



SYSTEMATIC OPTIMIZATION AND CHARACTERIZATION OF ALL-SOLID-STATE BATTERIES WITH SLURRY-CAST CATHODE

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Abstract

To address the ever-increasing demands for driving range and safety in electric vehicles, solid-state batteries (SSBs) have emerged as one of the most promising next-generation energy-storage technologies. Among various material configurations, the combination of sulfide solid electrolytes (SSEs), featuring high ionic conductivity and favorable processability, with layered Ni-rich oxide cathodes has demonstrated significant commercial potential. Furthermore, the adoption of slurry-casting processes for cathode fabrication provides a viable pathway toward the scalable manufacturing of SSBs. Nevertheless, complex interfacial reactions and the progressive emergence of electro-chemo-mechanical degradation during operation continue to severely limit the cycling stability and practical performance of such systems.

This dissertation focuses on polycrystalline $\text{LiNi}_{0.85}\text{Co}_{0.10}\text{Mn}_{0.05}\text{O}_2$ (PC NCM85) as the cathode active material (CAM) coupled with argyrodite $\text{Li}_6\text{PS}_5\text{Cl}$ (LPSCI) as the SSE. Through three complementary research directions, this work advances the mechanistic understanding of degradation phenomena in the cathode and develops systematic optimization strategies for SSBs.

The first section investigates interfacial (physicochemical) characteristics and associated degradation mechanisms. Using cryogenic transmission electron microscopy (cryo-TEM) combined with electron energy-loss spectroscopy (EELS), electrochemically induced reduction of transition-metal species and their dissolution from the CAM into the SSE are identified, leading to pronounced electrolyte poisoning. In parallel, a nanoparticle coating strategy is systematically investigated, resulting in substantial improvements in electrochemical performance. By designing a reliable three-electrode (3E) setup for SSBs, the second section focuses on interfacial kinetics between the working electrode (WE) and the counter electrode (CE). Emphasis is placed on the overlap of characteristic kinetic processes across relevant timescale regimes, as well as on the evolution of state-of-charge (SOC)-dependent overpotentials and interface-related kinetic responses from different CEs and their influence on cell performance. The third section addresses mechanical degradation of the cathode by employing $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) as the anode/CE in conjunction with a low negative-to-positive (n/p) capacity ratio design. By leveraging the lithiation profile of LTO near its terminal region, the volume changes in the cathode are effectively mitigated. Upon cycling, the capacity loss resulting from the incremental growth of cathode polarization can be partially mitigated through adaptive compensation. As a result, an optimal balance between attainable capacity and long-term capacity retention is achieved.

Collectively, the findings provide a comprehensive understanding of electro-chemo-mechanically induced degradation in the SSBs under investigation. The proposed strategies demonstrate pronounced performance improvements and strong transferability, offering effective methodologies and analytical perspectives for the rational design of high-performance SSBs.

Zusammenfassung

Um den stetig wachsenden Anforderungen an Reichweite und Sicherheit von Elektrofahrzeugen gerecht zu werden, haben sich Festkörperbatterien (SSBs) als eine der vielversprechendsten Energiespeichertechnologien der nächsten Generation etabliert. Unter den verschiedenen Materialkonzepten weist insbesondere die Kombination aus sulfidischen Festkörperelektrolyten (SSE), die sich durch hohe Ionenleitfähigkeit und vorteilhafte Verarbeitbarkeit auszeichnen, und Ni-reichen Schichtgitterkathoden ein hohes kommerzielles Potenzial auf. Darüber hinaus stellt der Einsatz von Schlickerbeschichtungsverfahren zur Kathodenherstellung einen praktikablen Ansatz für die skalierbare Produktion von SSBs dar. Dennoch führen komplexe Grenzflächenreaktionen sowie das fortschreitende Auftreten elektro-chemo-mechanisch-induzierter Degradationsprozesse während des Betriebs nach wie vor zu erheblichen Einschränkungen der Zyklenstabilität und praktischen Leistungsfähigkeit solcher Systeme.

Diese Dissertation konzentriert sich auf polykristallines $\text{LiNi}_{0.85}\text{Co}_{0.10}\text{Mn}_{0.05}\text{O}_2$ (PC NCM85) als Kathodenaktivmaterial (CAM) in Kombination mit dem Argyrodit $\text{Li}_6\text{PS}_5\text{Cl}$ (LPSCI) als SSE. Anhand von drei komplementären Forschungsansätzen wird das mechanistische Verständnis kathodenseitiger Degradationsphänomene vertieft und es werden systematische Optimierungsstrategien für SSBs entwickelt.

Der erste Abschnitt der Arbeit untersucht die physikochemischen Eigenschaften der Grenzflächen sowie die damit verbundenen Degradationsmechanismen. Mittels kryogener Transmissionselektronenmikroskopie (cryo-TEM) in Kombination mit Elektronenenergieverlustspektroskopie (EELS) werden elektrochemisch induzierte Reduktionsprozesse von Übergangsmetallspezies sowie deren Übertritt aus dem CAM in den SSE nachgewiesen, was eine ausgeprägte Elektrolytvergiftung zur Folge hat. Parallel dazu wird eine Nanopartikelbeschichtungsstrategie mit neu entwickelten Materialien systematisch untersucht, wodurch signifikante Verbesserungen der elektrochemischen Leistungsfähigkeit erzielt werden. Im dritten Abschnitt wird die mechanische Degradation der Kathode untersucht, indem $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) als Anode bzw. Gegenelektrode mit einem niedrigen negativ-zu-positiven (n/p) Kapazitätsverhältnis eingesetzt wird. Durch die gezielte Ausnutzung des Lithiatierungsprofils von LTO nahe seines Endbereichs können die Volumenänderungen in der Kathode effektiv reduziert werden. Im Zuge der Zyklierung lässt sich der Kapazitätsabfall, der aus dem inkrementellen Anstieg der Kathodenpolarisation resultiert, adaptiv kompensieren. Dies führt zu einer optimalen Balance zwischen erreichbarer Kapazität und langfristiger Zyklenstabilität.

Zusammenfassend liefern die Ergebnisse dieser Arbeit ein umfassendes Verständnis der elektro-chemo-mechanisch-induzierten Degradation in den untersuchten SSBs. Die vorgestellten Ansätze demonstrieren eine ausgeprägte Verbesserung der Leistungsfähigkeit sowie eine starke Übertragbarkeit. Sie bieten effektive Methodiken und analytische Perspektiven für die zielgerichtete Entwicklung von Hochleistungs-SSBs.

List of Abbreviations

2E	Two-electrode
3E	Three-electrode
ALD	Atomic layer deposition
ASSBs	All-solid-state batteries
ATR-IR	Attenuated total reflectance-infrared radiation
BMS	Battery management systems
c	The center of the peak in Gaussian function
c_p	Standard deviation of the Gaussian peak function
CAM	Cathode active material
CE	Counter electrode
CEI	Cathode electrolyte interface
Cryo-TEM	Cryogenic transmission electron microscopy
DEIS	Dynamic electrochemical impedance spectroscopy
DEMS	Differential electrochemical mass spectrometry
DRT	Distribution of relaxation times
DUP	Desired upper cut-off potential
ECM	Equivalent circuit model
EDS	Energy-dispersive X-ray spectroscopy
EELS	Electron energy loss spectroscopy
EIS	Electrochemical impedance spectroscopy
ESW	Electrochemical stability window
EV	Electric vehicle
f	Frequency
FFT	Fast Fourier transform
FIB-SEM	Focused ion beam-scanning electron microscopy
GCPL	Galvanostatic cycling with potential limitation
GPE	Gel polymer electrolyte

$g(\tau), \gamma(\ln\tau)$	The distribution function of relaxation time
HRTEM	High-resolution transmission electron microscopy
i	Imaginary unit
ICE	Initial Coulomb efficiency
In/InLi	Indium-lithium alloy
IUP	Initial upper cut-off potential
LFP	Lithium iron phosphate (LiFePO_4)
LGPS	Lithium germanium phosphorus sulfide ($\text{Li}_{10}\text{GeP}_2\text{S}_{12}$)
LIBs	Lithium-ion batteries
LLZO	Lithium lanthanum zirconium oxide ($\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$)
LTO	Lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$)
MIECs	Mixed ionic and electronic conductors
n/p ratio	negative-to-positive capacity ratio
NCA	Lithium nickel cobalt aluminium oxide ($\text{LiNi}_x\text{Co}_y\text{Al}_{1-x-y}\text{O}_2$)
NCM	Lithium nickel cobalt manganese oxide ($\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$)
NP	Nanoparticle
PC	Polycrystalline
PIB	Polyisobutylene ($[-\text{CH}_2 - \text{C}(\text{CH}_3)_2 -]_n$)
Q	Constant phase element (CPE)
R	Resistor
R_o	Ohmic resistance
RBF	Radial basis function
R_{ct}	Charge-transfer resistance
RE	Reference electrode
R_{int}	SEI/CEI resistance
R_p	Polarization resistance
SC	Single crystal
SEI	Solid electrolyte interface
SOC	State-of-charge

SPE	Solid polymer electrolyte
SSBs	Solid-state batteries
SSEs	Sulfide solid electrolytes
TM	Transition metal
TOF-SIMS	Time-of-flight secondary ion mass spectrometry
UP	Upper cut-off potential
W	Warburg element
WE	Working electrode
WLTP	Worldwide harmonized light vehicles test procedure
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
Z_{diff}	Diffusion-related impedance
$Z(f)$	Measured impedance
Z_L	Inductive-related impedance
Z_{ohm}	Ohmic-related impedance
$Z_{\text{pol}(f)}$	Polarization-related impedance
α	The exponential factor of Q
a_p	Peak height of the Gaussian peak function
λ	Regularization parameter
μ	Shape factor in the Gaussian function
μ_{Li}	Chemical potential of Li
$\tilde{\mu}_{\text{e}^-}$	Electrochemical potential of e^-
$\tilde{\mu}_{\text{Li}^+}$	Electrochemical potential of Li^+
σ_{e^-}	Electronic conductivity
τ	Time constant
τ_p	Peak center of the Gaussian peak function
$\phi_{\mu}(\mathbf{x}, \mathbf{c})$	Gaussian function

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1. Introduction

Lithium-ion batteries (LIBs), as one of the most successful energy-storage technologies to date, are not only widely deployed in portable consumer electronics, but also play a pivotal role in grid-scale storage systems and, in particular, in accelerating transportation electrification.^[1-3] For the latter, the demand for LIBs continues to expand at an unprecedented pace. According to recent market data from SNE Research, in 2025, global electric vehicle (EV) deliveries amounted to approximately 21.47 million units (+21.5% year-over-year), and global EV battery usage reached 1187 GWh (+31.7% year-over-year).^[4-5] These figures indicate that the electrification of transportation remains in an accelerated growth phase, with sustained and structurally increasing demand for high-performance battery systems.

Currently, LIB technology based on liquid electrolytes is highly mature. Since the commercialization of the first LIB in 1991, continuous advancements in material systems and engineering design have led to significant improvements in energy density, cost, and cycle life. In the EV industry, two representative technological routes have emerged based on cathode material selection: the LiFePO_4 (LFP) system, characterized by high safety, long lifetime, and low cost, and the layered Ni-rich oxide system ($\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ or $\text{LiNi}_x\text{Co}_y\text{Al}_{1-x-y}\text{O}_2$, $x \geq 0.6$, NCM or NCA), which offers high energy density.^[6-7]

According to teardown analyses and practical measurements of representative commercial cells, the BYD Blade (LFP) cell exhibits a specific energy of approximately 160 Wh/kg, corresponding to a driving range of ~500 km in corresponding packs (Worldwide Harmonized Light Vehicles Test Procedure: WLTP), whereas the Tesla 4680 (NMC811) cell reaches ~241 Wh/kg, enabling a range of ~580 km in the respective packs (WLTP).^[6] Under the current configuration using graphite as the anode, further improvements in energy density through cathode optimization (e.g., Mn doped LFP: LMFP or ultra-high-Ni NCM) and cell engineering are expected to be limited, gradually approaching the physicochemical ceiling at the cell-level (~280 Wh/kg for NCM systems).^[8] Although sodium-ion batteries exhibit great potential from the perspectives of cost and resource abundance,^[9] their current development status suggests that they are more likely to compete first with LFP-based systems, rather than high-energy NCM/NCA systems.^[10-11] For high-energy-density applications, lithium-based EV batteries are expected to remain dominant.

To further enhance energy density, one feasible pathway is to maintain Ni-rich cathodes while gradually transitioning from graphite to Si-containing anodes, with a projected upper limit of ~350 Wh/kg on cell level.^[12] To achieve further breakthroughs beyond this level, fundamental upgrades of key battery components are required, including the use of Li-rich, Mn-based cathodes, Li metal anodes (including anode-less configurations), and the development of advanced electrolytes.^[13-15] Notably, recent studies combining Ni-rich cathodes with Li metal anodes have demonstrated energy densities in the range of 380–700 Wh/kg,^[14-20] with a laboratory-level record of 707 Wh/kg, enabled by the design of hydrofluorocarbon electrolytes.^[15] However, such designs remain largely at the development stage due to insufficient cycling stability and critical safety concerns associated with Li metal.

1. Introduction

A highly promising strategy to achieve high energy densities is the adoption of solid-state batteries (SSBs).^[21-22] Moreover, quasi-SSBs (containing a limited amount of liquid electrolyte) have already begun to gain market acceptance. For example, Factorial Energy's FEST quasi-SSBs (based on Gel Polymer Electrolyte: GPE and Li metal anode) exhibit an energy density of ~375 Wh/kg and have established partnerships with Stellantis, Karma Automotive, and Mercedes-Benz, with demonstrations already conducted in real EVs.^[23-25]

The ultimate form of SSBs is the all-solid-state battery (ASSB), which can maximize energy density while offering enhanced safety compared to liquid or quasi-solid-state systems. In fact, Li-based ASSBs are not a new concept. As early as the 1970s, Li-I₂ primary SSBs were developed and successfully applied in implantable medical devices, such as pacemakers, due to their excellent safety and long-term stability.^[26] However, it was not until the breakthrough reported by Kanno *et al.* in 2011, with Li₁₀GeP₂S₁₂ (LGPS) exhibiting a room-temperature ionic conductivity comparable to liquid electrolytes (~1.2·10⁻² S/cm), that the feasibility of sulfide solid electrolyte (SSE)-based rechargeable batteries for EV applications was significantly advanced.^[27] Among various candidates, SSEs have attracted considerable attention due to their high ionic conductivity and relatively easy-to-process properties, and their combination with Ni-rich cathodes has become a mainstream approach.

To enable the transition from laboratory-scale fabrication to industrial-scale production, electrode processing methods for Ni-rich cathodes coupled with SSEs must be scalable.^[28-29] Currently, slurry-casting and dry processing represent the two main strategies for fabricating such sheet-type electrodes.^[30-31] The slurry-casting method, inherited from conventional LIB manufacturing, enables a more homogeneous electrode microstructure compared to dry composite mixing by introducing solvents and binders.^[32] However, SSEs are sensitive to the polarity of the solvent and binder, making the selection limited,^[33] and solvent recovery increases processing costs. In contrast, dry processing eliminates the need for solvents and relies on PTFE-based fibrillation networks to bind particles and maintain structural integrity. This method enables high mass loading, self-standing electrodes, and simplified processing, making it increasingly attractive for both solid-state and conventional battery manufacturing.^[34-36]

Despite the great potential of Ni-rich cathodes coupled with SSEs, their practical application remains hindered by the intrinsic instability of Ni-rich cathodes, the narrow electrochemical stability window (ESW) of SSEs, and interfacial degradation arising from their solid-solid contact.^[37-39] These challenges are further exacerbated by electrochemo-mechanical coupling effects.^[40-41] In addition, electrochemical measurements based on conventional two-electrode (2E) cell configurations may be significantly influenced by the counter electrode (CE), leading to misinterpretation of performance degradation.^[42-43]

Dedicated to advancing the electrochemical performance of Ni-rich cathodes coupled with SSEs, the objective of this PhD work is to first investigate the underlying mechanisms of interfacial failure and corresponding modification strategies, then identify the kinetic limitations within composite electrodes, and finally integrate these insights to propose feasible optimization strategies for the design of high-performance SSE-based SSBs.

1. Introduction

Based on this background, in this doctoral research, sheet-type cathodes were fabricated via slurry casting [with polyisobutylene (PIB) as binder and *o*-xylene as solvent],^[30, 44] and a systematic research framework was designed, with the corresponding results presented in **Publications I–VI**.

Focusing on the interface between the Ni-rich cathode [$\text{LiNi}_{0.85}\text{Co}_{0.10}\text{Mn}_{0.05}\text{O}_2$ (NCM85)] and the SSE [$\text{Li}_6\text{PS}_5\text{Cl}$ (LPSCI)], the electrochemical degradation mechanisms were systematically investigated and are summarized in section 3.1. Cryogenic transmission electron microscopy (cryo-TEM) was employed as an advanced characterization technique to analyze the cathode active material (CAM)|SSE interface. Pronounced transition metal (TM) dissolution and resulting SSE poisoning were revealed, as reported in **Publication I**.^[45] Furthermore, based on a nanoparticle (NP) coating concept, HfO_2 and $\text{HfO}_2/\text{Li}_2\text{HfO}_3$ coatings were successfully applied to the CAM surface (see **Publications II and III**).^[44, 46] Compared to uncoated counterparts, the coated cathodes exhibited significantly improved electrochemical performance, achieving an initial areal capacity of 2.3 mAh/cm^2 and 94% capacity retention after 200 cycles.^[44]

Recognizing that laboratory-scale anode/CE materials, such as $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) and indium-lithium alloy (In/InLi), can influence the cathode/working electrode (WE) performance and interfacial kinetic analysis, section 3.2 introduces the transition from 2E to three-electrode (3E) cell configurations, including an in-house designed setup with an LTO-based reference electrode (RE) (see **Publication VI**).^[47] Through 3E electrochemical impedance spectroscopy coupled with the distribution of relaxation times (EIS-DRT) analysis, the characteristic kinetic processes of LTO and In/InLi were identified. Furthermore, the polarization, state-of-charge (SOC)-dependent impedance growth, and overlapping time constants of interface-related kinetic processes among NCM85, LTO, and In/InLi were revealed. Importantly, the contribution from CE materials (e.g., In/InLi) to capacity fading and the potential overestimation of the contributions from the NCM85 WE were demonstrated (see **Publication V**).^[42]

Finally, to enhance the electrochemical performance of slurry-cast SSBs, a systematic cell-level optimization focusing on mechanical stability was conducted, as shown in section 3.3. For polycrystalline (PC) NCM85, LiNbO_3 coating effectively mitigated electrochemical degradation at the interface. Meanwhile, mechanical degradation induced by cell volume changes was significantly alleviated through a strategy based on negative-to-positive capacity (n/p) ratio optimization using LTO as a model anode/CE in **Publication VI**.^[48] By leveraging the lithiation tail of LTO, the initial upper cut-off potential (IUP) of NCM85 was reduced, resulting in a lower initial capacity, but enhanced mechanical stability. During prolonged cycling, the polarization-induced increase in upper cut-off potential (UP) enabled adaptive lithium extraction to compensate for capacity loss until reaching a predefined, desired upper cut-off potential (DUP). As a result, a pronounced balance between attainable capacity and capacity retention was achieved, with ~80% capacity retention after ~1300 cycles.

2. Fundamentals

2.1. Degradation Mechanisms and Corresponding Mitigation Strategies

In composite cathodes, the solid-solid contacts among Ni-rich CAM, SSE, and carbon additives give rise to multiple interfaces, the stability of which plays a decisive role in determining the electrochemical performance of SSBs.^[37] In this section, the interfacial degradation processes occurring within composite cathodes are systematically reviewed, followed by a discussion of the corresponding mitigation strategies.

2.1.1. Electro-Chemo-Mechanical Degradation

As summarized in **Figure 1**, electro-chemo-mechanical degradation effects coexist and interact synergistically within composite cathodes under practical operating conditions.^[38-39] In the following, the origin and impact of each degradation mechanism are discussed individually.

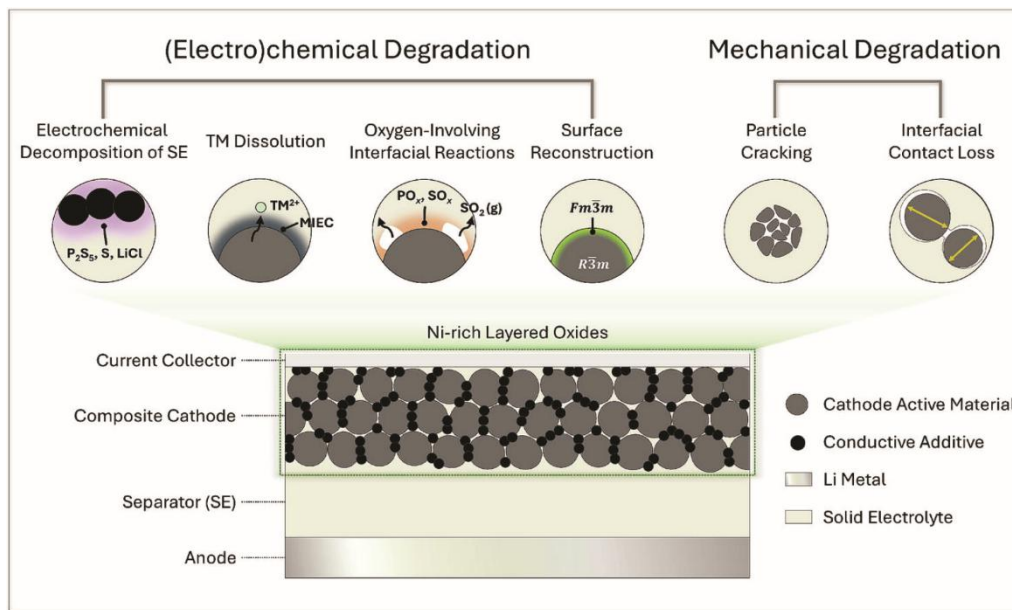


Figure 1. Schematics of the electro-chemo-mechanical degradation phenomenon in SSE-based SSBs. Adapted from Reference [38].

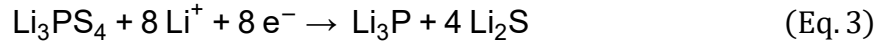
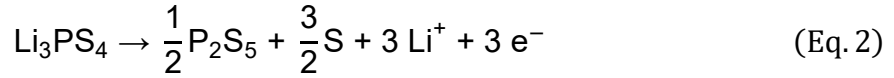
2.1.1.1 (Electro)chemical Degradation

Electrochemical Decomposition of SSE

SSEs such as LPSCI exhibit high ionic conductivity and favorable mechanical properties. However, first-principles calculations indicate that their intrinsic electrochemical stability window is rather narrow (~ 0.3 V).^[49] Specifically, the oxidative onset of sulfur ($S^{2-} \rightarrow S^0 + 2e^-$) occurs at approximately 2.0–2.6 V vs. Li^+/Li , while the reductive onset

2. Fundamentals

of phosphorus ($P^{5+} + 5e^- \rightarrow P^0$) takes place at around 1.0–1.7 V vs. Li^+/Li . The redox reactions of LPSCI proceed via intermediate phases (Li_3PS_4), as described in **Equations 1**, followed by further reactions to yield final products, as described in **Equations 2** and **3**.^[50] Considering the typical operating potential window of Ni-rich cathodes, SSE-based SSBs predominantly experience oxidative decomposition at the cathode side, which is irreversible.^[44-45]



Experimental studies have shown that the as-formed oxidized interphases from decomposed LPSCI exhibit high interfacial resistance, mainly due to the poor ionic and electronic conductivity of the decomposition products (e.g., S, P_2S_5 , and LiCl), leading to a sharp increase in charge-transfer resistance (R_{ct}) at the interface.^[37, 50-51]

Oxygen-Involved Interfacial Degradation Between CAM and SSE

When Ni-rich CAMs participate in interfacial reactions with SSEs, the degradation behavior becomes more complex. This originates from the high surface reactivity of Ni-rich cathodes, their structural instability at high states of delithiation, and the associated lattice oxygen release.^[38] The fundamental driving force for interfacial electrochemical reactions between CAM and SSE lies in the mismatch of Li chemical potential (μ_{Li}) at the interface,^[49] as detailed in section 2.1.2.1.

Even in the pristine state, direct contact between Ni-rich CAM and SSE leads to chemical incompatibility,^[52] which becomes more pronounced with increasing Ni content.^[53-54] The strong tendency for O–S exchange induces interdiffusion, potentially forming transition metal sulfides (e.g., Co_9S_8 , Mn_2S_3 , Ni_3S_4 , and $CoNi_2S_4$) and Li_2S as by-products.^[54]

Under highly delithiated conditions, structural instability of the CAM leads to lattice oxygen release near the surface,^[55-56] accompanied by a phase transformation from a layered structure to a rock-salt phase, further increasing the charge-transfer resistance. Differential electrochemical mass spectrometry (DEMS) measurements have confirmed O_2 release from uncoated Ni-rich CAMs in SSE environments, along with the evolution of SO_2 due to reactions with the SSE.^[57-58]

Oxygen-involved interfacial degradation results in the formation of oxygenated sulfur- and phosphorus-containing species (e.g., Li_2SO_4 , MSO_4 , Li_2SO_3 , Li_3PO_4 , $M_3(PO_4)_2$, where $M = Ni, Co, Mn$).^[37, 59-61] These interphases significantly hinder Li^+ transport, increase interfacial resistance, and lead to capacity fading during cycling.

Recently, Hartel *et al.* compared the performance of $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ -based SSBs coupled with NCM83 and Li–S SSBs. Compared with the relatively stable Li–S systems, oxygen-involved SSBs exhibited pronounced performance degradation due to oxygen-driven interfacial reactions, highlighting the critical importance of chemical compatibility between SE and active materials for interfacial stability and long-term cycling.^[62]

TM Dissolution

Another electrochemically relevant phenomenon is the dissolution of TM elements from Ni-rich CAMs into the SSE, followed by SSE poisoning.^[38, 45, 63] Such phenomena have recently gained attention. Notably, despite the absence of solvation effects and conventional migration pathways (as in liquid electrolytes), TM species can still dissolve and migrate within SSEs.

Early studies reported that, in LiCoO_2 -based systems, Co can diffuse into the SSE via interdiffusion, forming Co-containing by-products and penetrating up to ~50 nm from the interface to SSE, possibly in the form of crystalline CoS.^[64-65] More recent studies indicate that TM dissolution is not limited to Co and that diffusion depths can reach the micrometer scale.^[45, 63] This process is often accompanied by oxygen release and reduction of TMs which further reacts with the SSE, promoting interfacial side reactions and interphase growth. Possible by-products associated with TM dissolution include TM sulfides and phosphides.^[39, 66]

On the other hand, while intergranular cracking within PC CAMs is frequently observed via TEM, the enrichment of sulfur species within cracks or along grain boundaries has rarely been systematically discussed.^[44-45, 67] Such observations imply the penetration of sulfur species along grain boundaries or voids during cycling. Whether this penetration facilitates Li^+ transport remains unclear. However, it may also significantly increase the number of reactive sites for interfacial side reactions.

2.1.1.2 Mechanical Degradation

CAM Cracking and Contact Loss

During delithiation, Ni-rich CAMs undergo significant volume contraction, accompanied by the H2–H3 phase transition at high potentials. In PC Ni-rich CAMs, orientation mismatch among primary particles leads to strain incompatibility, resulting in intergranular cracking and particle fragmentation.^[38-40, 68]

In addition, electrochemical degradation induced oxygen release and surface reconstruction further weakens the CAM surface, allowing defects to propagate into the bulk.^[68] The repeated volume changes during cycling lead to severe contact loss between CAM and SSE, which is further exacerbated by SSE decomposition.^[40]

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As indicated by **Equation 2**, the molar volume of SSE decreases upon oxidation (e.g., for LPSCI, from 163.7 cm³/mol to 142.8 cm³/mol),^[40, 69-70] contributing to additional contact loss. Meanwhile, inhomogeneous contact between CAM and SSE leads to SOC heterogeneity within particles, creating localized hotspots that induce stress concentration and accelerate cracking.

Overall, mechanical degradation aggravates charge-transfer limitations, increases polarization resistance, and ultimately leads to significant performance decay.

In fact, although electrochemical degradation can be effectively mitigated through surface coating of CAMs, mechanical degradation remains the key factor limiting long-term cycling stability. This has been systematically analyzed in studies that decouple electro-chemo-mechanical degradation effects and evaluate their individual contributions.^[48, 71]

Finally, electro-chemo-mechanical degradation is not limited to the cathode. At the anode side, especially when employing high energy density materials such as Li metal and Si, similar coupled challenges arise. The opposing volume change behaviors of the cathode and anode may lead to structural compatibility as a favorable perspective,^[72] while effective suppression of interfacial side reactions remains essential for realizing high-performance SSBs. In the following, mitigation strategies from the perspective of the cathode are discussed.

2.1.2. Strategies Against (Electro)chemical Degradation in the Cathode

An effective strategy to mitigate the (electro)chemical degradation at the interface between Ni-rich cathodes and SSEs is to introduce a buffer layer between the two components, which can be achieved via coating approaches. It should be noted that the coating material can be applied either on the CAM or on the SSE.^[73-75] Within the scope of this PhD work, the primary focus is placed on CAM coatings. In the following, the principles, functionalities, materials, and methods of CAM coating are reviewed.

2.1.2.1. Principles of CAM Coating

As illustrated in **Figure 2**, a significant difference exists in the chemical potential of Li (μ_{Li}) between the SE and the CAM.^[49] Without an intermediate coating layer, the μ_{Li} at the interface can exceed the onsite potential for SE oxidation, thereby triggering interfacial side reactions. In contrast, an as-formed interphase layer [cathode electrolyte interface (CEI)] or an intentionally introduced coating layer (both assuming negligible electronic conductivity (σ_{e-}) compared to the SE) can reduce the μ_{Li} gap between the CAM and SE, thereby shifting the μ_{Li} at the interface into the electrochemical stability window of the SE. As a result, the thermodynamic driving force for SE decomposition is suppressed, preventing further propagation into the bulk.

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The μ_{Li} can be expressed as the sum of the electrochemical potentials of Li^+ and e^- ($\mu_{\text{Li}} = \tilde{\mu}_{\text{Li}^+} + \tilde{\mu}_{\text{e}^-}$). At equilibrium, $\tilde{\mu}_{\text{Li}^+}$ and $\tilde{\mu}_{\text{e}^-}$ redistribute across the interface, giving rise to a potential difference. While $\tilde{\mu}_{\text{Li}^+}$ remains in equilibrium across the coating layer, the $\tilde{\mu}_{\text{e}^-}$ from the CAM to the SE is significantly suppressed due to the low σ_{e^-} of the coating layer.

To note, as discussed in section 2.1.1.1, in practically operating conditions, the oxidative interphases formed at the interface are often mixed ionic and electronic conductors (MIECs). In such cases, μ_{Li} at the interfaces cannot be sufficiently lowered into the SE stability window, and the interphase growth is no longer self-limited, leading to continuous oxidative reactions. Such diffusion-driven solid-state reactions can be well described by the Wagner model.^[76]

Overall, an effective CAM coating layer should possess sufficiently low σ_{e^-} while still enabling efficient Li^+ transport and charge transfer across the interface. Typical oxide materials are widely employed as coating layers due to their intrinsically low σ_{e^-} . However, excessively low σ_{e^-} may hinder charge transfer. Therefore, both the coating content and thickness must be carefully optimized.

2.1.2.2. Functionalities of CAM Coating

As described above, the primary function of CAM coatings is to reduce the μ_{Li} at the interfaces, thereby suppressing detrimental interfacial side reactions, lowering interfacial resistance, and improving overall electrochemical performance. In addition, CAM coatings can partially suppress the dissolution of TMs from the CAM.^[64-65] Moreover, lithium residuals on the CAM surface might adversely affect interfacial stability.^[77-78] The designed coating process can consume these residual species, simultaneously forming the coating layer and improving interfacial stability, which contributes to enhanced cycling performance.^[46, 79]

2.1.2.3. Materials and Methods

A wide range of coating materials has been reported for high energy density cathode materials, including binary oxides, lithium-containing ternary and quaternary oxides, phosphate-based materials, and even polymer coatings.^[80-85] The morphology, structure, and performance of the coating layer strongly depend on the synthesis method employed.^[81-82]

Among various approaches, wet-chemical methods such as the sol–gel process are widely adopted due to their simplicity and flexibility in material selection, enabling relatively good control over coating thickness and uniformity. LiNbO_3 , used as a representative sol–gel coating material, has been extensively applied in SSBs and has demonstrated effective suppression of interfacial side reactions.^[78, 86-87] For more precise control over thickness, uniformity, and conformality, atomic layer deposition (ALD) is typically employed.^[88-89] However, due to its complexity and high cost, ALD remains

limited in practical applications. Dry coating methods, on the other hand, offer a simple and scalable approach but often result in non-uniform, island-like coatings, making process optimization essential.^[90-91]

In recent years, several innovative strategies for CAM coating in SSBs have been reported. For example, Ma *et al.* proposed a nanoparticle-based coating strategy, where highly dispersed nanoparticles are pre-synthesized and well-dispersed, subsequently applied via solution mixing with CAM particles followed by post-annealing, resulting in a uniform and ultrathin coating layer.^[44, 46, 92] Huang *et al.* reported a surfactant-assisted coating approach, which notably does not require high-temperature annealing and can be performed under ambient conditions, demonstrating strong potential for commercialization.^[93] Inspired by the properties of decomposition products (e.g., Li_2SO_4 and Li_3PO_4), Zuo *et al.* and Kissel *et al.* designed artificial CEI layers as coating layers, achieving significant performance improvements.^[94-95] Finally, Henkel *et al.* developed a method to coat CAMs with antiperovskite materials via melt-infiltration, expanding the design space for both coating materials and processing strategies.^[96]

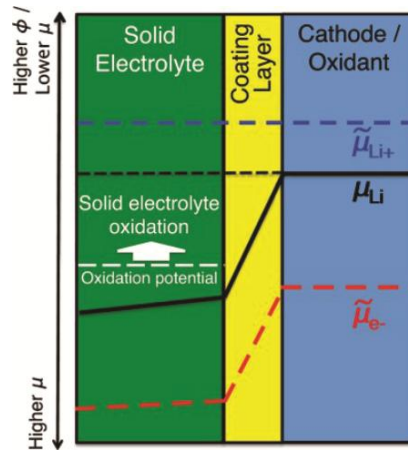


Figure 2. Schematic diagram of chemical potential of Li (μ_{Li}), electrochemical potential of Li^+ ($\tilde{\mu}_{\text{Li}^+}$), and e^- ($\tilde{\mu}_{\text{e}^-}$) across the coating layer between SE and CAM in equilibrium state. Adapted from reference [49].

2.1.3. Strategies Against Mechanical Degradation in the Cathode

Although, under high external pressure, the volume change at the cathode is much smaller than that at the anode (such as in In/InLi , Si , or Li metal-based anode), in practical applications under low stack pressure, the chemomechanical behavior of the cathode itself can already dominate the performance of SSBs.^[72] Therefore, focusing on Ni-rich CAMs coupled with SSEs, the mechanical degradation at the cathode can be mitigated at the material-, electrode-, and cell-levels. The following summarizes representative strategies reported in SSE-based SSBs.

2.1.3.1. Material-Level Strategies

Compositional Modification of CAM

Modification of Ni-rich CAMs is commonly achieved through bulk or near-surface elemental doping, aiming to enhance structural stability. Dopants such as Ti, Zr, Nb, Ta, W, and Mo strengthen the TM–O bonds, thereby mitigating lattice distortion during deep delithiation, suppressing oxygen release and phase transitions, and ultimately reducing stress concentration and crack propagation.^[97-102]

Morphological Modification of CAM

Conventional PC secondary particles, although mature in processing, are prone to intergranular cracking due to stress concentration at grain boundaries. An effective strategy is the adoption of SC CAMs, where internal cracking within secondary particles is largely mitigated, leading to reduced charge-transfer limitations. SC-based Ni-rich cathodes coupled with SSEs have consistently demonstrated superior cycling stability in the literature.^[68, 86]

In addition, designing internal porosity within polycrystalline particles represents another viable strategy. For example, Li *et al.* proposed a gradient-porous Ni-rich CAM, which effectively buffers the anisotropic volume change of primary particles, alleviates intergranular cracking, and suppresses impedance growth.^[103]

Polymer Coating on CAM

The function of coatings extends beyond suppressing interfacial side reactions. They also provide a mechanical buffering effect, mitigating stress and strain arising from volume changes between the CAM and SSE. This is critical when coated CAMs deliver higher capacities yet associated with larger cell volume change. Due to their intrinsic flexibility, polymer coatings serve as an effective strategy to alleviate mechanical degradation. Their soft nature allows them to accommodate deformation while maintaining structural integrity during volume changes of the CAM.^[84-85, 104] This strategy not only benefits the cathode but is also relevant for stabilizing high volume change anodes, such as Si-based materials.

2.1.3.2. Electrode-Level Strategies

Binder-Assisted Electrode Preparation

Numerous studies on binder-assisted, sheet-type cathodes have shown that, compared to conventional pelletized composite cathodes prepared by simple mixing, the introduction of a binder not only provides the necessary adhesion for the preparation of sheet-type electrodes but also significantly enhances the mechanical stability within the electrode.^[105-106]

Polymer binders effectively connect different components within the cathode, improve the interfacial contact between CAM and SSE, suppress contact loss during cycling, and enhance the overall mechanical strength of the electrode. Interestingly, binder-

assisted cathodes also exhibit a more uniform microstructure and significantly reduced porosity compared to pelletized composite cathodes.^[48]

2.1.3.3. Cell-Level Strategies

Balance Between Attainable Capacity and Capacity Retention

The degree of delithiation directly affects the cell volume change and the H2–H3 phase transition of Ni-rich CAMs, leading to stress and strain accumulation that induces inter- and intragranular cracking within the CAMs. A practical approach to control the delithiation state is to reduce the UP of the cathode. However, lowering the UP inevitably reduces the attainable capacity, resulting in a decrease in energy density. Therefore, a trade-off exists between attainable capacity and capacity retention. Recently, Zhang *et al.* proposed a strategy to enhance the mechanical stability of the cathode by using LTO as a model anode.^[48] By leveraging the deviation from the plateau potential during LTO lithiation and optimizing the n/p ratio, significant improvements in both mechanical stability and cycling performance of the cathode were achieved.

2.2. Interface-Related Kinetic Analysis

In solid-state systems based on Ni-rich layered oxide cathodes coupled with SSEs, the interfacial resistance plays a dominant role in determining the fading of electrochemical performance. The interfacial degradation mechanisms and corresponding mitigation strategies discussed in the previous section can be qualitatively and quantitatively evaluated through electrode- and interface-related kinetic analysis.

Non-destructive probing of the physicochemical processes at the interface is typically achieved by EIS. Owing to the distinct characteristic time constants of individual electrochemical processes, the complex processes occurring within SSBs can be deconvoluted in the frequency (f) domain. Furthermore, when combined with the DRT analysis, electrochemical processes at the interfaces can be more intuitively distinguished, making it a powerful tool for investigating interfacial kinetics.

Therefore, in this section, the fundamental principles of EIS and DRT are first introduced. Subsequently, DRT-assisted interface-related kinetic analysis is summarized, with a focus on SSE-based SSBs. Finally, the kinetic hindrance arising from the CE is critically reviewed.

2.2.1. On the Functionality of Electrochemical Impedance Spectroscopy

SSBs represent complex electrochemical systems, in which the underlying physicochemical processes span multiple length and time scales, ranging from the fastest ionic conduction within the SEs to the slowest ion diffusion within electrode materials.^[107-108] EIS, as a technique in the frequency-domain based on small-signal linear perturbation, enables the probing of these processes by applying a small current or voltage perturbation and measuring the corresponding voltage or current response. In this way, kinetic processes can be captured over a broad frequency range spanning from MHz to mHz, allowing for the effective separation of electrochemical processes occurring on different time scales.

A reliable impedance measurement must satisfy three fundamental conditions: stability, causality, and linearity. In addition, the real and imaginary components of the impedance should fulfill the Kramers–Kronig (K–K) relations.^[109-110] It is worth noting that recent developments in dynamic electrochemical impedance spectroscopy (DEIS) have demonstrated significant advances in battery research.^[111-113] By satisfying the assumptions of local stationarity and local validity of the K–K relations, DEIS enables real-time tracking of variations in SOC, interface, and contact resistance during operation. A detailed discussion of DEIS can be found in the literature.^[114]

In the frequency domain, electrochemical impedance is commonly represented in the form of a Nyquist plot, often combined with equivalent circuit model (ECM) fitting for the qualitative and quantitative analysis of the involved kinetic processes.^[108] Equivalent circuits simulate different processes using combinations of basic elements. For example, a resistor (R) is used to represent the ohmic resistance of the system (high-

frequency intercept), while a parallel combination of R and Q (constant phase element, CPE) that commonly referred to as a $ZARC$ element, is used to describe interfacial processes, such as grain boundary within SEs and the as-formed interfaces (typically manifested as depressed semicircles).^[115] At low frequencies, capacitive and diffusion-related processes are often modeled using a Q or a Warburg element (W), giving rise to the characteristic inclined line in the Nyquist plot. For a given interface-related process, the corresponding time constant (τ) is related to the peak frequency of the semicircle according to: $\tau = (RQ)^{(1/\alpha)}$, where α is the exponential factor of Q , with a value between 0 and 1. A more intuitive identification of characteristic processes can be achieved in the Bode plot by locating the corresponding phase peaks.

However, the ECM approach suffers from intrinsic limitations. Kinetic processes with similar time constants often appear overlapped in the frequency domain, making them difficult or even impossible to separate.^[47, 107] Moreover, the selection of ECMs involves a certain degree of empiricism and subjectivity, as different circuit models can fit the same impedance data, leading to ambiguous interpretations of the underlying electrochemical processes. To address these limitations, the DRT analysis, which transforms impedance data from frequency into the time domain, has become a widely adopted approach in battery research and will be discussed in detail in the following section.

2.2.2. On the Functionality of Distribution of Relaxation Times

DRT has become an indispensable analytical tool in the field of battery research.^[42, 47, 107, 116-117] Compared with conventional ECM-based analysis, DRT does not rely on a predefined ECM. Instead, by transforming EIS data from the frequency domain into the time domain and applying DRT deconvolution, the resulting peaks can be directly used for the qualitative and quantitative analysis of the involved electrochemical processes.

For a typical SSB system, the measured impedance $Z(f)$ may consist of contributions from the bulk of the SE (Z_{ohm}), a possible inductive contribution at high frequencies (Z_L), a series of interface-related polarization processes ($Z_{pol(f)}$), and a diffusion-related impedance (Z_{diff}) with pronounced capacitive characteristics when featuring blocking electrodes. DRT analysis is based on decomposing interfacial electrochemical processes into an infinite series of $ZARC$ elements and involves the deconvolution of the measured impedance to obtain the distribution function of relaxation times.^[107, 118] After subtracting the contributions from inductive and diffusion components, the DRT formulation can be expressed as:

$$Z(f) = R_o + R_p \int_0^{\infty} \frac{g(\tau)}{1 + i2\pi f\tau} d\tau \quad (1)$$

with normalized integration:

$$\int_0^{\infty} g(\tau) d\tau = 1 \quad (2)$$

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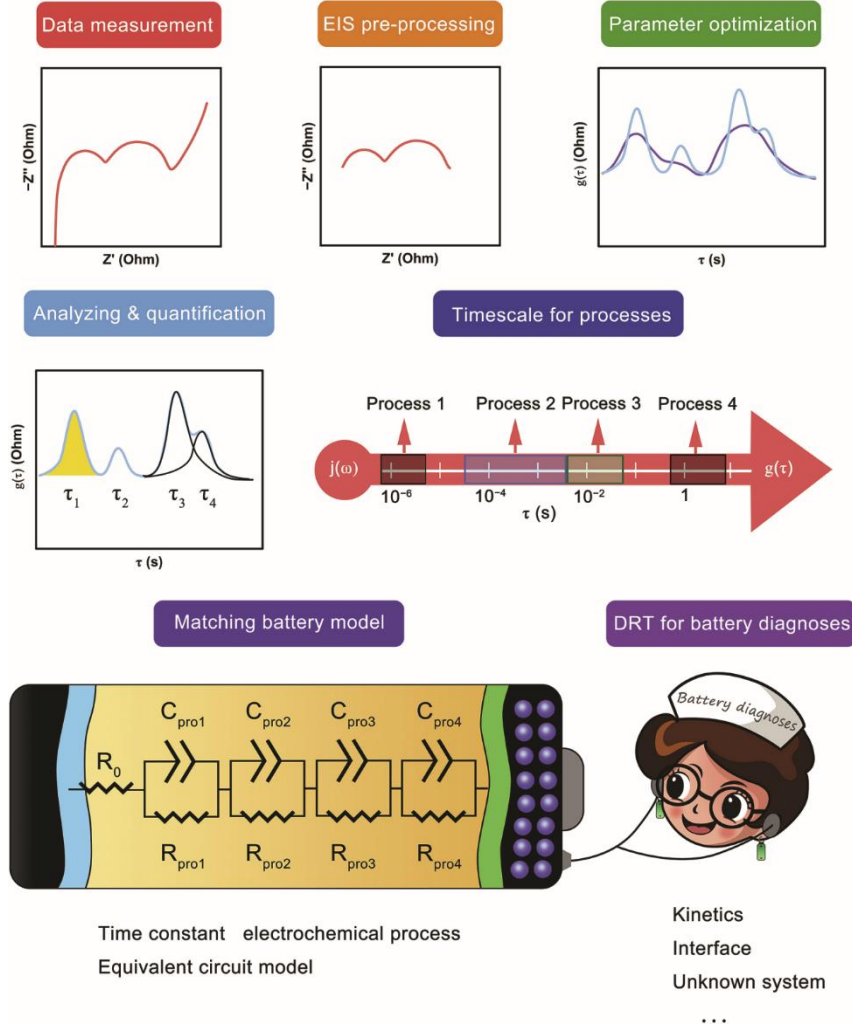


Figure 3. Workflow for DRT-based kinetic analysis for the battery system. Adapted from reference [107].

where i refers to the imaginary unit, R_0 refers to the ohmic resistance, R_p refers to the interface-related polarization resistance, and $g(\tau)$ is the distribution function of relaxation time. Since EIS data are typically acquired on a logarithmic frequency scale, the integral equation can be further transformed into a logarithmic form, yielding:

$$Z(f) = R_0 + R_p \int_0^{\infty} \frac{\gamma(\ln\tau)}{1+i2\pi f\tau} d\ln\tau \quad (3)$$

where $\gamma(\ln\tau) = \tau g(\tau)$.

The deconvolution process from $Z(f)$ to $\gamma(\ln\tau)$ is inherently an ill-posed problem. The Tikhonov regularization provides an effective solution. The discretization of $\gamma(\ln\tau)$ can be represented as a linear combination of radial basis functions (RBF),^[119] where Gaussian functions are commonly employed and expressed as:

$$\phi_{\mu}(\mathbf{x}, \mathbf{c}) = \exp(-\mu \|\mathbf{x} - \mathbf{c}\|^2) \quad (4)$$

where c refers to the center of the peak, and μ is the shape factor. Accordingly, $\gamma(\ln\tau)$ can be written as:

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$$\gamma(\ln\tau) = \sum_{m=1}^M x_m \phi_{\mu}(|\ln\tau - \ln\tau_m|) \quad (5)$$

where x_m refers to the unknown parameter to be fitted, and τ_m refers to the time constant.

By applying Tikhonov regularization, the optimization problem between the reconstructed impedance from DRT and the experimental impedance data can be formulated as:

$$S(\mathbf{x})_{\min} = \|\mathbf{Ax} - \mathbf{b}\|^2 + \lambda \|\mathbf{x}\|^2 \quad (6)$$

where $\lambda \|\mathbf{x}\|^2$ refers to the penalty term, and λ is the regularization parameter.

Therefore, when employing a Gaussian function as the RBF basis together with Tikhonov regularization for deconvolution, two key parameters must be carefully considered, namely λ and μ .

For λ , a larger value leads to a smoother DRT pattern, which may suppress peak intensity or even eliminate peaks, thereby masking relevant electrochemical processes. In contrast, an excessively small λ results in overfitting, amplifying noise, and potentially giving rise to oscillations or pseudo-peaks. The effect of μ is the opposite. An excessively large μ can induce oscillatory behavior, whereas an overly small μ leads to overly broad basis functions, which may smooth out the DRT patterns and obscure the identification of characteristic peaks. Therefore, depending on the measurement conditions and the specific system under investigation, a moderate and well-balanced parameter selection is essential for reliable timescale diagnosis based on DRT analysis.

At this stage, the characteristic kinetic processes appear as distinct peaks in the DRT pattern, where the peak position corresponds to the time constant of a given electrochemical process, enabling a qualitative analysis of interface-related kinetic processes.

Furthermore, a quantitative analysis can be performed. It is noted that, in the DRT pattern, the area of each peak corresponds to the respective polarization resistance. Therefore, the DRT pattern can be fitted using a series of Gaussian peak functions, expressed as:

$$\gamma(\ln\tau) = \sum_{p=0,1,2\dots}^P a_p \cdot \exp\left(-\frac{(\ln\tau - \ln\tau_p)^2}{2 \cdot c_p^2}\right) \quad (7)$$

where a_p refers to the peak height, τ_p refers to the peak center (characteristic time constant), and c_p refers to the standard deviation. The area, A_p , can be calculated as:

$$A_p = a_p \cdot c_p \cdot \sqrt{2\pi} \quad (8)$$

In this way, a quantitative evaluation of characteristic interface-related kinetic processes can be achieved. A general workflow of DRT-assisted kinetic analysis can be found in **Figure 3**.

2.2.3. DRT-Assisted Interface-Related Kinetic Analysis

In the DRT pattern, each peak corresponds to a specific electrochemical process. The interpretation of its underlying physical or chemical origin requires a fundamental understanding of the possible kinetic processes involved in the studied system. Compared with the frequency-domain analysis based on ECM, DRT analysis can reveal fruitful information that is otherwise masked. For unknown electrochemical processes, an initial assignment can be made based on their characteristic time constants, which should then be further validated through carefully designed complementary experiments.^[107]

For both liquid- and solid-state lithium-ion batteries, each component of the system and their interactions may contribute to distinct electrochemical processes. These include interfacial contact at the current collector, diffusion processes within electrode materials, as well as various interfacial phenomena, such as interface formation, side reactions, charge transfer, and ionic transport across grain boundaries in SEs.^[42, 86, 120-121] Representative battery systems and their corresponding electrochemical processes, categorized by their characteristic time constant ranges, are summarized in **Figure 4**.

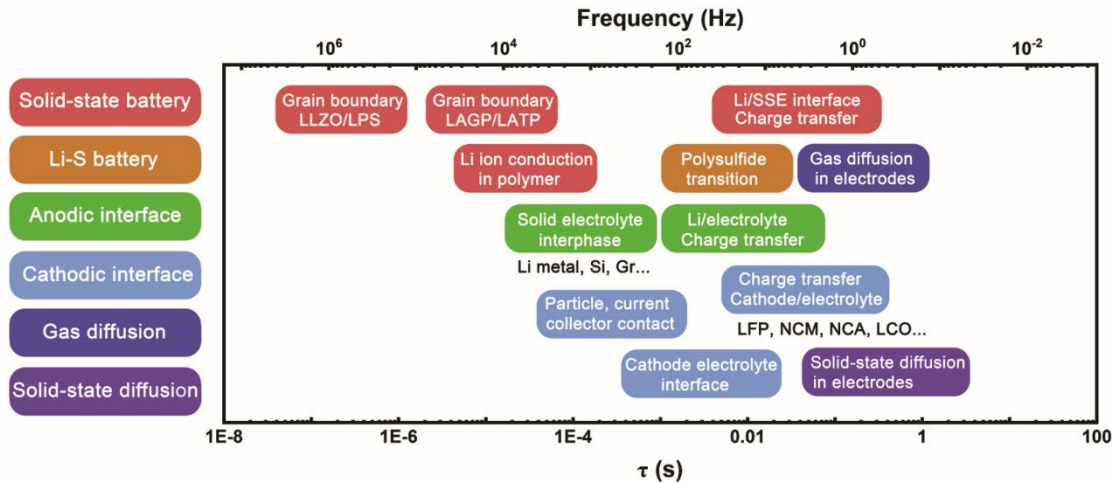


Figure 4. Representative kinetic processes associated with their time constants. Adapted from reference [107].

Focusing on SSBs based on Ni-rich cathodes coupled with SSEs, and for the anode side involves laboratory-scale materials such as LTO or In/InLi, or high energy-density anodes including graphite, Si, and Li metal. Their typical kinetic processes reported in

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the literature can be categorized into different time constant regimes. For SSEs containing grain boundaries, Li^+ transport across grain boundaries exhibits the shortest relaxation times ($< 10^{-6}$ s) and represents the fastest process in the system. The particle-to-particle contact within cathode materials and their contact with the current collector are generally located in the 10^{-6} to 10^{-5} s regime. Typically, ion transport through coating layers or solid electrolyte interface (SEI)/CEI layers occurs in an intermediate time range (10^{-5} to 10^{-2} s), while the charge transfer processes at both cathode and anode fall within the 10^{-3} to 1 s regime. The interparticle contact in Si electrodes is assigned to the 10^{-3} to 10^{-2} s regime. Finally, diffusion processes driven by concentration gradients within electrode materials correspond to the slowest processes (< 1 s).^[42, 47, 121-122]

In fact, by comparing the characteristic time constants of typical energy storage materials (see **Table 1**), it becomes evident that, for the same type of kinetic process, materials commonly used as cathodes, anodes, and even laboratory-scale CE materials exhibit close time constants. This overlap often leads to coupled DRT peaks originating from different electrodes under 2E testing conditions. This issue becomes particularly critical when performance degradation is directly attributed to the WE, while the contribution from the CE cannot be neglected. Therefore, in the following section, the kinetic hindrance arising from the CE will be discussed in detail.

Table 1. A summary of time constants of typical interface-related kinetic processes for energy storage materials.

Materials	Time constant / s	System	Reference
Grain boundary of SSE			
$\text{Li}_6\text{PS}_5\text{Cl}$	$< 1.6 \times 10^{-7}$	SSB	[120, 123]
$\text{Li}_7\text{P}_3\text{S}_{11}$	2.5×10^{-6} (273 K), $> 1.6 \times 10^{-7}$ (298 K)	SSB	[124]
SEI/CEI			
Graphite	$10^{-3} - 10^{-2}$	LIB	[125]
Si	$10^{-5} - 10^{-3}$	SSB	[121]
Li metal	$10^{-3} - 1$	SSB	[120]
NCM	$10^{-5} - 10^{-3}$	SSB	[42, 121]
NCA	$1.6 \times 10^{-4} - 1.6 \times 10^{-3}$	LIB	[126]
LTO	$10^{-5} - 10^{-2}$	SSB	[42, 47]
Li_xIn ($0 < x < 1$)	$10^{-5} - 10^{-2}$	SSB	[42, 47]
Charge transfer			
Graphite	$10^{-2} - 10^{-1}$	LIB	[125]
Si	$10^{-2} - 10^{-1}$	SSB	[121]
Li metal	$10^{-3} - 1$	SSB	[120]
NCM	$10^{-2} - 1$	SSB	[42, 121]
NCA	$10^{-2} - 10^{-1}$	LIB	[126]

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LTO	$10^{-2} - 1$	SSB	[42, 47]
Li_xIn ($0 < x < 1$)	$10^{-3} - 10^{-2}$	SSB	[42, 47]

2.2.4. Kinetic Hindrance from CE

In studies of SSBs, electrochemical characterization is typically conducted based on 2E cell configurations. Among the commonly used materials of the CE, In/InLi, as a representative example, exhibits favorable (electro)chemical stability in contact with SSE and is therefore widely employed as a CE/RE for performance evaluation and interfacial kinetic analysis at the WE. However, recent studies have shown that, in practical operation conditions, the intrinsic stability issues and characteristic kinetic processes of the In/InLi CE itself can interfere with the interpretation of WE behavior during the interfacial impedance analysis, and may even become a non-negligible factor contributing to the apparent performance degradation of the WE.^[42-43]

In the analysis of interface-related kinetic processes and their evolution, as discussed in section 2.2.3, the application of EIS-DRT analysis enables the identification of electrochemical processes in the time domain, where characteristic peaks appear in the DRT patterns. However, when examining the time constants of the involved interfacial processes listed in **Table 1**, it becomes evident that the characteristic time constants of typical CE materials used in SSBs, such as In/InLi and LTO, fall within the range of 10^{-5} to 1 s, which overlaps significantly with those of most energy storage materials, including not only typical cathode materials such as NCM, LFP, and NCA, but also typical anode materials such as graphite and Si.

Specifically, this broad timescale range covers from 10^{-5} to 10^{-2} s, typically associated with SEI/CEI formation (R_{int}), as well as from 10^{-2} to 1 s, corresponding to the charge transfer process (R_{ct}). In particular, the charge transfer process dominating at the CE contributes to the overall impedance and cannot be excluded from the results tested in a 2E configuration. When the interfacial stability of the CE deteriorates significantly, this contribution can strongly interfere with the objective evaluation of WE degradation during cycling. Indeed, performance fading induced by severe degradation of the In/InLi CE, as well as a pronounced increase in R_{ct} at specific SOC, has recently been reported in the literature.^[42] For the analysis of SSB full cells, such as Si|NCM, Kim *et al.* employed 3E measurements combined with EIS-DRT analysis to investigate the kinetics of individual electrodes after cycling.^[121] The results clearly show that almost all DRT peaks associated with both NCM and Si overlap. Specifically, in the 10^{-5} to 10^{-3} s regime, the response is primarily dominated by NCM, whereas in the 10^{-2} to 10^{-1} s regime, the charge-transfer impedance of Si dominates; however, the contribution from NCM in this regime remains non-negligible. Therefore, similar to the ambiguity encountered in assigning semicircles in ECM fitting, a comparable dilemma arises in the interpretation of DRT peaks in 2E systems.

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In addition, another form of kinetic hindrance associated with conventionally prepared foil-stacked In/InLi CE arises from their limited fast kinetics and the progressive deterioration of phase homogeneity within the In/InLi electrode during long-term operation.^[42] Overpotential tracking serves as an effective indicator of kinetic limitations. However, in 2E cell configurations, the overall voltage profile masks the evolution of the overpotential associated with the In/InLi CE.

As recently reported in the literature, both the preparation methods of the indium-lithium alloy and the lithiation approach have a significant impact on their kinetics.^[127-129] The limitation of the In/InLi electrode is mainly attributed to the formation of a Li-depleted, In-rich interfacial layer within the electrode, adjacent to the In/InLi|SSE interface, during delithiation, which hinders Li⁺ transport. For brevity, typical strategies for mitigating the kinetic hindrance arising from the In/InLi CE are not discussed here. The major scope of this work is to identify and objectively evaluate the interfacial kinetic processes for individual electrodes through advanced electrochemical methodologies.

The 3E cell configuration represents the most direct and effective approach to address the above issues. However, the implementation of a reliable RE in solid-state systems remains highly challenging. The development and application of such configurations will therefore be discussed in detail in the following section.

2.3. Three-Electrode Setup Design and Measurement

As discussed in section 2.2.4, the identification and objective evaluation of polarization and interface-related kinetic processes are essential for better understanding the observed fading of electrochemical performance and for assessing interfacial engineering and modification strategies. However, during practical electrochemical measurements, the stability issue and polarization from the CE can exert a non-negligible influence on the evaluation of the WE.^[42, 130] This issue becomes particularly pronounced when measurements are conducted in the conventional 2E half-cell, where the observed response is often implicitly attributed entirely to the WE, potentially obscuring or misinterpreting contributions arising from the CE. Therefore, the introduction of a RE associated with 3E measurements becomes important for probing the electrochemical behavior of individual electrodes in SSB systems.

Against this background, this section first briefly overviews the fundamental concepts of cell configurations. Consequently, the functionality and critical parameters of the 3E cell configuration are discussed. Finally, the challenges of the design and representative 3E setups for SSBs reported in the literature are compared and summarized, providing guidance for experimental design and interpretation in future studies.

2.3.1. Principles and Configurations of Two- and Three-Electrode Cells

In electrochemical studies of lithium-based rechargeable batteries, the electrode represents an essential component of the basic structural unit of a battery, namely the cell. However, depending on the cell configuration and its position, different terminologies and conventions are often adopted to describe the electrodes, reflecting variations in the investigated systems and research objectives. Meanwhile, these terms are closely related across different configurations, which may lead to potential confusion or ambiguity in their usage. Therefore, these fundamental concepts are briefly reviewed and summarized in **Table 2** at the beginning, to establish the conceptual basis for the subsequent discussion.^[131-132]

In fact, the commonly used terminology referring to NCM and LFP, etc., as cathode materials, and graphite, LTO, Si, In/InLi, and lithium metal, etc., as anode materials, is defined based on the redox reactions occurring during discharge. Among these materials, lithium metal represents a special case. In principle, it does not behave as an ideal non-polarizable electrode.^[131, 133] Therefore, when lithium metal is used as a RE or CE/RE in a half-cell setup, it is generally regarded as a pseudo-RE.

When RE is independently introduced as a separate electrode, a 3E cell configuration is established. A comparison between the 3E and 2E cell configuration is shown in **Figure 5**. It can be seen that in a half-cell setup, the WE and CE/RE are part of the same current circuit in a 2E cell configuration. As a result, the recorded voltage corresponds to the potential difference between the WE and the CE/RE, and the potential changes at the individual electrodes cannot be distinguished. This limitation becomes particularly significant when the CE/RE does not exhibit ideal non-polarizable behavior.

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In contrast, in a 3E cell configuration, the RE is not involved in the current circuit between the WE and CE. Therefore, the potentials of the WE and CE can be

Table 2. Terminologies of electrodes used in lithium-based rechargeable batteries.

Term	Brief definition/description
Common terminology in the battery field	
Positive Electrode	The electrode with a higher potential relative to the other electrode
Negative Electrode	The electrode with a lower potential relative to the other electrode
Electrochemical reaction perspective	
Cathode	The electrochemical reaction at the electrode is predominantly reduction. PE = Cathode during discharge; NE = Cathode during charge.
Anode	The electrochemical reaction at the electrode is predominantly oxidation. NE = Anode during discharge; PE = Anode during charge.
Electrochemical measurement perspective	
Working Electrode	In a half-cell setup, the electrode of WE contains the primary material under investigation. Its potential and electrochemical behavior are of interest.
Reference Electrode	In a half-cell setup, RE provides a stable and constant potential, enabling the potential control and measurements of the WE.
Counter Electrode	In a half-cell setup, CE serves only to supply or accept electrons/ions, thereby completing the electric current circuit and supporting the study of the WE. It plays an auxiliary role and is therefore also referred to as the auxiliary electrode. The electrochemical processes occurring at the CE are not the focus of the investigation. In a 2E cell configuration, the CE simultaneously functions as the RE and is therefore often denoted as CE/RE.

Half-cell setup

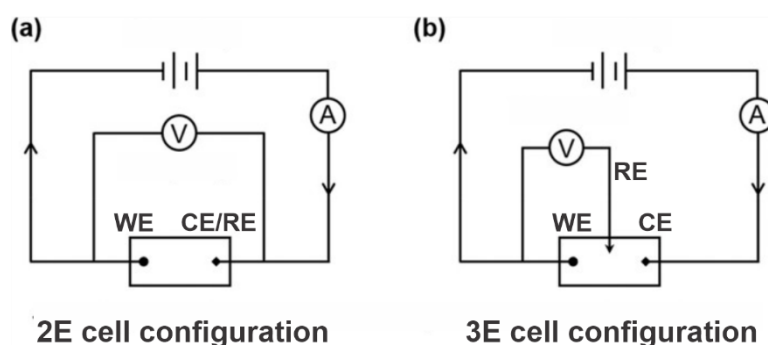


Figure 5. 2E and 3E cell configuration in the half-cell setup. The figure was adapted and modified from the reference [133].

independently measured with respect to the RE. Since the RE only experiences a nA-level current for the measurement, its polarization can be considered negligible.^[133] Consequently, the 3E cell configuration enables the decoupling of the CE contribution during the analysis of the WE under different testing conditions.

It should be noted that, in addition to the two main cell configurations used for electrochemical measurements discussed above, several specially designed functional cell configurations have also been developed to investigate the physicochemical properties of electrode and electrolyte materials, including symmetric cells,^[134-136] electron/ion-blocking cells,^[137-138] four-electrode cells,^[139] and Hebb–Wagner cells.^[140-141] These configurations are not discussed in further detail here.

2.3.2. The Functionality of Three-Electrode Configuration

3E cell configurations have been widely adopted in the development of LIBs. Their applications primarily focus on two key functionalities enabled by the 3E configuration:

- (1) Tracking the potentials of individual electrodes.
- (2) Analyzing the kinetic characteristics of single electrodes associated with the interfaces using electrochemical techniques such as EIS.

On the one hand, typical potential-based applications include characterization and optimization of charge-discharge protocols to avoid lithium plating on anode materials;^[142-144] investigating the rate capability of electrode materials and the influence of operating temperature;^[145-147] evaluating the effectiveness of functional electrolyte additives;^[148-149] and identifying issues such as overcharge/overdischarge arising from electrode aging during cycling.^[147, 150] On the other hand, typical impedance-based kinetic analyses involve the use of EIS-DRT analysis to resolve kinetic processes in porous electrodes at medium and high frequencies;^[113, 151] separating the impedance evolution of cathode and anode materials in terms of their SOC-dependency and during long-term cycling;^[149, 152-154] and identifying the non-negligible influence of the CE on the degradation and impedance analysis of the WE upon cycling.^[130]

Despite the extensive applications in LIBs, the implementation of 3E in SSBs remains significantly challenging due to the difficulties of the 3E cell design in solid-state environments. As a result, their use in SSBs is far less widespread. However, considering that interfacial issues are even more severe in SSBs, the creative design of 3E cells and their use in elucidating the characteristics of the electrode associated with interfacial kinetic processes represent an important research topic. In the following, representative studies reported in the literature that apply the 3E cell configuration for the investigation of SSBs are discussed.

2.3.2.1. Potential Tracking

In applications where a RE is used to track the potentials of the WE and CE in SSBs individually, research mainly focuses on the kinetic limitations of typical anode/CE materials and the behavior of electrodes under different testing conditions. One important research direction is the improvement of fast-charging performance. For example, graphite and silicon anodes possess significant potential in SSB systems, particularly the latter. However, under conditions of high areal capacity and high charging rates, lithium plating and dendritic growth can still be triggered on the graphite surface or at the Si|SSE interface, leading to the risk of internal short circuits. Using 3E measurements, Zhang *et al.* monitored the lithium deposition behavior on structurally modified graphite electrodes and verified that lithium plating could be significantly suppressed on the modified electrode.^[155] Similarly, Cao *et al.* revealed that incomplete alloying reactions in nanosized silicon, together with low electronic conductivity and slow lithium diffusion, lead to sluggish kinetics at high current densities, which subsequently induce lithium plating at the interface. Based on these findings, strategies to improve reaction kinetics were proposed.^[156]

Another important issue arises from the reduction of the upper cut-off potential of the WE caused by CE polarization during high-rate testing. Zhang *et al.* investigated two typical laboratory-scale CE materials, LTO and In/InLi, and demonstrated that their polarization behaviors during cycling exhibit distinct symmetric and asymmetric characteristics as the current density increases. As a result, CE polarization leads to a reduced upper cut-off potential of the WE and prematurely terminated charge-discharge processes.^[42] To avoid overcharge issues caused by inappropriate cell voltage window settings under high areal capacity and large current densities conditions, Dorrer *et al.* conducted rate capability tests of the WE under 3E conditions. With the assistance of the RE, the WE could reach the preset upper cut-off potential, which further enabled a rational adjustment of the cell voltage window for 2E cells.^[157] In addition, in studies employing In/InLi as the CE in SSBs, 3E measurements have been used to investigate and verify the relationship between varied fabricating methods of the indium-lithium alloy and their kinetics.^[128-129]

2.3.2.2. EIS analysis

Regarding kinetics, the application of the 3E measurement plays an important role in studying interfacial degradation in SSBs, particularly when considering that the characteristic interface-related kinetic processes of the WE and CE may overlap in the frequency or time domains. In studies focusing on anode materials, Riegger *et al.* revealed that with LPSCI SSE, the SEI evolution strongly depends on the surface properties of the lithium metal used. Through 3E EIS analysis, the self-limiting and non-self-limiting growth behaviors of the SEI formed under different lithium metal conditions were distinguished and quantitatively analyzed in detail.^[158] Wang *et al.* further explored the SEI passivation layer in lithium metal anodes in solid polymer electrolyte (SPE)-based SSBs. By employing 3E EIS-DRT analysis, they demonstrated that a modified lithium-based composite anode exhibits more uniform SEI growth and stable

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lithium deposition behavior.^[159] Similarly, Fukunishi *et al.* systematically investigated the irreversible lithiation behavior of graphite composite electrodes during the first cycle in SSE-based SSBs and the electrochemical degradation induced by high-temperature cycling.^[160]

In addition, kinetic analyses of cathode materials in SSBs are mainly focused on the qualitative and quantitative evaluation of interface-related electrochemical degradation. For instance, through independent analysis of the WE enabled by 3E measurements, studies have examined the interfacial stability between the SE and the Ni-rich cathode,^[161-162] as well as the significant role of the upper cut-off potential in the evolution of interfacial impedance.^[76]

Overall, the 3E cell configuration enables operando characterization of electrode and interfacial processes, allowing the decoupling of single-electrode information that is otherwise masked in conventional 2E measurements, including electrode potential evolution, impedance characteristics, and polarization development. This capability enables more precise identification of electrochemical degradation mechanisms and makes the 3E approach a practical tool during research in the laboratory-scale.

In fact, although such LIBs have been widely deployed as EV batteries, the 3E cell configuration has not yet been implemented in practical applications. Nevertheless, the RE can function as an implantable potential sensor, which could enable smart battery design and potentially contribute to the development of next-generation intelligent battery management systems (BMS).^[163-166]

2.3.3. Critical Design and Validation Parameters

The core of a 3E cell configuration lies in the incorporation of RE. The selection of the RE material, its geometry, and position within the cell serve as critical design parameters, which collectively determine the quality of the RE and consequently influence the resulting outputs in terms of electrode potentials and impedance measurements.^[133, 167] Furthermore, in order to accurately reproduce the electrochemical behavior observed under conventional 2E testing conditions, the reliability of the results obtained from 3E measurements should be carefully validated using appropriate validation criteria. In the following, the critical design and validation perspective for 3E cell configurations are summarized.

2.3.3.1. Design Parameters

RE Materials

Ideally, non-polarizable electrodes are preferred as REs, meaning that the potential of the electrode remains constant and does not vary with the applied current, corresponding to a stable equilibrium potential as defined by the Nernst equation. However, in practice, electrodes inevitably experience polarization and deviate from their thermo-

dynamic equilibrium potential. Under such circumstances, the RE material should exhibit a high exchange current density, enabling rapid recovery toward equilibrium after perturbation.^[133, 167]

In solid-state systems, due to the intrinsically narrow electrochemical window of SSEs such as LPSCI, the direct use of lithium metal as the RE, or as the CE/RE in a 2E cell configuration, is generally considered unsuitable. Nevertheless, there are reports demonstrating successful 3E measurements using *in situ* plated lithium on wire-type REs as well as lithium for ring-type REs, without showing significant chemo-mechanical failure.^[157, 168] This may be attributed to two factors: (1) when the RE is embedded within the separator, the SEI growth of freshly plated lithium is self-limiting, and the amount of deposited lithium is negligible;^[158] (2) when commercial lithium metal is used as the RE, it is not located within the Li^+ flux pathway, and the SEI growth is spatially constrained.

In SSE-based SSBs, materials widely used as RE or CE/RE include the indium-lithium alloy, as representative lithium-based alloys (others such as Li–Au, Li–Al, Li–Sn, and Li–Bi), as well as intercalation-type materials such as LTO (with others such as LFP).^[133, 167] When they are used as CE/RE in a 2E cell configuration, the lithium content and the areal capacity of the electrode must be carefully adjusted to ensure a stable reference potential throughout the entire charge-discharge process.^[86, 92] In contrast, when used as a RE in 3E cell configurations, careful pre-lithiation is required to achieve a predefined reference potential for subsequent measurements.^[47, 168]

Geometry and Position

Since the geometry and position of the RE are closely related, their selection and design have a significant influence on the functionality and quality of 3E measurements and are discussed together here. Owing to the limited internal space and constrained design flexibility in solid-state systems, some well-established and reliable configurations used in LIBs, such as the T-shaped Swagelok cell, cannot be directly transferred to 3E designs for SSBs.

Reported RE geometries for SSBs include wire-, mesh-, ring-, sheet-, and strip-type designs, with representative setups shown in **Figure 6**.^[157-158, 168-170] The RE can be positioned either embedded within the separator or placed outside the Li^+ flux pathway between the WE and CE. Although certain designs, such as strip- or mesh-type REs, may induce an ion-blocking effect, thereby affecting high-rate performance measurements, most reported 3E setups for SSBs are capable of monitoring the individual electrode potentials reliably under proper conditions.

However, 3E EIS measurements impose tougher requirements on the geometry and position of the RE. Therefore, not all of the aforementioned designs are suitable for achieving reliable impedance measurements or for obtaining high-quality and (quasi-) artefact-free EIS results. Such representative configurations typically involve asymmetric arrangements of the WE, CE, and RE, or designs in which the RE is positioned outside the space between the WE and CE.^[155, 169] Improper size, geometric symmetry

of RE, or misalignment between the WE and CE can lead to locally distorted electric fields, which are a primary source of measurement artefacts.^[167, 171-172]

Among the various designs, mesh-type REs are considered particularly promising for achieving near artefact-free impedance measurements, as they can provide a spatially averaged potential.^[158, 172] Nevertheless, considering the simplicity of manufacturing, wire-type REs remain a practical and widely adopted choice. By reducing the wire diameter, maintaining structural symmetry of the electrodes, and ensuring proper alignment between the WE and CE, wire-type RE-based 3E setups for SSBs can also deliver high-quality EIS results. In addition, the impedance of the RE itself, as well as factors such as the length of measurement cables, are known to contribute to artefacts in the high-frequency region.^[171, 173]

Overall, an ideal 3E setup that can simultaneously satisfy the requirements of potential tracking and EIS analysis requires a multi-dimensional design of the RE. More importantly, the purpose of 3E measurements is to unveil the electrochemical “black box” in 2E cell configurations, which presupposes the ability to faithfully mimic the electrochemical processes occurring under 2E testing conditions. Therefore, the validation of the reliability and durability of the RE in the 3E configuration, as well as an objective comparison of the electrochemical performance obtained from 2E and 3E measurements under identical testing conditions, are essential steps. Accordingly, it is recommended that the designed 3E setup and the resulting measurements be evaluated from the following three validation perspectives.

2.3.3.2. Validation Perspectives

(1) Monitoring the Drifting of the Reference Potential

Due to the limited thermodynamic stability of RE materials in some of the solid electrolyte environments, lithium dissolution from alloy-based REs, and the influence of testing temperature, the potential of the RE may gradually drift during prolonged operation time.^[47, 174] A qualified RE should exhibit a stable reference potential over a certain period, with any deviation occurring as a gradual fading process rather than an abrupt shift. Monitoring the potential drift of the RE is therefore a crucial step, particularly in such applications, where the conclusions are primarily derived from potential tracking. An objective evaluation and effective correction of RE potential drift can significantly improve the fidelity with which the true electrochemical behavior is captured. In addition, appropriate *in situ* recalibration strategies, such as re-lithiation, should be considered.

(2) Performance Gap Between 2E and 3E Measurements

Considering the challenges associated with introducing the RE in solid-state systems, it is inevitable that the thickness of the separator layer increases and that the RE itself introduces an ion-blocking effect.^[175] These factors are unfavorable for 3E measurements under large dynamic conditions. Under scenarios such as high C-rate operation or lithium plating investigations, significant electrochemical performance gaps may

arise between 2E and 3E measurements, mainly due to additional ohmic polarization and possible kinetic hindrances. This discrepancy can affect the reliability of performance evaluation and the determination of critical failure thresholds based on 3E potential tracking. Therefore, when the potential of electrodes is used as a key criterion, the performance gap between 2E and 3E configurations must be carefully considered.

(3) Consistency Between Summed WE/CE Impedance and 2E Impedance

The impedance of the WE and CE can be measured independently under 3E conditions, and their sum can be compared with the impedance obtained from the 2E configuration. This comparison serves as an important indicator for evaluating the quality of 3E impedance data. In practice, perfect agreement is rarely achieved due to external factors such as the measurement environment, electrical contacts, and temperature variations. Deviations are typically observed in the high- and low-frequency regions. However, in SSBs, interface-related kinetic processes are generally located in the mid-frequency range. Therefore, a quantitative assessment of the deviation between 2E and 3E measurements, together with a targeted qualitative and quantitative analysis within the frequency range of interest, represents a rational approach for impedance analysis based on 3E configurations.^[167-168]

2.3.4. Challenges and Representative 3E Setup Designs for SSBs

The design of 3E setups in solid-state systems faces significantly more challenges and constraints compared to liquid-based systems. Even for 2E cell configurations, a fully standardized setup or commercialized format has not yet been established.^[176] As a result, testing cells vary substantially among different research groups, making the extension toward 3E cell configurations inherently case-dependent.

Moreover, for different types of SE, the pronounced differences in mechanical properties and cell assembling procedures lead to distinct requirements for design parameters of RE. For example, when selecting RE materials, their chemical compatibility with the SE must be carefully considered. In addition, when setting the potential of RE, approaches such as *in situ* pre-lithiation may introduce additional challenges, including mechanical failure caused by volume expansion and interfacial side reactions induced by local redox reactions.

For both the assembling and operation of SSBs, the application of high external pressure is often necessary to ensure proper interfacial contact. However, the introduction of a RE and its corresponding placement can significantly increase the likelihood of structural instability, potentially leading to issues such as internal short circuits. Furthermore, due to the spatial constraints within SSBs, the design of the RE tends toward miniaturization.

Overall, the design and validation of 3E configurations for SSBs represent a system-level engineering challenge. As summarized in **Figure 6**, representative 3E designs reported in the literature, particularly for SSE-containing designs, are presented. Each

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design demonstrates distinct features in terms of RE material, position, or geometry, thereby providing valuable insights and inspiration for the development of more advanced 3E configurations for SSBs.

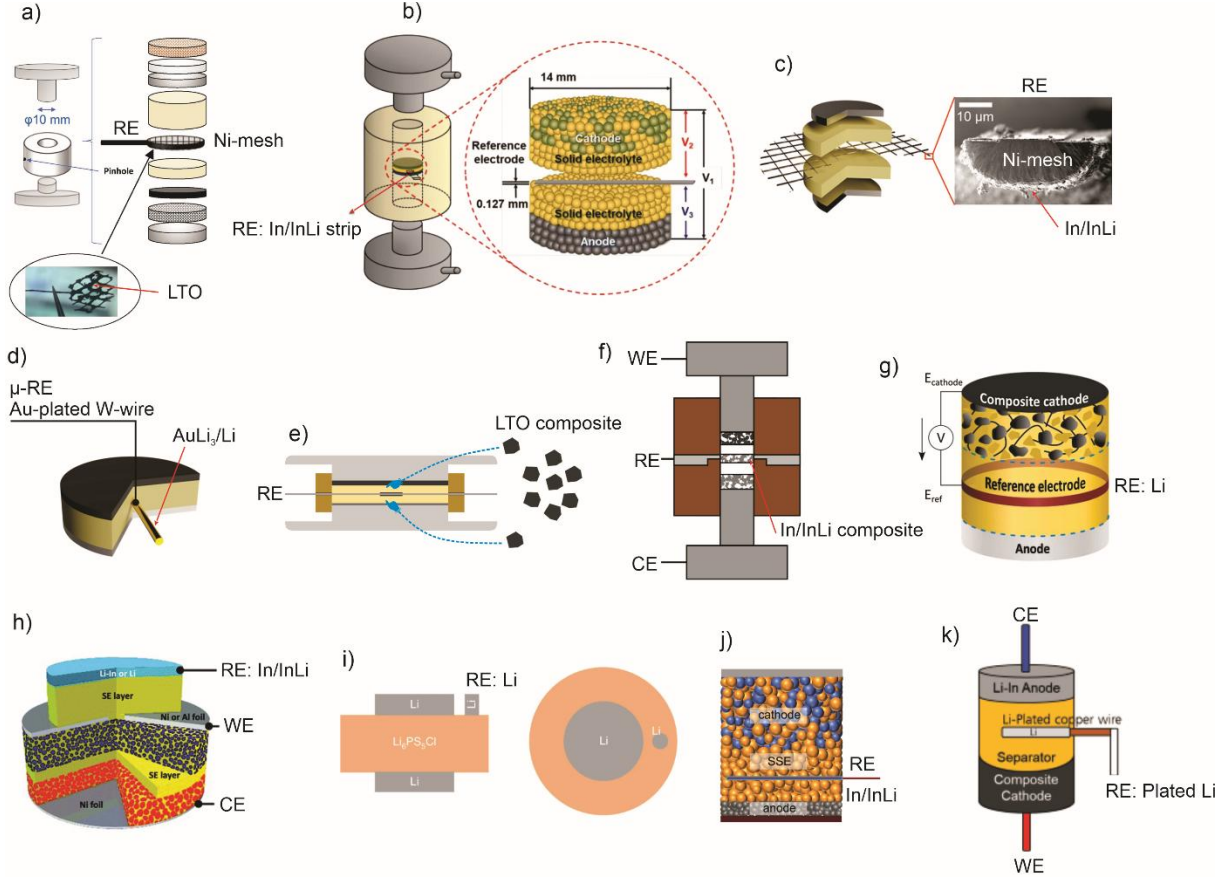


Figure 6. Representative 3E setups for SSE-based SSBs. (a) Chemically pre-lithiated LTO coated Ni-mesh as RE. (b) In/InLi strip as RE. (c) In/InLi-coated Ni-mesh as RE. (d) *In situ* lithiated Au-plated W-wire as RE. (e) Electrochemically *ex situ* lithiated LTO composite as wire-type RE. (f) In/InLi composite as RE. (g) Ring-type lithium metal as RE. (h) In/InLi foil as RE. (i) Li metal as RE, RE was placed next to WE on the SSE separator. (j) In/InLi plated Cu-wire as RE. (k) Li plated Cu-wire as RE. Figures were adapted and modified from Ikezawa *et al.* for (a),^[177] Chang *et al.* for (b),^[170] Riegger *et al.* for (c),^[158] Hertle *et al.* for (d),^[168] Zhang *et al.* for (e),^[47] Dugas *et al.* for (f),^[178] Doerr *et al.* for (g),^[157] Nam *et al.* for (h),^[169] Kasemchainan *et al.* for (i),^[179] Fan *et al.* for (j),^[180] and Yanev *et al.* for (k).^[128]

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3.1. Investigation of Degradation at the CAM|SSE Interface and Novel Nanoparticle Coatings

In SSBs employing Ni-rich cathodes coupled with SSEs, the microstructure and composition of the CAM|SSE interface, as well as strategies to enhance its stability, have long been central research topics. Interfacial degradation is among the key factors limiting the electrochemical performance of SSBs. The characterization of decomposition interphases typically involves multiple aspects and complementary techniques. From a microstructural perspective, focused ion beam-scanning electron microscopy (FIB-SEM) enables direct observation of physical contact failure at the interface, while high-resolution TEM (HRTEM) allows atomic-scale visualization of interfacial layers with thicknesses on the order of several tens of nanometers. From the standpoint of chemical composition and oxidation states of interfacial reaction products, techniques such as X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (TOF-SIMS), and electron energy loss spectroscopy (EELS) can be employed to identify decomposition products from the SSE, oxygenated phosphorus/sulfur species, as well as their oxidation states, and further to elucidate their spatial distribution. DEMS, as an *operando* characterization technique, provides access to gaseous products generated by interfacial side reactions, thereby deepening the understanding of the electrochemical stability between Ni-rich cathodes and SSEs. Finally, for qualitative and quantitative analysis of interfacial kinetics, EIS-DRT analysis serves as a nondestructive tool that can be used to directly correlate the interface-related kinetic processes with electrochemical performance. Such multi-scale and multi-technique characterization approaches have been widely applied to the study of interfacial failure in SSBs and are extensively reported in the literature.

When the focus is narrowed to interfacial layers with thicknesses of only several tens of nanometers, the oxidation state and spatial distribution of key elements within the interphase become critical points of interest. At this length scale, only TEM offers the spatial resolution required for meaningful analysis. More importantly, the SSEs and sulfur-containing interphases investigated here are extremely sensitive to electron irradiation, air, and moisture. This imposes strict requirements on both sample preparation and characterization conditions and implies that, during conventional lamella preparation and TEM analysis, beam damage can lead to discrepancies between the actual interfacial structure and the observed results, potentially obscuring underlying degradation mechanisms.

Therefore, in **Publication I**, we employed cryogenic conditions throughout the entire workflow: from lamella preparation via cryo-FIB to cryo-TEM characterization to minimize beam-induced damage to the interface. This approach enabled reliable analysis of the interfacial layer, as well as the adjacent regions. Through EELS line scans and point analyses, we provided experimental verification of TM dissolution and interdiffusion in a solid-state electrolyte system, a phenomenon that has rarely been reported

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in this context. Furthermore, we revealed long-range TM migration, which was found to exert a poisoning effect on the SSE within the catholyte.

Given the intrinsically narrow electrochemical stability window of SSEs and their limited tolerance toward interdiffusion between TM, sulfur, and phosphorus species, two interfacial engineering studies based on a novel nanoparticle coating concept were further explored during my PhD research. Although not constituting the core focus of this dissertation, these studies are closely related to the overall research framework and are presented as **Publication II** and **Publication III**, using HfO_2 and $\text{HfO}_2/\text{Li}_2\text{HfO}_3$ nanoparticle coatings, respectively. Compared with their bare counterparts, the coated Ni-rich cathodes exhibited pronounced improvements in electrochemical performance.

3.1.1. Publication I: Transition-Metal Interdiffusion and Solid Electrolyte Poisoning in All-Solid-State Batteries Revealed by Cryo-TEM

As the first core investigation in this doctoral thesis, cryo-FIB and cryo-TEM were applied to characterize the CAM|SSE interface. The primary objective was to analyze the as-formed interface/interphase owing to the electrochemical degradation, with particular emphasis on the oxidation state of key elements. Based on oxidation products suggested by prior experimental and computational studies, the degradation mechanisms at the interface and in adjacent regions were systematically investigated.

In this work, PC NCM85 was employed as the CAM, together with LPSCI as the SSE, and LTO composite was applied as the anode for the electrochemical testing. To deliberately amplify interfacial failure induced by electrochemical degradation, no surface coating was applied to the CAM. The cathode electrode was prepared via a slurry-casting method using 1 wt.% PIB as the binder and *o*-xylene as the solvent.

Electrochemical results show a relatively low initial Coulomb efficiency (ICE: 82%), which can be attributed to the absence of surface coating on the CAM, while the charge/discharge capacities from low to high C-rates remained as expected. After long-term cycling at 1C, the capacity retention remained excellent, with nearly no observable decay. Notably, during the later stages of cycling, a continuous decrease in CE was observed, indicating the occurrence of pronounced side reactions within the cell.

Cryo-TEM combined with EELS analysis was subsequently employed to perform an in-depth characterization of the cycled samples in the vicinity of the interface. Five representative locations, denoted as P1 to P5, were selected for detailed analysis, covering the bulk CAM, the as-formed CAM|SSE interface, the SSE region approximately 100 nm away from the interface, and regions far from the interface within the SSE (around 1 μm). Leveraging the high spatial resolution of EELS and its capability to resolve elemental oxidation states, particular attention was paid to oxygen and the transition metals (TM) Ni, Co, and Mn within these selected regions. The results led to several key conclusions. (1) Even in a solid-state system, TM elements can dissolve into the solid electrolyte, with diffusion extending beyond the interfacial layer and leading to poisoning of the SSE. (2) TMs were found to exist in reduced oxidation states at the interface and even in the SSE regions far from the interface, indicating interdiffusion with sulfur and phosphorus species and supporting previous experimental and computational reports on the formation of sulfides and oxygenated phosphorus/sulfur species. (3) Energy-dispersive X-ray spectroscopy (EDS) mapping revealed that mobile sulfur-containing compounds are able to penetrate into intergranular cracks within the PC NCM85 particles, even under solid-state conditions.

The significance of this work lies in the identification of new possible degradation pathways in SSBs. In particular, the as-formed interphase at the interface and the dispersed species within the SSE, which may exhibit MIEC characteristics, are likely to be closely associated with the continuous and accelerated deterioration of side reactions. These

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findings further highlight the necessity of interfacial engineering strategies aimed at suppressing TM dissolution and interdiffusion.

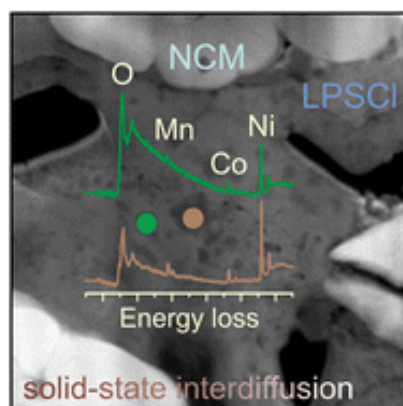
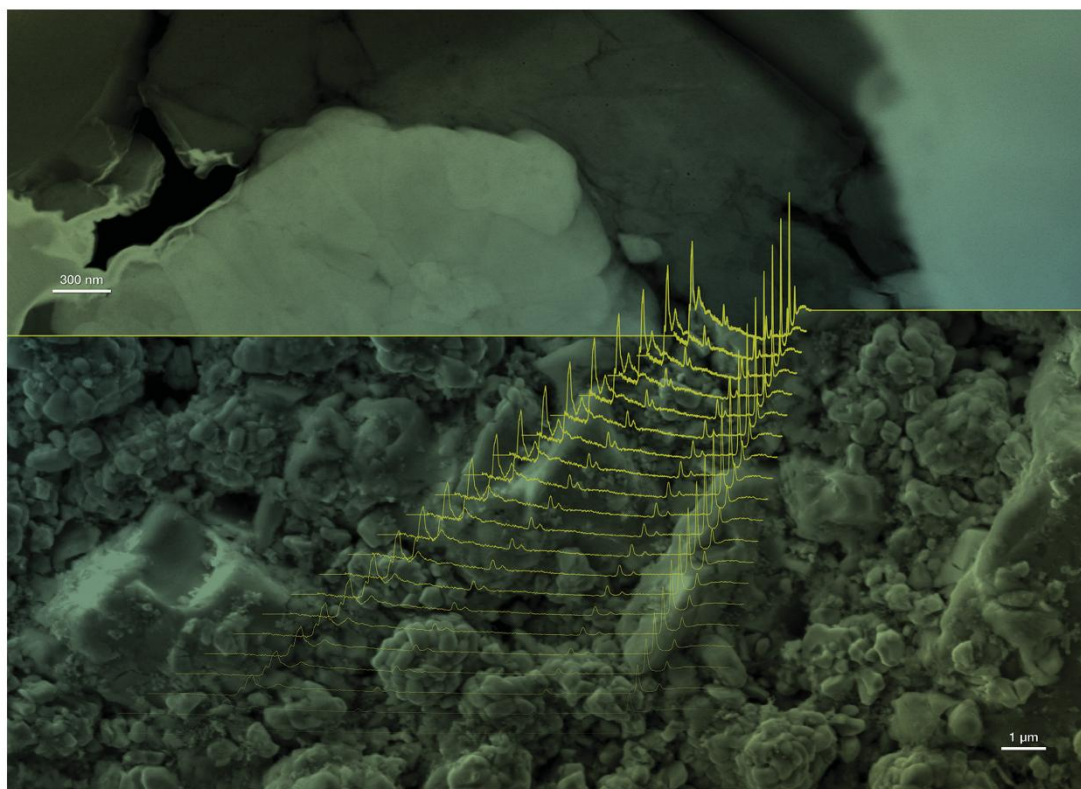


Figure 7. Table of contents graphic of Publication I. Adapted from reference [45].

The experiments were designed and planned by the first author R. Zhang, under the supervision of J. Janek, A. Kondrakov, and T. Brezesinski. Cryo-FIB and cryo-TEM measurements were conducted at Thermo Fisher Scientific (Eindhoven, Netherlands). The first author prepared the cathode tape, conducted the electrochemical testing, harvested the samples, and performed the data analysis. L. Li conducted the preparation of the lamella by cryo-FIB. L. Jiang and L. Casalena carried out the cryo-TEM measurements with the assistance of R. Zhang. The gathered data were analyzed by R. Zhang, L. Jiang, and L. Li. R. Zhang, F. Strauss, and T. Brezesinski discussed the data and established the mechanism. F. Strauss supported the design of figures. The draft was written by R. Zhang and further polished by F. Strauss. The final version of this manuscript was then edited by all co-authors.

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Showcasing research from the Battery and Electrochemistry Laboratory (BELLA), Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), Germany.

Transition-metal interdiffusion and solid electrolyte poisoning in all-solid-state batteries revealed by cryo-TEM

Scanning transmission electron microscopy investigations under cryogenic conditions into the degradation of thiophosphate-based all-solid-state batteries not only reveal interphase formation, due to side reactions between solid electrolyte and cathode material during cycling, but also transition metal dissolution and solid electrolyte poisoning.

As featured in:



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Torsten Brezesinski *et al.*,
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Transition-metal interdiffusion and solid electrolyte poisoning in all-solid-state batteries revealed by cryo-TEM†

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Using scanning transmission electron microscopy, along with electron energy loss spectroscopy, under cryogenic conditions, we demonstrate transition-metal dissolution from a layered Ni-rich oxide cathode material and subsequent diffusion into the bulk of a lithium thiophosphate solid electrolyte during electrochemical cycling. This problem has previously only been considered for liquid-electrolyte-based batteries.

Solid-state batteries (SSBs) hold great promise as a next-generation energy storage technology for powering future portable electronics and electric vehicles. This is due in part to their potentially superior energy and power densities and improved safety over conventional batteries.¹ However, commercial implementation is plagued by detrimental interfacial side reactions occurring at the cathode and anode, causing performance decay and ultimately cell failure.^{2–5} Many efforts have been made to reveal the underlying degradation mechanisms and to prevent or alleviate such intrinsic problems.^{6–8} The solid and gaseous degradation products formed during cycling at the interface between the cathode active material (CAM) and superionic solid electrolyte (SE) are usually probed using techniques such as X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS) and differential electrochemical mass spectrometry (DEMS).^{9–12} The latter techniques, however, have limited spatial resolution capabilities. To gain detailed insights into the composition and structure

of the CAM/SE interface (decomposition interphase), transmission electron microscopy (TEM) appears to represent the method of choice.¹³ Unfortunately, sulfide-based SEs are prone to beam damage (degradation),¹⁴ and they are also highly reactive towards ambient atmosphere (moisture/oxygen), thereby complicating specimen preparation procedures.¹⁵ To overcome these hurdles, sample handling under inert atmosphere and microscopy investigation, including TEM lamella sample preparation, at cryogenic temperature are required. Following this, here we study the evolution of the cathode interface/interphase in bulk-type SSB cells using a non-coated LiNi_{0.85}Co_{0.1}Mn_{0.05}O₂ (NCM851005) CAM and an argyrodite Li₆PS₅Cl SE via scanning TEM (STEM) in combination with energy-dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS).

The cathode was prepared by slurry casting (see ESI† for details) and tested in pellet-stack cells with a Li₄Ti₅O₁₂ anode. The areal CAM loading was around 9.4 mg cm^{−2}. Representative voltage profiles for the first and second cycles at a rate of 0.1C are depicted in Fig. 1a. They are typical of Ni-rich NCM CAMs. In the initial cycle, specific charge and discharge capacities of about 233 and 192 mA h g^{−1} were achieved, corresponding to a Coulomb efficiency (CE) of 82%. The cells delivered a similar capacity of $q_{\text{dis}} \approx 191 \text{ mA h g}^{-1}$ in the second cycle, and the CE increased to 98%. After the first two cycles, the rate capability was tested (Fig. 1b). To this end, the C-rate was increased in a stepwise manner from 0.2C ($q_{\text{dis}} \approx 179 \text{ mA h g}^{-1}$) to 2C ($q_{\text{dis}} \approx 99 \text{ mA h g}^{-1}$) (Fig. S1, ESI†), followed by cycling at 1C for 150 cycles. As can be seen from the data, there was no significant capacity fading over the first 160 cycles despite the absence of a protective surface coating on the CAM secondary particles. The CE stabilized above 99.9% during long-term cycling, with some decay towards 99.8% after around 100 cycles due to continuous (but relatively minor) SE decomposition.

For cryo-TEM analysis, cycled cells in the discharged state were disassembled and specimens from the cathode side were prepared by focused-ion beam (FIB) slicing. An illustration of

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† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d3cc00516j>

Communication

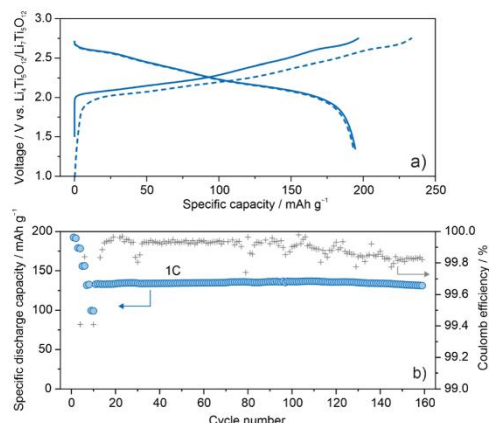


Fig. 1 Cycling performance of the slurry-cast cathode in pelletized SSB cells at 45 °C. (a) First- and second-cycle voltage profiles at 0.1C are shown as dashed and solid lines, respectively. (b) Specific discharge capacities over 160 cycles, including a rate capability test in the beginning of cycling (see ESI† for details), and corresponding Coulomb efficiencies.

the workflow process is shown in Fig. S2a–e (ESI†). Low-magnification images of a FIB-cut lamella are presented in Fig. S3a and b (ESI†), showing no signs of cracking or delamination. The interface region of interest (ROI) between CAM and SE, indicated by arrows in Fig. 2a, was probed using STEM [primarily in high-angle annular dark-field (HAADF) mode] and EDS. As shown in the inset of Fig. 2a, a mostly amorphous decomposition layer of approximate thickness 10 nm had formed after cycling. Such an interphase was not visible for the pristine cathode (Fig. S4a, ESI†). EDS mapping was conducted to reveal the elemental distribution across the CAM/SE interface (Fig. 2b). Both Ni and O are evenly distributed throughout the CAM particle (Fig. 2c and d), whereas the S and Cl maps show a non-uniform distribution (Fig. 2e and f). Increased signal intensity is evident near the interface region, which is corroborated by the O, S and Cl overlap map in Fig. 2g. The ion accumulation at the ROI originates from the (electro)-chemical SE decomposition during cycling (also considering oxygen release from the CAM at high states of charge), leading to the formation of LiCl, polysulfides and oxygenated phosphorus and sulfur species, to name some degradation products, as determined by XPS and ToF-SIMS in recent years.^{9,12,16–18} This is in contrast to the pristine cathode, where clear spatial separation of elements points towards the presence of a well-defined (“clean”) CAM/SE interface (Fig. S4b–f, ESI†).

EELS was conducted on three different spots, the CAM (P1), the CAM/SE decomposition interphase (P2) and the SE (P3), as can be seen in Fig. 3a. The corresponding energy loss spectra are depicted in Fig. 3b. For P1 and P2, the O K-, Mn L-, Co L- and Ni L-edges are clearly visible, and even for P3, weak signals pertaining to the transition metals (TMs) can be observed. This result suggests that TM dissolution occurs

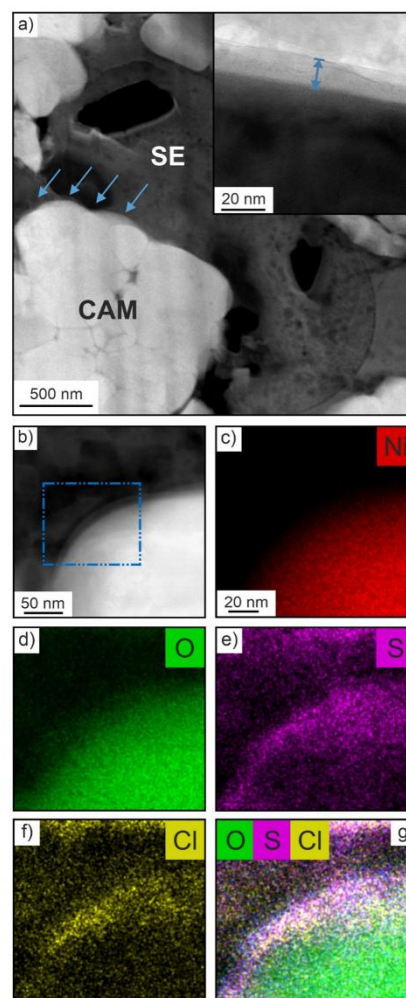


Fig. 2 Cross-sectional cryo-STEM/EDS analysis of the cycled cathode. (a) HAADF overview image showing both CAM and SE, with the interfacial ROI denoted by arrows. The inset is a high-magnification annular bright-field image of the decomposition interphase. (b) HAADF image of the CAM/SE interface and (c–g) elemental maps from EDS for Ni, O, S and Cl of the area indicated by the rectangle in (b).

during battery operation (apparent detection of TM species in the decomposition interphase and within the argyrodite SE). Note that the O K-edge is also detected for P3, either due to the presence of impurities or oxygen incorporation from the CAM, which is the only source of oxygen in the electrode. Wang *et al.* recently reported signs of TM dissolution into a $\text{Li}_{10}\text{Si}_{0.3}\text{PS}_{6.7}\text{Cl}_{1.8}$ SE, in agreement with our findings.¹⁹



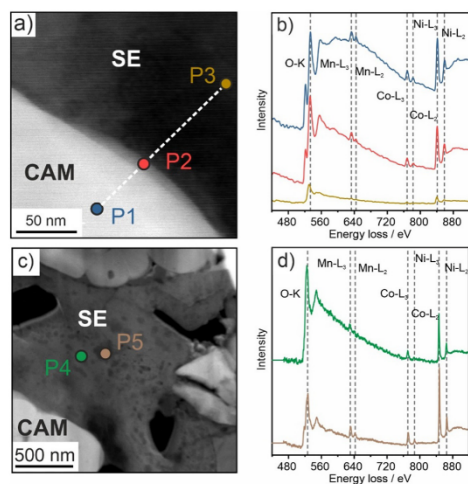


Fig. 3 (a) High-magnification HAADF image of the CAM/SE interface, with the highlighted areas probed by EELS, and (b) corresponding energy loss spectra. (c) Low-magnification HAADF image of the bulk SE in the cycled cathode and (d) corresponding energy loss spectra collected from the areas denoted in (c). The O K- and TM L-edges are indicated by dashed lines in the spectra.

To gain further insights into the morphological evolution of the cathode, low-magnification STEM images were taken prior to and after cycling. As is evident from the data in Fig. S5a and b (ESI†), the SE appearance changes from uniform to non-uniform with cycling. Brighter and darker areas/spots are visible all over the SE, hinting at different relative densities. For this reason, EELS was conducted on two representative areas, denoted as P4 (bright) and P5 (dark) in Fig. 3c. The K- and L-edges that can be assigned to O and Ni, Co and Mn, respectively, are apparent in the corresponding spectra in Fig. 3d. Because the areas probed were more than 500 nm away from the CAM secondary particles, this provides evidence for TM dissolution and subsequent diffusion into the bulk of the SE. In conventional liquid-electrolyte-based Li-ion batteries (LIBs), TM dissolution has been shown to be detrimental to the cycling performance by poisoning of the graphite anode, among others.^{20–23} However, a similar effect in SSBs has not been reported yet. To compare the oxidation numbers for all of the TM species in the different areas, the EELS data were analyzed in some more detail. In particular, the L_3/L_2 ratios from the integrated peak areas were calculated (see ESI† for details and Fig. S6) for Mn, Co and Ni.^{24,25} The results are given in Table S1 and depicted in Fig. S7 (ESI†). For the CAM (P1 in Fig. 3a), Ni/Co and Mn were determined to be in +3 and +4 state, respectively, as usually observed for Ni-rich NCM-type materials.²⁶ Both Ni and Co remained on average in +3 state in the CAM/SE interface region (P2 in Fig. 3a), whereas the slightly increased L_3/L_2 ratio for Mn suggests partial reduction towards mixed +4/+3 states. In contrast, for the SE at a distance around

100 nm away from the interface (P3 in Fig. 3a), the L_3/L_2 ratio increased for all three TMs, especially for Co and Ni. This is indicative of distinct reduction of Co and Ni from originally +3 to +2 state. The data also suggest partial reduction of Mn to mixed +3/+2 states.^{24,27,28} In the bulk SE (P4 and P5 in Fig. 3c), *i.e.*, several hundreds of nanometers away from the interface, areas of different appearance/contrast were detected by STEM (Fig. S5a and b, ESI†), as described above. As expected, analysis of the L_3/L_2 ratios revealed differences in the oxidation numbers. Mn was found to be present in states ranging from +4 to +2 and Ni from +3 to +2. By contrast, Co was closer to +2 state. Taken together, the results corroborate the inhomogeneous nature of the SE after cycling. More in-depth characterization, including phase identification, is very challenging though. Nevertheless, it can be assumed that TM-containing oxide and sulfide species are formed.^{3,9,19,29}

In addition, the difference in energy loss between the O K-edge and the pre-edge (referred to as ΔE hereafter) can be considered. As shown in Table S1, ΔE decreased from 12.0 eV for P1 (CAM) to 8.7 eV for P5 (bulk SE) [$\Delta E = 10.8$ eV for P2 (CAM/SE interface region)], thus confirming TM reduction upon dissolution/diffusion.³⁰

Apart from that, we also noticed sulfur diffusion into the CAM secondary particles. Fig. 4a–d shows a high-magnification HAADF image of a fractured NCM851005 particle and elemental maps from EDS for Ni and S. The spectra collected from the different areas denoted in Fig. 4d reveal an increased sulfur signal for the grain boundary region (Fig. 4e), corroborating sulfur accumulation in the particle interior. We hypothesize that this is related to the mechanical degradation of the CAM and the (electro)chemical SE oxidation during cycling, leading to a loose grain boundary structure and formation of mobile species. Similar observations (Cl/P accumulation) have been made recently.^{31,32}

In summary, we have demonstrated that not only interphase formation occurs at the CAM/SE contact points in thiophosphate-based SSBs, but also distinct TM dissolution and diffusion into the bulk of the SE. Although the dissolution (and migration/deposition) of TM species from NCM materials in liquid-electrolyte-based LIBs is a well-known and understood phenomenon, to our knowledge, it has not received attention in prior research on solid-state cells. Our data emphasize the highly dynamic nature of thiophosphate-based SSBs, with (electro)chemically driven solid-state interdiffusion reactions occurring during cycling. Taken together, the findings uncover a previously unknown degradation mechanism that needs to be considered in future SSB research and development. It may well be that TM interdiffusion is responsible, at least to some degree, for electro-chemo-mechanical degradation and fracture processes. Further studies are needed to clarify this (including elucidating the driving force for TM dissolution/diffusion) and also to determine if protective surface coatings on the CAM particles are capable of suppressing SE poisoning by preventing direct contact between CAM and SE. Apart from that, it is unclear if similar effects would occur in SSBs using organic, hybrid or other types of inorganic SEs (oxide, halide *etc.*).



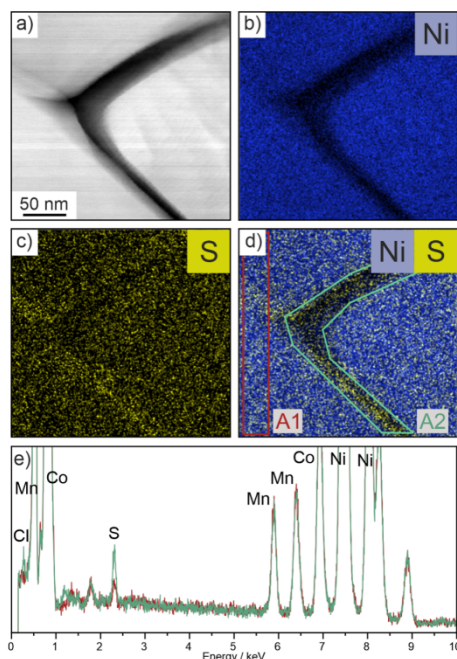


Fig. 4 (a) High-magnification HAADF image of a cycled CAM particle showing intergranular fracture and (b–d) corresponding elemental maps from EDS for Ni and S. (e) Spectra collected from the areas A1 and A2 indicated in (d).

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Conflicts of interest

There are no conflicts to declare.

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3.1.2. Publication II: Single-to Few-Layer Nanoparticle Cathode Coating for Thiophosphate-Based All-Solid-State Batteries

Based on the knowledge obtained from **Publication I**, interfacial engineering becomes a necessary step for cell configurations using Ni-rich cathodes coupled with SSEs. Inspired by a novel NP coating strategy, we further explored the feasibility of employing HfO₂ NPs as single- to few-layer coatings on the CAM surface.

Building on a favorable workflow previously established using ZrO₂ NPs for NCM85, **Publication II** successfully extended this strategy to the implementation of well-dispersed HfO₂ NPs. PC NCM85 and LPSCI were used as CAM and catholyte, respectively, with the latter also serving as the separator. An LTO-based composite electrode was employed as the anode.

The key to achieving interfacial stabilization and enhanced electrochemical performance through a nanoparticle coating strategy lies in obtaining a uniform and conformal coating. Realizing this requirement critically depends on achieving good dispersion of the NPs in the solvent. However, as-prepared NPs typically exhibit high surface energies, leading to pronounced agglomeration, which makes subsequent dispersion in solvents highly challenging. Moreover, the dispersion strategy must be tailored on a case-by-case basis for different materials. Therefore, the first focus of this work was on the dispersion of as-prepared HfO₂ NPs. Unlike the treatment used for ZrO₂, well-dispersed HfO₂ NPs were achieved, based on prior reports, by synergistically employing two surfactants (oleic acid + oleylamine) to stabilize the NPs in chloroform.^[181] By optimizing the coating parameters, including content and calcination conditions, the most pronounced performance enhancement was achieved for 0.83 wt.% HfO₂-coated NCM85 calcined at 400 °C in an oxygen atmosphere.

The results indicate that the coating has a thickness of approximately 11 nm and that the NPs are uniformly deposited on the CAM surface. Galvanostatic cycling tests conducted on pelletized cells showed that the initial specific discharge capacity at 0.1C and the Coulomb efficiency reach 203 mAh/g and 90%, respectively, which are significantly higher than those of the uncoated counterpart (175 mAh/g and 79%). During long-term cycling at 0.2C, the HfO₂-coated NCM85 maintained a capacity retention of 69% after 200 cycles. In-depth interfacial characterization further demonstrated that the HfO₂ NP coating effectively suppresses detrimental (interfacial) side reactions and enhances the microstructural stability of the cathode during cycling. Notably, in further cathode optimization, the use of a glassy SSE (1.5Li₂S–0.5P₂S₅–LiI) combined with slurry-cast cathode fabrication enabled both high areal capacity and excellent capacity retention (~2.3 mAh/cm² and 94% after 200 cycles). This improvement can be attributed to more intimate interfacial contact and the stabilizing contribution of the binder to the electrode structure during cycling.

3. Results

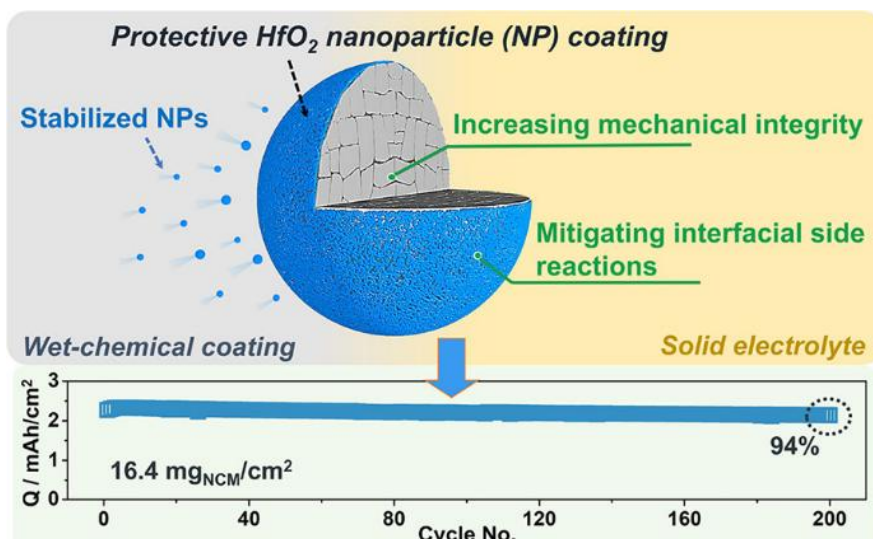


Figure 8. Table of contents graphic of Publication II. Adapted from reference [44].

Publication II has a shared first authorship between Y. Ma and R. Zhang. The experiments were designed by Y. Ma under the supervision of J. Janek, M. Bianchini, and T. Brezesinski. R. Zhang synthesized the HfO_2 NPs, dispersed them in chloroform, conducted the CAM coating, prepared the cathode tape, performed the electrochemical tests as well as the X-ray diffraction (XRD) measurements. Y. Ma conducted the SEM measurements. Y. Tang performed the cross-sectional imaging by FIB and TEM measurements. J.H. Teo and T. Diemant conducted the DEMS and XPS measurements, respectively. D. Goonetilleke conducted the *operando* XRD, refined and analyzed all XRD results. Y. Ma and R. Zhang analyzed and interpreted the results with all co-authors. The first draft was mainly written by Y. Ma, with support by R. Zhang. The final paper was edited by all co-authors.

Single- to Few-Layer Nanoparticle Cathode Coating for Thiophosphate-Based All-Solid-State Batteries

Yuan Ma,^{*,#} Ruizhuo Zhang,[#] Yushu Tang,^{*} Yanjiao Ma, Jun Hao Teo, Thomas Diemant, Damian Goonetilleke, Jürgen Janek, Matteo Bianchini, Aleksandr Kondrakov, and Torsten Brezesinski^{*}



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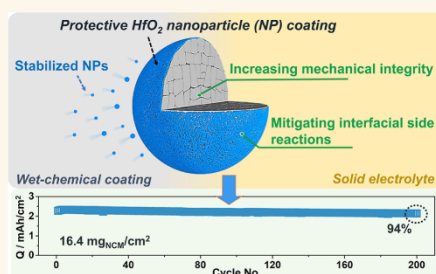
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Supporting Information

ABSTRACT: Bulk-type solid-state batteries (SSBs) composed of lithium thiophosphate superionic solid electrolytes (SEs) and high-capacity cathode active materials (CAMs) have recently attracted much attention for their potential application in next-generation electrochemical energy storage. However, compatibility issues between the key components in this kind of battery system are difficult to overcome. Here, we report on a protective cathode coating that strongly reduces the prevalence of detrimental side reactions between CAM and SE during battery operation. This is demonstrated using preformed HfO_2 nanoparticles as a secondary particle coating for a layered Ni-rich oxide CAM, $\text{Li-Ni}_{0.85}\text{Co}_{0.1}\text{Mn}_{0.05}\text{O}_2$ (NCM85). The preparation of a stable dispersion of the HfO_2 nanoparticles enabled the deposition of a uniform coating of thickness ≤ 11 nm. When incorporated into $\text{Li}_6\text{PS}_4\text{Cl}$ -based, pellet-stack SSBs, the coated NCM85 showed superior performance in terms of reversibility, cell capacity, longevity, and rate capability over its uncoated counterpart. The effectiveness of the protective coating in mitigating electro-chemo-mechanical degradation was investigated using a suite of physical and electrochemical characterization techniques. In addition, the adaptability to wet processing of the coated NCM85 is demonstrated in slurry-cast SSBs and liquid-electrolyte-based Li-ion cells.

KEYWORDS: solid-state battery, secondary particle coating, Ni-rich cathode, argyrodite solid electrolyte, electro-chemo-mechanical degradation



INTRODUCTION

Solid-state batteries (SSBs) have been investigated intensively as a promising next-generation energy-storage technology in recent years.^{1,2} The adoption of inorganic solid electrolytes (SEs) in these systems can enhance safety, due to the replacement of flammable (organic) liquid electrolytes in conventional lithium-ion batteries (LIBs).^{2–4} More importantly, the use of SEs can facilitate the implementation of Li metal or alloy anodes, ultimately leading to improvements in cell-level energy density (thanks to their large Li transference number and increased mechanical rigidity).^{1,3,5,6} For example, lithium thiophosphate superionic SEs (e.g., $\text{Li}_6\text{PS}_4\text{Cl}$ with $\sigma_{\text{ion}} \approx 3 \times 10^{-3}$ S/cm at room temperature) have been thoroughly examined recently, with the goal of ensuring satisfactory rate capability of the respective SSBs, among others.^{2,7,8} However, the main drawback of sulfide SEs is their narrow electrochemical stability window.^{2,7–9} When using industrially relevant cathode active materials (CAMs), such as Li-

$\text{Ni}_{0.85}\text{Co}_{0.1}\text{Mn}_{0.05}\text{O}_2$ (NCM851005, hereafter referred to as NCM85), the poor stability at the CAM/SE interface induces side reactions, resulting in resistance buildup and inferior electrochemical performance.^{2,8–11}

To address interfacial stability problems, numerous studies have proposed the application of a protective coating to the CAM surface to prevent direct physical contact with the SE.^{2,9,12,13} In principle, a coating should have the following characteristics: (i) nanoscale thickness, (ii) structural/morphological uniformity, (iii) high (electro)chemical stability, and (iv) reasonable ionic conductivity.^{2,10,13} However, the

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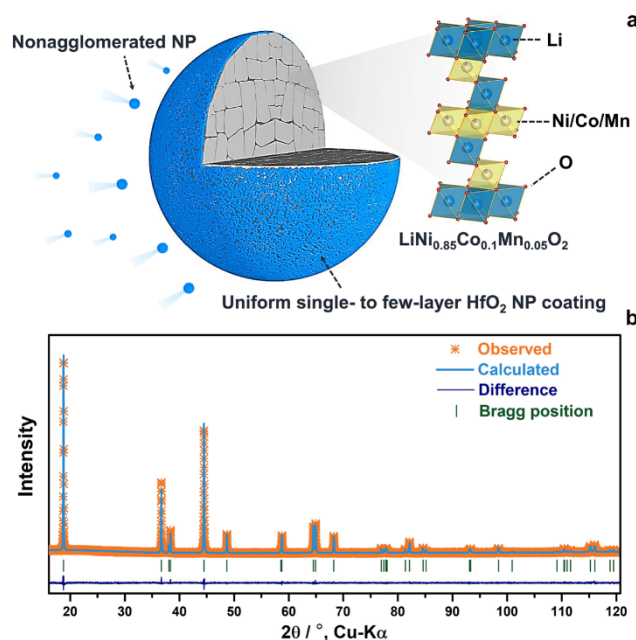


Figure 1. (a) Schematic depiction of the bulk and surface (coating) structure for HfO_2 -NCM85. (b) XRD pattern collected from the HfO_2 -NCM85 particles and corresponding Rietveld refinement plot. Observed, calculated, and difference profiles are shown in orange, cyan, and blue, respectively. Green markers indicate the expected Bragg reflections for NCM85. Refinement results are shown in Table S2.

available coating methods, especially wet-chemical (sol-gel) techniques, have some limitations for the preparation of conformal surface films on complex substrates (regarding uniformity/degree of coverage, coating chemistry, etc.).^{10,14–18} Despite progress made with physical deposition techniques, their widespread application has been hampered by difficulties in the scalability and high production costs, caused by complex processes.^{19,20}

In this work, we present an optimized wet-chemistry route to apply nanoparticles (NPs) dispersed in solution as a coating material.⁸ Different from previous NP-derived coatings, surface stabilization effectively solved problems associated with particle agglomeration, thus practically realizing the deposition of single NPs (Figure 1a).^{8,21–23} The effectiveness of NP coatings, in general, was studied by using HfO_2 -coated NCM85 (HfO_2 -NCM85) as a model-type CAM in $\text{Li}_6\text{PS}_5\text{Cl}$ -based SSB cells with an $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) anode. Note that HfO_2 has already been demonstrated to be an (electro)-chemically stable coating material.²⁰ Electrochemical testing of the CAM in LIBs and slurry-cast SSBs also highlights the practicality of the NP coating for wet-processing techniques. The combination of both physical and electrochemical characterization techniques offered insights into the working principle of the protective coating, which helped to understand differences in cyclability between the bare and coated NCM85 samples.

RESULTS AND DISCUSSION

The HfO_2 NPs were prepared using a surfactant-free solvothermal process (characterization results can be found in the Supporting Information, see Figures S1 and S2).^{8,24,25} After synthesis, a white suspension (Figure S1a) was obtained, indicative of particle agglomeration (by virtue of their high surface energy).^{26,27} It should be noted that NPs present in such an agglomerated state are not well suited for coating applications.^{8,27} To this end, we also found that redispersing them in apolar or polar solvents does not lead to any improvements. Surface modification was thus performed to increase their dispersibility. A quasi-transparent dispersion in chloroform (Figure S1b) was achieved by adding small amounts of oleic acid and oleylamine, offering stabilization owing to steric hindrance.²⁴ Transmission electron microscopy (TEM) images taken after surface treatment (Figure S1c–e) showed elongated (crystalline) NPs of size 6–7 nm (Figure S1f,g) that were virtually free of agglomeration.

HfO_2 -NCM85 was produced via a typical wet-chemistry coating route, by combining the NPs dispersed in chloroform with bare CAM and subsequent heating at 400 °C in O_2 . The Hf content from inductively coupled plasma-optical emission spectroscopy (ICP-OES, Table S1) was found to be 0.72 wt % (0.83 wt % HfO_2). It should be noted that both the heating temperature and coating content were optimized based on a series of experiments. After the coating process, the CAM was found to retain the expected layered structure with space group $R\bar{3}m$. X-ray diffraction (XRD) and Rietveld refinement profiles and refined structural parameters are shown in Figure 1b and

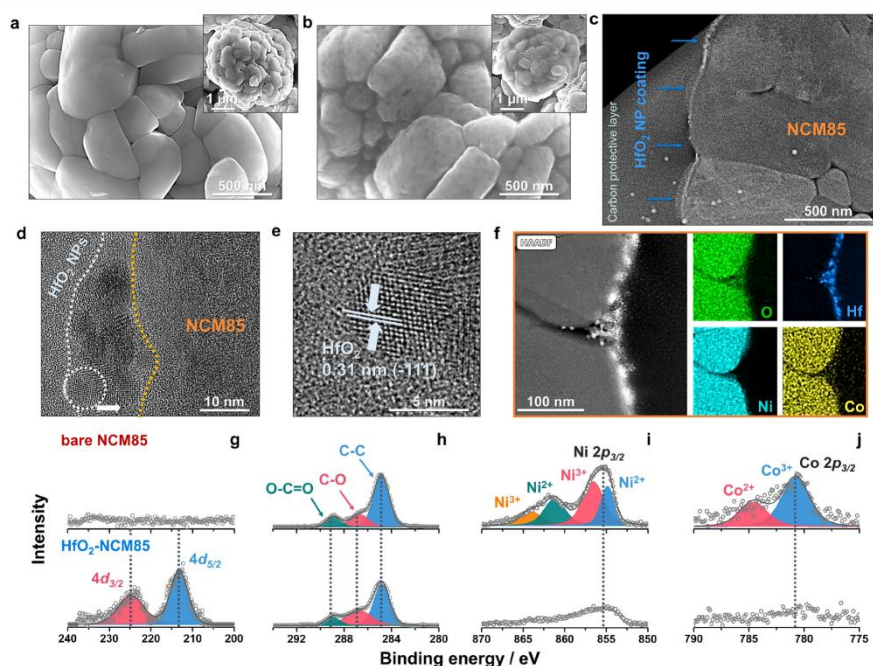


Figure 2. SEM images at different magnifications of the (a) bare NCM85 and (b) HfO₂-NCM85 particles. (c) HAADF STEM and (d) TEM images of FIB-prepared particle cross sections. (e) High-resolution TEM image of the area denoted by the white circle in (d). (f) STEM EDS mapping results. (g) Hf 4d, (h) C 1s, (i) Ni 2p, and (j) Co 2p XPS detail spectra for bare NCM85 (top) and HfO₂-NCM85 (bottom). Note that the C 1s, Ni 2p, and Co 2p spectra have the same y-axis scaling for both CAMs.

Table S2, respectively. Compared to the uncoated reference material (Figure S3), a subtle increase in cell volume was observed after coating, by $\sim 0.1 \text{ \AA}^3$, while the degree of Ni²⁺/Li⁺ cation mixing remained similar for both samples, 3.9(3) and 3.4(2)% for bare NCM85 and HfO₂-NCM85, respectively. This demonstrates that the coating process is not detrimental to the structural properties of the CAM.²⁸ No reflections from the HfO₂ NPs were apparent in the XRD pattern (zoom presented in Figure S4), which could be expected given the low weight content of the coating.

To gain more insight into the structural characteristics of the NCM85 prior to and after coating, scanning electron microscopy (SEM), high-angle annular dark-field (HAADF) scanning TEM (STEM), and X-ray photoelectron spectroscopy (XPS) measurements were conducted on the samples. As can be seen from the high- and low-magnification SEM images in Figure 2a,b (lower magnification images are shown in Figure S5), unlike bare NCM85, the HfO₂-NCM85 CAM exhibits a rougher surface structure, without visible NP agglomeration at this scale, but the particle morphology is well maintained. Results from (S)TEM analysis and energy-dispersive X-ray spectroscopy (EDS) mapping of focused ion beam (FIB)-prepared specimens are presented in Figure 2c–f. The HAADF STEM image in Figure 2c shows the presence of a uniform shell-like structure on the surface of HfO₂-NCM85. The coating thickness is around 11 nm. TEM imaging unveiled that the surface shell can be described as a single- to few-layer

nanoparticle coating (Figure 2d,e and Figure S6). In agreement with the (S)TEM results, EDS mapping (Figure 2f) confirmed that the HfO₂ NPs are primarily located on the free (outer) surface of the NCM85 secondary particles. Compared with previous reports on NP coatings, significant improvements regarding uniformity and thickness were achieved in this work (Table S3).

The surface composition was probed by XPS (Figure 2g–j). As expected, Hf 4d signals were detected only for HfO₂-NCM85 (Figure 2g). Their binding energies (213.2/224.8 eV) are characteristic of Hf⁴⁺.^{29,30} The detail spectrum of the C 1s region for bare NCM85 revealed three peaks (Figure 2h), which can be assigned to C=C/C–C (284.8 eV), C–O (286.8 eV), and O=C–O (288.8 eV) species.^{31–33} Interestingly, the intensity of the carbonaceous signals did not change much with coating, suggesting that the surface ligands are decomposed during the final heat treatment. The Ni 2p and Co 2p detail spectra of HfO₂-NCM85 showed much decreased peak intensities over the bare NCM85 (Figure 2i,j). Considering the surface sensitivity of XPS, the weaker signals indicate a high degree of surface coverage by the HfO₂ nanoparticles.²⁸

The electrochemical behavior of the HfO₂-NCM85 CAM was tested in thiophosphate-based, pellet-stack SSB cells and compared with bare NCM85, which served as a reference material. Both samples were mixed with Li₆PS₅Cl SE and Super C65 carbon black additive for the preparation of cathode

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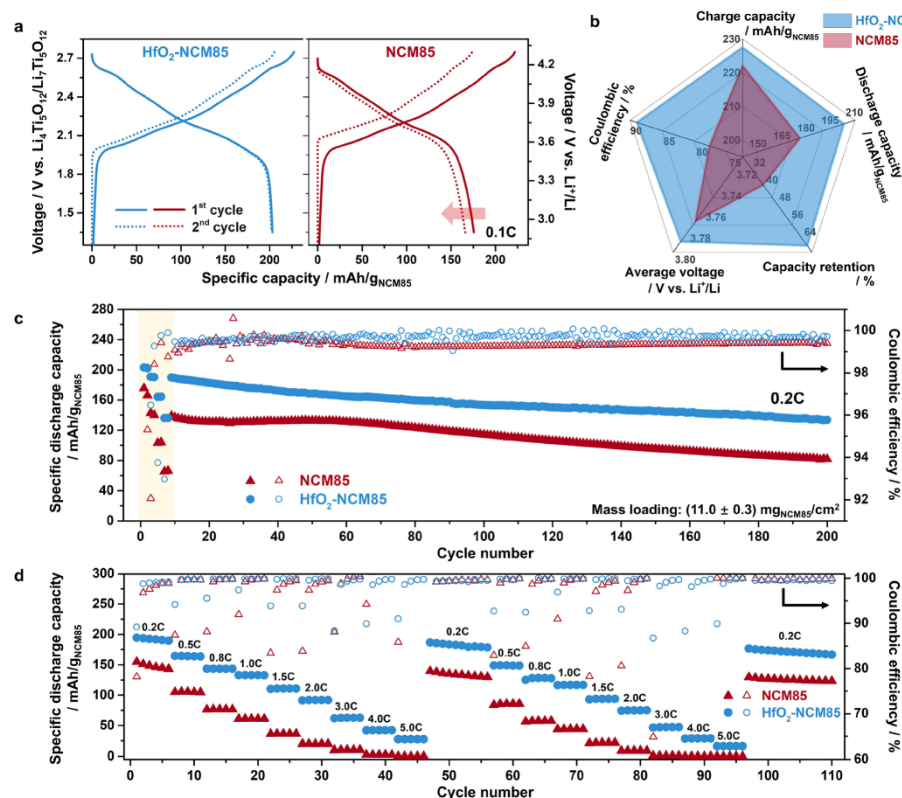


Figure 3. Cycling performance of the bare NCM85 and HfO₂-NCM85 CAMs in pellet-stack SSB cells at 45 °C. (a) Voltage profiles for the first two cycles at 0.1 C rate and (b) first-cycle performance parameters. The capacity retention was calculated by dividing the discharge capacity at 1.0 C by the initial discharge capacity at 0.1 C. (c) Rate capability from 0.1 to 1.0 C during the first eight cycles (highlighted by the shaded area) and long-term cycling performance at 0.2 C. (d) Specific discharge capacities (and Coulomb efficiencies) for various C-rates versus the cycle number.

composite in powder form. The cathodes employed had a relatively high areal loading of $(11.0 \pm 0.3) \text{ mg}_{\text{NCM85}}/\text{cm}^2$, corresponding to $\sim 2 \text{ mAh}/\text{cm}^2$. The anodes in this setup were produced from LTO, Super C65, and Li₆PS₄Cl. All cells were tested at 45 °C in the voltage range 1.35–2.75 V vs Li₄Ti₅O₁₂/Li₇Ti₅O₁₂ (~ 2.9 – 4.3 V vs Li⁺/Li).

The voltage profiles for the first two cycles at 0.1 C rate in Figure 3a indicate major improvements in cyclability after coating. The performance parameters for the initial cycle are compared in the radar plot in Figure 3b. For HfO₂-NCM85, the specific discharge capacity and Coulomb efficiency reached high values of 203 mAh/g and 90%, respectively. In contrast, bare NCM85 only delivered 175 mAh/g, with a much lower first-cycle Coulomb efficiency of 79%. HfO₂-NCM85 also showed a smaller voltage drop (Figure S7) and higher mean voltage (Figure 3b) compared with bare NCM85. This suggests that the NP coating is capable of somewhat suppressing side reactions occurring at the CAMISE interface, thus effectively reducing resistance buildup upon cycling.^{2,34} The second-cycle voltage profiles confirmed this trend. In

particular, a large overpotential was evident for bare NCM85 at the beginning of the charge cycle and HfO₂-NCM85 showed virtually no capacity decay, indicating good reversibility.

For rate and long-term performance testing, the cells were charged and discharged at different C-rates of 0.1, 0.2, 0.5, and 1.0 C over the first eight cycles, followed by cycling at 0.2 C (Figure 3c). As expected, HfO₂-NCM85 showed much improved cyclability. For example, $\sim 65\%$ of the specific capacity was retained at 1.0 C (relative to that at 0.1 C in the initial cycle), compared to less than 40% for bare NCM85, and the capacity retention after 200 cycles was $\sim 70\%$ (135 mAh/g), compared to $\sim 58\%$ (81 mAh/g) for bare NCM85 (with reference to q_{dis} at 0.2 C in the ninth cycle). From the data, it can be seen that bare NCM85 showed minor capacity fading between the ninth and 60th cycle (lower overall degree of de/lithiation), with accelerated degradation thereafter (mechanical contact loss etc.). This kind of cycling behavior has also been observed by other groups when using polycrystalline CAMs.³⁵

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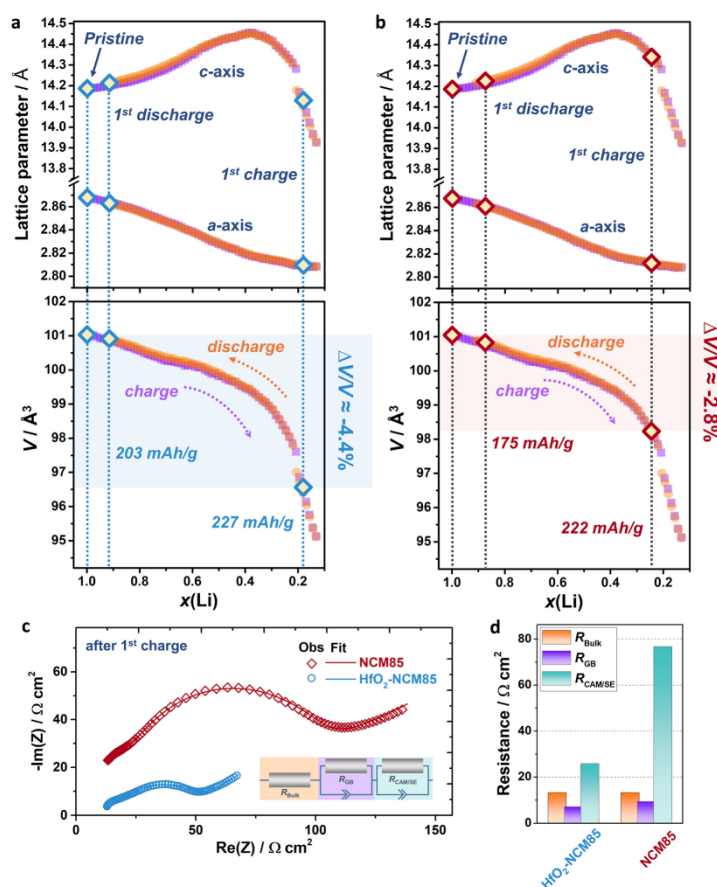


Figure 4. (a and b) Changes in lattice parameters (top) and cell volume (bottom) as a function of $x(\text{Li})$ from Rietveld refinement of *operando* XRD data obtained on a liquid-electrolyte-based Li|NCM85 reference cell, and structural evolution of (a) $\text{HfO}_2\text{-NCM85}$ and (b) bare NCM85 in pellet-stack SSB cells during the initial cycle at 0.1 C rate and 45 °C from *ex situ* XRD. Note that the $x(\text{Li})$ was calculated from the electrochemical data. Refined lattice parameters and cell volume (see also Figure S12 and Table S4) are denoted by blue and red diamond symbols. Measured specific capacities are also indicated. (c) Nyquist plots of the electrochemical impedance of SSB cells with $\text{HfO}_2\text{-NCM85}$ (blue) and bare NCM85 (red) after the initial charge. The inset shows the equivalent circuit used for fitting. (d) Summary of the impedance results.

More detailed rate capability testing was done on the cells from 0.2 to 5.0 C (Figure 3d). Because the NP coating exerted a positive effect on the cathode stability, $\text{HfO}_2\text{-NCM85}$ showed a satisfactory performance. In particular, stable specific discharge capacities of >60, 40, and 20 mAh/g were achieved at rates of 3.0, 4.0, and 5.0 C, respectively. In contrast, bare NCM85 delivered <10 mAh/g at ≥ 3.0 C. Comparing the voltage profiles of the bare and coated NCM85-based cells, we found that the protective coating lowers the increase in overpotential with increasing C-rate (Figure S8). Considering the negligible (ionic/electronic) conductivity of HfO_2 , it could be expected that lithium transport across the CAMISE interface is negatively affected after coating. However, the above results rather suggest that interfacial side reactions are responsible for the performance degradation (sluggish kinetics).²⁰ Galvano-

static intermittent titration technique (GITT) analysis (Figure S9) further confirmed this by demonstrating more severe polarization for bare NCM85 than $\text{HfO}_2\text{-NCM85}$.

In contrast to $\text{HfO}_2\text{-NCM85}$, for bare NCM85, the major capacity decay occurred in the initial cycles. To better understand the working principle of the NP coating, a series of *operando* and *ex situ* measurements were conducted on the cathodes. In general, interfacial stability problems and (chemo)mechanical degradation have been identified as two of the root causes of capacity fading and cell failure.^{36,37} Mechanical degradation (particle fracture, contact loss, etc.) primarily results from the anisotropic volume variation in NCM-type materials.^{38,39} An elegant way to probe the state of charge (SOC) of SSB cells and learn about the mechanical behavior is *via* monitoring the structural evolution of the CAM

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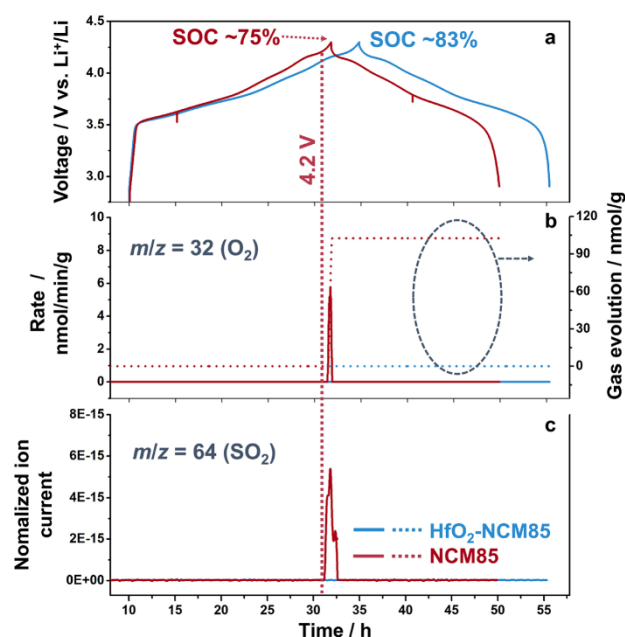


Figure 5. *In situ* gas analysis of SSB cells with bare NCM85 (red) and HfO₂-NCM85 (blue). (a) First-cycle voltage profiles at 0.05 C rate and 45 °C, (b) time-resolved evolution rates (left y-axis) and cumulative amounts (right y-axis) of O₂, and (c) normalized ion currents for SO₂.

during cycling.⁴⁰ To this end, *operando* XRD measurements were performed using liquid-electrolyte-based coin cells containing the NCM85 and a Li metal anode (Figures S10 and S11). This allows the changes in structural parameters to be directly correlated with the lithium content in the CAM [$x(\text{Li})$]. The data were then used as a reference and compared with results from *ex situ* XRD measurements conducted on the SSB cathodes in the pristine state and after the first charge and discharge (Figure S12 and Table S4). The evolution trends with Li extraction and reintercalation are depicted in Figure 4a,b. During charge (delithiation), the lattice parameter a decreased steadily, due to Ni oxidation, leading to continuous contraction of the ab -plane.⁴⁰ In contrast, the c -axis revealed a different behavior, namely, an initial gradual increase because of increasing electrostatic repulsion between the oxygen layers, followed by a strong decrease for $x(\text{Li}) \leq 0.3$ (see also Figure S11).^{40,41} The latter is caused by a collapse of the layered structure.^{42,43} The cell volume also decreased considerably upon achieving high degrees of delithiation, which typically impairs the cycling stability.^{43–45} XRD analysis revealed a more pronounced volume shrinkage for HfO₂-NCM85 ($\Delta V/V \approx -4.4\%$ vs -2.8% for bare NCM85 at ~ 4.3 V vs Li⁺/Li). This result suggests that the anisotropic volume variation has no profound effect on the initial cycling performance, especially the first-cycle reversible capacity. We believe that the small particle size of NCM85 ($d_{50} \approx 4$ μm) allows for intimate physical contact with the SE in the cathode, thereby mitigating mechanical degradation. Similar observations have been made previously for LiNiO₂.⁴⁰

Using this approach, both the reversible and irreversible capacity contributions can be determined from the Li

content.⁴⁰ The specific charge capacities were calculated to be 222 and 205 mAh/g for HfO₂-NCM85 and bare NCM85, respectively, based on the cell parameters determined from *ex situ* XRD. Both values are lower than the measured capacities (227 mAh/g for HfO₂-NCM85 and 222 mAh/g for bare NCM85). Thus, the “additional” charge capacity can be attributed to the oxidative degradation of the Li₆PS₃Cl SE (among others), deteriorating the reversibility of the cell.^{2,46} A significantly larger irreversible capacity was observed for the bare NCM85, again indicating that the NP coating is capable of suppressing to some degree adverse side reactions. Note that the as-formed interphase negatively affects the charge-transport properties, thus leading to inferior capacities.

Electrochemical impedance spectroscopy (EIS) measurements conducted after the first charge confirmed this conclusion (Figure 4c,d and Table S5). The CAMISE interfacial resistance (R_{CAMISE}) for bare NCM85 was three times larger than that for HfO₂-NCM85. Both the bulk resistance (R_{Bulk}) and SE grain boundary resistance (R_{GB}) were similar for the different cells. The overall trend in R_{CAMISE} matched the results from the electrochemical testing.

The first-cycle specific discharge capacities were also calculated, amounting to 202 and 173 mAh/g for HfO₂-NCM85 and bare NCM85, respectively, in good agreement with the electrochemically measured ones (Figure 4a,b). This corroborates the effectiveness of the approach in determining the SOC of SSBs and further suggests that SE degradation is most pronounced during the course of the initial charge.

The gassing behavior of the bare and coated NCM85-based SSB cells was probed using differential electrochemical mass spectrometry (DEMS). In recent years, it has been shown that

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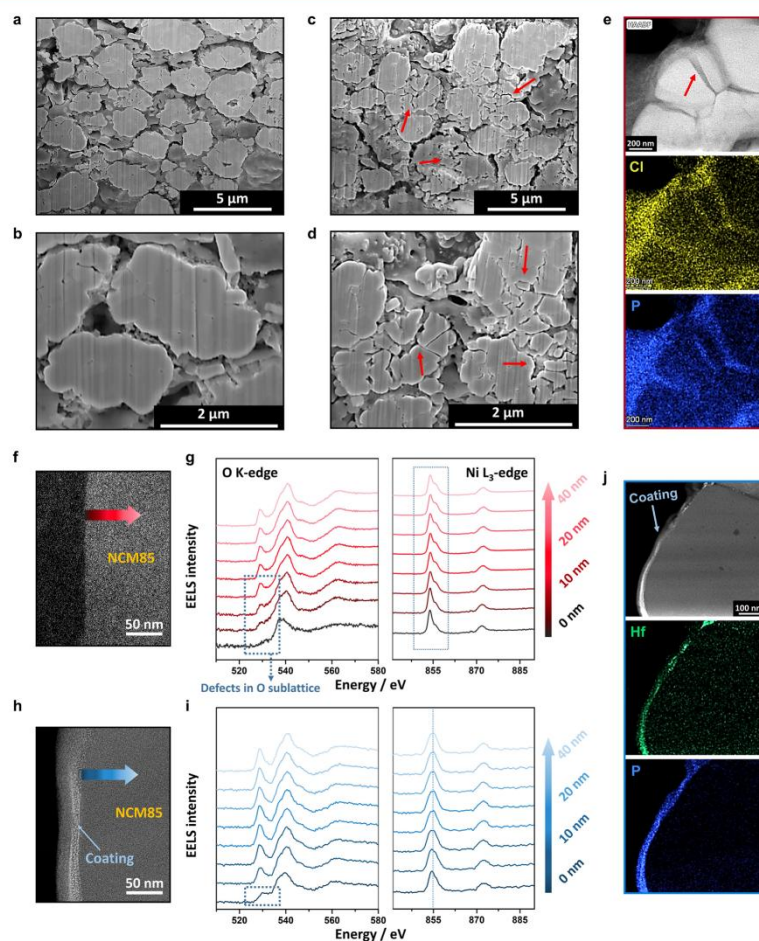


Figure 6. CAM degradation after SSB cell cycling at 0.2 C rate and 45 °C (60 cycles) probed by SEM and HAADF STEM including EELS and EDS. Cross-sectional SEM images at different magnifications of the cathodes with (a and b) HfO₂-NCM85 and (c and d) bare NCM85. EDS mapping results for (e) bare NCM85 and (j) HfO₂-NCM85. HAADF STEM images and EELS line scans from the surface inward to the bulk for (f and g) bare NCM85 and (h and i) HfO₂-NCM85. Intergranular cracking is indicated by red arrows in (c–e) and the coating by blue arrows in (h) and (j).

certain coating chemistries can help to suppress the formation of gaseous degradation products.^{8,28} For both CAMs, four different gases were detected in the first two cycles, namely, H₂, O₂, CO₂, and SO₂ (Figure 5 and Figure S13). Among these, the formation and release of O₂ and SO₂ are of importance in the discussion of side reactions occurring at the CAM/SE interface.⁸ In general, oxygen in a reactive state has been demonstrated to be released at a high SOC, *e.g.*, ≥ 80% for NCM811 (80% Ni), due to destabilization of the crystal lattice.^{47,48} The requirement of 80% SOC was not realized for bare NCM85 (Figures 5a). While cells using the latter CAM achieved an SOC closer to 75% (~206 mAh/g) in the initial cycle, those with HfO₂-NCM85 revealed an SOC of about 83% (~229 mAh/g). However, because of cathode inhomogene-

ities, O₂ release may even occur below 80%. For thiophosphate-based SSBs, side reactions of the SE with O₂ have been reported, with the formation of SO₂ as a gaseous product (clear indication of SE decomposition).^{49,50} Thus, correlated O₂ and SO₂ evolution should be observed, which was indeed the case for bare NCM85, where sharp *m/z* = 32 and 64 signals were detected around 4.2 V vs Li⁺/Li (Figure 5b,c). In contrast, no O₂ and/or SO₂ gas evolved in the HfO₂-NCM85-based cells. A possible explanation for this result is that the coating inhibits the release of lattice oxygen. Recently, Guo et al. showed that oleic acid-induced surface engineering leads to (spinel/layered) heterostructure formation, which apparently strengthened the surface by preventing the layered to spinel/rocksalt phase transformation.⁵¹ Given that oleic acid

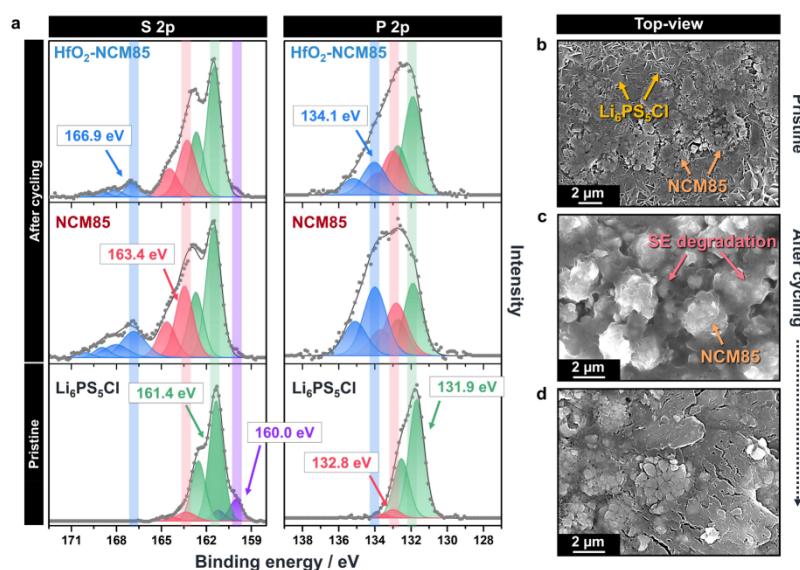


Figure 7. (a) XPS detail spectra of the S 2p (left) and P 2p (right) regions for pristine Li₆PS₅Cl and cathodes using bare NCM85 and HfO₂-NCM85 after SSB cell cycling (60 cycles at 0.2 C rate and 45 °C). Top-view SEM images of cathodes with (b and d) HfO₂-NCM85 and (c) bare NCM85 taken (b) prior to and (c and d) after cycling (200 cycles).

was used in the HfO₂ NP dispersion, the possibility of a similar effect cannot be excluded. The data presented provide profound evidence that the coating helps to stabilize cathode interfaces, which has a positive effect on the cell cyclability (less capacity fading despite more severe volume variation).

Apart from the first-cycle characteristics and rate capability, there were also major differences in the long-term cycling performance between the bare and coated NCM85 CAMs. To better understand these, EIS measurements were conducted on the cells after 60 and 200 cycles at 0.2 C rate and 45 °C (Figure S14 and Table S5). The cathode interfacial resistance grew upon cycling in both cases. For bare NCM85, the R_{CAMISE} increased by a factor of ~ 10 relative to the initial (charge) cycle and was ~ 4.5 times larger than that for HfO₂-NCM85. This means that side reactions occurred continuously at the interfaces with the SE during cycling but much more pronounced in the case of bare NCM85.

Next, FIB-prepared samples were probed using cross-sectional SEM for visualizing the microstructural evolution. As shown in Figure 6a,b, the structure/morphology of HfO₂-NCM85 (after 60 cycles) was well preserved; the degree of particle fracture was very low. By contrast, SEM and HAADF STEM imaging (Figure 6c–e) revealed cracking of the bare NCM85 secondary particles, leading to the formation of reactive surfaces and inducing unwanted side reactions, as confirmed by EDS mapping of Cl and P (Figure 6e).²⁸ These results are consistent with the trends seen from electrochemical testing and EIS analysis. Several studies have attributed intergranular CAM cracking in LIBs to the anisotropic volume variation during cycling.^{52,53} However, as demonstrated by XRD, the absolute change in cell volume of HfO₂-NCM85 was larger than that for bare NCM85 as a result of the larger capacity delivered. Thus, it seems likely that the

particle fracture might be rather related to the (electro)-chemical side reactions occurring at the CAMISE interface. A recent report by Han et al. supports this hypothesis.⁵⁴ The protective coating somewhat suppressed unfavorable side reactions, thereby ensuring particle integrity and longevity.

This was further corroborated by *ex situ* studies combining STEM with electron energy-loss spectroscopy (EELS). The O K-edge spectrum for bare NCM85 (Figure 6f,g) showed a gradual fading of the pre-edge feature from the bulk toward the surface, indicating the presence of vacancies in the O sublattice and transition-metal reduction.⁵⁵ The latter was also evident from the Ni L-edge spectrum in Figure 6g (decrease in intensity of the shoulder peak at ~ 856 eV).⁵⁶ In contrast, much weaker signs of O-defect formation and Ni reduction were found for HfO₂-NCM85 (Figure 6h,i). This suggests that the surface degradation of NCM85 is closely connected to the interfacial side reactions.⁵⁴ The NP coating mitigated this effect and preserved high surface coverage after cycling, as demonstrated by STEM and EDS (Figure 6j).²⁸

XPS was used to identify the chemical nature of the degradation products formed at the interfaces with the SE. In the following, we limit the discussion to the S 2p and P 2p core-level regions (Figure 7a), which revealed the most significant changes. The S 2p (reference) detail spectrum collected from the pristine Li₆PS₅Cl SE showed three doublet peaks. The main peak at 161.4 eV (S 2p_{3/2}) could be assigned to PS₄^{3−}. The minor one at the lower binding energy side (160.0 eV) is probably due to the free S^{2−} in the argyrodite structure (or Li₂S), while that at 163.4 eV indicated the presence of a small amount of polysulfides.^{40,57,58} The P 2p detail spectrum contained two doublet peaks, due to the PS₄^{3−} units (P 2p_{3/2} peak at 131.9 eV) and some impurity species (P₂S₆^{2−}, Li₃PO₄, etc., with the P 2p_{3/2} peak at 132.8 eV).^{46,59}

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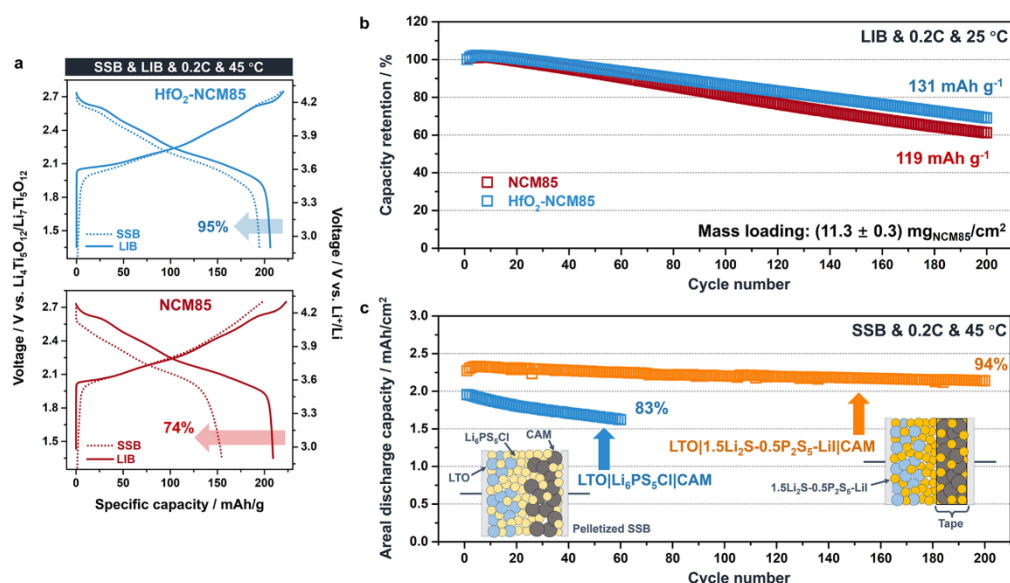


Figure 8. (a) Initial voltage profiles of pelletized SSB and LIB cells using cathodes with $\text{HfO}_2\text{-NCM85}$ (top) and bare NCM85 (bottom). (b) Long-term cycling performance of LIB cells. (c) Cyclability of slurry-cast (with $1.5\text{Li}_2\text{S}-0.5\text{P}_2\text{S}_5\text{-LiI}$ SE) and pelletized (with $\text{Li}_6\text{PS}_5\text{Cl}$ SE) SSB cathodes with $\text{HfO}_2\text{-NCM85}$.

The intensity of the polysulfide peaks in the S 2p spectrum was increased for the bare NCM85 and $\text{HfO}_2\text{-NCM85}$ cathodes after cycling (60 cycles). At the same time, new doublet peaks appeared at binding energies beyond 166.0 eV, suggesting the formation of oxygenated sulfur (SO_x) compounds.^{38,58,60} The latter can be directly attributed to the side reactions occurring at the CAMISE interface (note that the NCM85 CAM was the only oxygen source present in the positive electrode of the cells).⁸ As expected, lower intensities of the respective peaks (lower relative amounts) were observed for $\text{HfO}_2\text{-NCM85}$ (Figure S15), confirming the above results. A similar trend was also seen in the P 2p data, with the appearance of a new doublet peak (P 2p_{3/2} peak at 134.1 eV) resulting from the formation of metal phosphates and/or metaphosphates (i.e., oxygenated phosphorus (PO_x) compounds due to CAMISE side reactions).^{8,60} This is in agreement with the interdiffusion observed by STEM EDS (Figure S16). Overall, the interfacial degradation leads to buildup of a resistive passivation layer containing, among others, SO_x and PO_x species, thereby impeding charge transfer and transport.^{8,28,34}

The pristine (Figure 7b and Figure S17) and cycled cathodes (Figure 7c,d) were also imaged using SEM. As can be seen from the data, the CAM secondary particles were well embedded in the SE matrix (indicated by arrows in the respective images). In the pristine state (prior to cycling), there were no visible differences between the cathodes using the bare NCM85 or $\text{HfO}_2\text{-NCM85}$. However, for bare NCM85, SE degradation (indicated by arrows) was very evident from the change in electrode morphology after cycling (200 cycles). In the case of $\text{HfO}_2\text{-NCM85}$, the cathode largely maintained its initial appearance, further emphasizing the robustness of the CAMISE interface. Notably, void formation and contact loss

on the micrometer level were not observed, neither for $\text{HfO}_2\text{-NCM85}$ nor for bare NCM85. This agrees with the XRD results, indicating that mechanical effects, due to volume changes of the CAM particles, play a minor role in the capacity-fading behavior.

Taken together, the findings collectively demonstrate that the side reactions at the CAMISE interface not only cause the formation of a passivation layer and loss of active material but also negatively affect the integrity of the NCM85 particle structure. These problems were mitigated, to a large extent, by coating the CAM free surface with HfO_2 NPs, leading to considerable improvements in cycling performance.

The effectiveness of the coating in liquid-electrolyte-based LIB cells was studied too. To this end, high-loading cathodes ($11.3 \pm 0.3 \text{ mg}_{\text{NCM85}}/\text{cm}^2$) were tested in the voltage range 2.9–4.3 V vs Li^+/Li in coin half-cells. The first-cycle voltage profiles at 0.2 C rate and 45 °C and corresponding differential capacity curves are shown in Figures S18 and S19, suggesting a similar electrochemical behavior for the bare NCM85 and $\text{HfO}_2\text{-NCM85}$, with specific discharge capacities of 209 and 206 mAh/g and Coulomb efficiencies of 93.8 and 93.6%, respectively. Figure 8a presents a performance comparison of both CAMs in pellet-stack SSB and conventional LIB cells. The solid-state environment resulted in a lower Coulomb efficiency in the initial cycle and some drop in capacity due to interfacial stability problems.^{37,40} Upon applying the NP coating to the NCM85, the capacity retention, relative to the corresponding LIB cells, improved from 74% for bare NCM85 to 95% for $\text{HfO}_2\text{-NCM85}$. $\text{HfO}_2\text{-NCM85}$ also showed better long-term cycling in LIBs, with 70 vs 61% capacity retention after 200 cycles at 0.2 C rate and 25 °C (Figure 8b).

Slurry-cast electrodes were also prepared and incorporated into SSBs to learn about the adaptability of HfO_2 -NCM85 to wet processing.⁴⁹ The slurry-cast cathodes tested in this work had an areal loading of $16.4 \text{ mg}_{\text{NCM85}}/\text{cm}^2$, with a similar composition to the pelletized counterparts, but using glassy $1.5\text{Li}_2\text{S}-0.5\text{P}_2\text{S}_5\text{-LiI}$ as SE and 1 wt % polyisobutylene binder. The cycling behavior of slurry-cast and pelletized (binder-free) cathodes with $1.5\text{Li}_2\text{S}-0.5\text{P}_2\text{S}_5\text{-LiI}$ and $\text{Li}_6\text{PS}_3\text{Cl}$, respectively, in cells at 0.2 C rate and 45°C is shown in Figure 8c. Using the slurry-cast cathode in the SSB setup, high area-specific capacities ($\sim 2.3 \text{ mAh}/\text{cm}^2$) were achieved in the initial cycles and also a much better capacity retention of 94% after 200 cycles, compared to 83% after 60 cycles for the dry-processed (binder-free) cathode. This improvement could be linked to (i) enhanced contact between cathode and SE, (ii) higher uniformity of the slurry-cast cathode, and (iii) the fact that the Young's modulus of glassy SEs is typically beneficial for mitigating mechanical degradation.^{49,61}

CONCLUSIONS

A homogeneously distributed secondary particle coating on a Ni-rich NCM cathode material and its benefits to the electrochemical performance has been presented. Surface stabilization using an appropriate solvent mitigated issues with particle agglomeration and allowed for the uniform deposition of individual nanoparticles on the CAM surface. Electrochemical testing showed that the coated material exhibits improvements in specific capacity, capacity retention, and Coulomb efficiency compared with its uncoated counterpart when employed in thiophosphate-based SSBs. Complementary characterization conducted on the positive electrodes prior to, during, and after cycling indicated that the protective coating not only suppresses interfacial side reactions but also inhibits particle fracture and outgassing, thereby improving the stability of the cathode structure/morphology and CAM/SE interface. The coated material was also tested in high-loading, slurry-cast cathodes with a glassy $1.5\text{Li}_2\text{S}-0.5\text{P}_2\text{S}_5\text{-LiI}$ solid electrolyte and found to maintain stable, long-term cycling at 45°C . Compatibility with wet processing of electrodes is essential for the practical application of inorganic solid-state batteries. The nanoparticle coating also improved the cycling stability of the Ni-rich NCM cathode in conventional liquid-electrolyte-based Li-ion cells. While the results presented are encouraging, we believe that the overall performance can be increased further by using this generic surface-modification strategy and tailoring the coating chemistry.

EXPERIMENTAL SECTION

Preparation of HfO_2 Nanoparticles and CAM Coating. The solvothermal synthesis of HfO_2 nanoparticles and their surface functionalization using oleic acid and oleylamine are detailed elsewhere.^{24,25} Quasi-transparent chloroform-based nanoparticle dispersions having a solid content of $\sim 20 \text{ mg}/\text{mL}$ were achieved in this work. The HfO_2 nanoparticles were then applied as coating material to the NCM85 CAM (BASF SE) following a procedure reported previously.⁸ Prior to coating, the as-received CAM was heated at 750°C in oxygen flow to eliminate surface impurities (residual Li). Depending on the solid content, a certain volume of nanoparticle dispersion was added to 2 g of NCM85 in a beaker. Finally, chloroform was added to achieve 20 mL of total volume, and the beaker was sealed using Parafilm. Next, the suspension was agitated by ultrasonication for 15 min, thereby enabling uniform mixing of the HfO_2 nanoparticles and the NCM85 CAM. Afterward, the Parafilm was removed and the suspension was placed in an oil

bath at 60°C with continuous stirring until the chloroform was evaporated. The resulting black powder was collected and treated at ambient temperature in a vacuum overnight, followed by heating at 400°C in oxygen flow for 2 h. After natural cooling, the coated NCM85 CAM was transferred to an Ar glovebox for further processing.

Electrode Preparation. The composites used for the preparation of pelletized and slurry-cast electrodes were prepared as reported elsewhere.^{8,49} Two types of SEs were used in this work, argyrodite $\text{Li}_6\text{PS}_3\text{Cl}$ (NEI Corp.) and glassy $1.5\text{Li}_2\text{S}-0.5\text{P}_2\text{S}_5\text{-LiI}$. For the latter material, stoichiometric amounts of precursors (LiI, 99.99%, Alfa Aesar; P_2S_5 , 99%, Sigma-Aldrich; Li_2S , 99.9%, Sigma-Aldrich) were mixed in a 70 mL zirconia jar under an Ar atmosphere. The sealed jar was then transferred to a planetary ball mill (FRITSCH) and the powder mixture milled at 450 rpm for 12 h.⁶¹ The as-prepared SE was used as separator, as well as in the cathode and anode of tape-cast SSBs. For the cathode composite, CAM, SE ($\text{Li}_6\text{PS}_3\text{Cl}$ for pelletized cells and glassy $1.5\text{Li}_2\text{S}-0.5\text{P}_2\text{S}_5\text{-LiI}$ for tape-cast cells), and Super C65 carbon additive (TIMCAL Ltd.) were mixed in a weight ratio of 69.3:29.7:1.0. For the anode composite, the weight ratio of carbon-coated LTO (NEI Corp.), SE to Super C65 was set to 30:60:10. Slurry-cast electrodes were prepared from the glassy SE-based cathode composite described above. The latter was first prewetted with anhydrous *o*-xylene (97%, Sigma-Aldrich) and mixed at 600 rpm for 2 min using a centrifugal planetary mixer. The solid content in the slurry was set to 64 wt %. Next, polyisobutylene binder (Oppanol N 150, BASF SE) solution was added dropwise to achieve a CAM/SE/Super C65/binder weight ratio of 68.6:29.4:1.0:1.0. After further mixing at 2000 rpm for 6 min, the as-obtained slurry was cast onto Al foil under an Ar atmosphere using a mini tape casting coater from MTI Corp. The different mixing steps and casting conditions are described in more detail elsewhere.^{49,61} The slurry-cast cathode tape was first dried in the glovebox at room temperature and ambient pressure for 4 h and then subjected to further drying in a vacuum for 12 h. For the testing in LIBs, the CAM was incorporated into an *N*-methyl-2-pyrrolidone slurry with Super C65 and polyvinylidene difluoride binder in a weight ratio of 94:3:3 using a centrifugal planetary mixer. The slurry was cast onto Al foil at a thickness of $140 \mu\text{m}$ and dried at 120°C in a vacuum. Finally, the electrode was calendared at 15 N/mm and cut into circular electrodes of diameter 13 mm. The areal loading was $\sim 11.3 \text{ mg}_{\text{NCM85}}/\text{cm}^2$.

Cell Assembly. A customized setup was used for the pelletized SSBs, containing stainless steel dies as current collectors and a 10 mm diameter PEEK ring.⁸ First, about 100 mg SE was compacted at 62.5 MPa. Then, 65–66 mg anode composite and 12–13 mg cathode composite were placed on either side of the SE pellet. A 440 MPa pressure was applied to the assembled cell to ensure intimate contact between the different components. For the tape-cast SSBs, a 9 mm diameter cathode was punched out and then placed onto the compacted glassy SE separator layer. The amounts of SE separator and anode were the same as for the pelletized cells described above. During galvanostatic cycling, an external pressure of 81 MPa was maintained. Coin cells (2032) were used to probe the cycling performance of LIBs. Lithium metal served as the counter electrode (Albemarle Germany GmbH). The separator (GF/D from Whatman) soaked with 95 μL of LP57 (1 M LiPF_6 in 3:7 by weight ethylene carbonate (EC)/ethyl methyl carbonate (EMC), BASF SE) was placed between the working and counter electrodes.

Electrochemical Measurements. Both the cell cyclability and rate performance were tested at 25 and 45°C , with 1.0 C corresponding to $190 \text{ mA}/\text{g}_{\text{NCM85}}$ using a MACCOR battery cycler. The voltage range was set to 1.35–2.75 V vs $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_7\text{Ti}_5\text{O}_{12}$ (about 2.9–4.3 V vs Li^+/Li) and 2.9–4.3 V vs Li^+/Li for the SSBs and LIBs, respectively. EIS was conducted on the SSB cells at 45°C (7 mV voltage amplitude, 7 MHz to 100 mHz frequency change) using an SP-300 multichannel potentiostat (Bio-Logic). GITT measurements were also performed at 45°C on a MACCOR battery cycler. After the initial cycle, the cells were given 30 min constant charge or discharge current pulses at 0.05 C, with a 4 h relaxation period between each pulse.

Characterization. SEM imaging was done using a Zeiss Leo 1530 microscope equipped with a field emission source. TEM measurements (HRTEM, SAED, STEM EDS, and EELS) were conducted at an accelerating voltage of 300 kV using a double-corrected Themis-Z microscope (Thermo Fisher Scientific) equipped with a HAADF STEM detector, a Super-X EDX detector, and a Gatan Continuum 970 HighRes image filter. The STEM EDS maps were acquired at a beam current of 200 pA. Sample cross sections were prepared using a dual-beam focused Ga-ion beam (FIB) in an FEI Strata 400 at 30 kV. Carbon layers were deposited by ion beam-induced deposition to protect the surface coating. The thinned samples were further cleaned at 5 kV/2 kV. ICP-OES measurements were carried out using an iCAP 7600 Duo (Thermo Fisher Scientific) and a PerkinElmer Optima 4300 DV. XRD data were acquired using a STOE Stadi-P diffractometer with a DECTRIS MYTHEN 1K strip detector in Debye–Scherrer geometry ($\lambda = 1.5406 \text{ \AA}$). The instrumental contribution to the peak broadening was obtained by measuring a NIST 640f Si standard reference material as line broadening reference. Rietveld refinement was performed using GSAS-II.⁶² For refinement of NCM structural models against the diffraction data, the scale factor, zero shift, and size/strain broadening parameters were allowed to vary. A fixed background was fitted to the data using a Chebyshev polynomial function with 13 terms. In the structural model, the unit cell parameters, the oxygen z-coordinate, and the atomic displacement parameters (isotropic) for each site were refined. Atoms occupying the same site were constrained to have the same atomic parameters, and site occupancy factors were constrained such that each site remained fully occupied. XPS measurements were carried out on a SPECS XPS system with a PHOIBOS 150 energy analyzer using monochromatic Al K α radiation ($\lambda = 1486.6 \text{ eV}$), a takeoff angle of 45° , and pass energies of 30 and 90 eV for detail and survey scans, respectively. The C 1s peak (adventitious carbon) at 284.8 eV was used for binding energy calibration. Peak fitting was done with the CasaXPS software assuming Shirley-type backgrounds and mixed Gaussian–Lorentzian peak shapes. For peak doublets in the P 2p and S 2p core-level regions, the intensity ratio (2:1) and spin–orbit splitting (0.84 eV for P 2p, 1.18 eV for S 2p) were set to the expected values.⁶³ The DEMS setup used for *in situ* gas analysis is described in detail elsewhere.^{8,49} In this case, galvanostatic cycling was done at a rate of 0.05 C and 45°C in the voltage range 2.3–3.7 V vs In/InLi (about 2.9–4.3 V vs Li $^+$ /Li) using a VMP3 multichannel potentiostat, with a 10 h OCV period prior to testing.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsnano.2c07314>.

Figures of characterization of the HfO $_2$ NPs, XRD analysis of the CAMs and microscopy results, SEM images, first-cycle discharge curves and voltage profiles of SSB cells, GITT data, results from *operando* and *ex situ* XRD, additional DEMS and XPS data, Nyquist plots of the electrochemical impedance and fitting results, post mortem STEM EDS analysis, voltage profiles of LIB cells and differential capacity plots, tables of ICP-OES results, refined structural parameters, comparison of nanoparticle coatings in the battery field, and results from fitting of EIS data (PDF)

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Notes

The authors declare no competing financial interest.

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3.1.3. Publication III: Conformal $\text{Li}_2\text{HfO}_3/\text{HfO}_2$ Nanoparticle Coatings on Layered Ni-Rich Oxide Cathodes for Stabilizing Interfaces in All-Solid-State Batteries

During the synthesis and storage of Ni-rich cathodes, the excess use of lithium precursors often leads to the formation of residual lithium on the particle surface, including Li_2O , LiOH , Li_2CO_3 , etc. In particular, lithium carbonate exhibits electrochemical instability at high potentials, generating gaseous decomposition products, among which oxygen can further oxidize the SSE and thereby exacerbate interfacial degradation. In addition, although lithium carbonate can be used as a coating material, its microstructural characteristics in the as-formed coating and its ability to suppress interfacial side reactions, especially when present as an accompanying phase, remain insufficiently understood. It is also well recognized that these factors have a pronounced impact on electrochemical performance.

Therefore, in my PhD research, when exploring new coating strategies and coating materials, the as-received Ni-rich cathodes were subjected to a preliminary heat-treatment step (denoted as regeneration) to remove surface contaminants, particularly lithium carbonate. This treatment yields a relatively clean surface of CAM and minimizes the influence of residual lithium carbonate on the functionality and effectiveness of the investigated coating materials and strategies, as investigated in **Publication II**. However, two issues still remain: (1) a certain amount of lithium carbonate persists on the cathode surface even after heat-treatment, and (2) thermal decomposition of Li_2CO_3 and LiOH essentially converts them into Li_2O . As Li_2O is known for its electronically insulating nature, its presence could increase the interfacial charge-transfer resistance.

Therefore, in **Publication III**, we explored an *in situ* approach that combines the advantages of NP coating strategies with the simultaneous consumption of residual lithium species during coating formation. Through this approach, a partially lithiated $\text{Li}_2\text{HfO}_3/\text{HfO}_2$ (denoted as LHO) mixed NP coating was constructed, enabling a uniform and conformal nanoparticle deposition with a thickness of approximately 12 nm. To form the desired surface layer, an annealing step was carried out at 700 °C under oxygen. PC NCM85, LPSCI, and LTO composite were used as CAM, SSE, and anode, respectively, for electrochemical evaluation.

The coexistence of Li_2HfO_3 and HfO_2 was confirmed by two sets of Hf 4f doublets, together with fast Fourier transform (FFT) and EELS analyses of the NPs, while attenuated total reflectance-infrared radiation (ATR-IR) data further supported the consumption of residual lithium carbonate. The nearly identical degree of $\text{Li}^+/\text{Ni}^{2+}$ intermixing before and after coating suggests that lattice lithium consumption can be neglected, indicating that the residual lithium participated in the lithiation of the HfO_2 NPs. Electrochemical testing demonstrated that, compared with the uncoated counterpart, LHO-NCM85 exhibits improvements in both initial specific discharge capacity and Coulomb efficiency (187 vs. 162 mAh/g and 83 vs. 79%, respectively). In terms of long-term cycling stability, LHO-NCM85 showed markedly enhanced capacity retention, reaching 81% after 200 cycles, in contrast to 45% for the uncoated counterpart. Upon cycling,

3. Results

LHO-NCM85 was found to maintain good microstructural integrity and to exhibit significantly reduced interfacial impedance, consistent with its superior electrochemical performance.

Objectively, the performance demonstrated in **Publication III** does not represent the best results reported for the effective utilization of nanoparticle coatings, as pronounced kinetic hindrance at 3.5 V vs. Li^+/Li limits the attainable capacity of LHO-NCM85. Nevertheless, the strategy of *in situ* residual lithium consumption combined with nanoparticle coating formation clearly demonstrates its feasibility. Further optimization could be achieved by introducing additional lithium sources and by tailoring both the location and the mode of lithium-source incorporation.

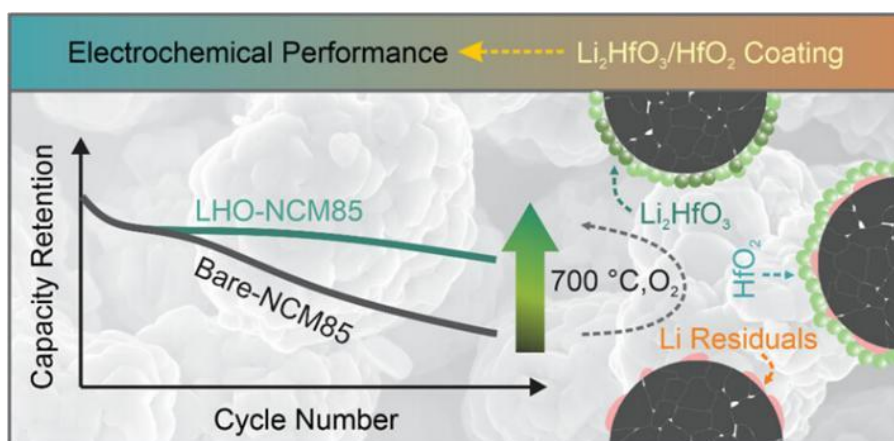


Figure 9. Table of contents graphic of Publication III. Adapted from reference [46].

The experiments were designed and planned by the first author R. Zhang, under the supervision of Y. Ma, J. Janek, and T. Brezesinski. R. Zhang conducted all of the synthesis steps, including preparation of the nanoparticle solution, CAM coating, and calcination, performed the cycling test, XRD, SEM-EDS, ATR-IR, and EIS measurements together with the data analysis. Y. Tang carried out the sample preparation and TEM measurements. D. Goonetilleke analyzed and refined the XRD data. T. Diemant performed the XPS measurements. Y. Ma supported the analysis and interpretation of the gathered TEM and XPS results. The first draft was written by the first author and then edited by all co-authors.

Conformal $\text{Li}_2\text{HfO}_3/\text{HfO}_2$ Nanoparticle Coatings on Layered Ni-Rich Oxide Cathodes for Stabilizing Interfaces in All-Solid-State Batteries

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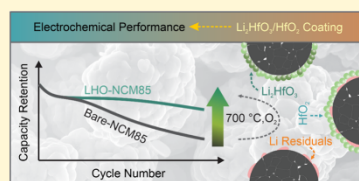
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ABSTRACT: Solid-state batteries (SSBs) are a promising next-generation energy-storage solution to complement or replace current battery technologies in the wave of automotive electrification. Especially SSBs using sulfide solid electrolytes (SEs) hold great potential; however, (electro)chemical instability when in contact with layered oxide cathode active materials (CAMs) remains an obstacle to further implementation. SE degradation occurring during cycling adversely affects the ion/electron transport and may possibly cause mechanical failure. In the present work, a protective surface coating composed of Li_2HfO_3 and HfO_2 nanoparticles (NPs) was produced on the secondary particles of a high-capacity $\text{LiNi}_{0.85}\text{Co}_{0.1}\text{Mn}_{0.05}\text{O}_2$ (NCM85) CAM to mitigate side reactions and enable robust interfacial charge transfer. HfO_2 NPs dispersed in solution served both as a coating material and as a precursor to react with residual lithium during post-deposition annealing. The $\text{Li}_2\text{HfO}_3/\text{HfO}_2$ -coated NCM85 showed much improved cycling performance over uncoated CAM in all-inorganic SSB cells with $\text{Li}_4\text{PS}_3\text{Cl}$ SE and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode. Thorough characterization using a series of techniques helped to elucidate the role that the coating plays in stabilizing interfaces and preserving structural integrity of the cathode.



INTRODUCTION

While extensive investigation and commercialization of lithium-ion batteries have made the electrification of automobiles possible, the intrinsic flammability of (ordinary) organic, liquid electrolytes and dendrite formation associated with the lithium metal anode pose safety concerns and challenges to fast charging.^{1–5} Therefore, considerable attention is directed toward solid-state batteries (SSBs), particularly those using layered Ni-rich oxide cathode active materials (CAMs), e.g., $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ (NCM or NMC) or $\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$ (NCA) (with $x + y + z = 1$ and $x \geq 0.8$),⁶ and superionic thiophosphate solid electrolytes (SEs) such as $\text{Li}_6\text{PS}_5\text{X}$ (with $\text{X} = \text{Cl}, \text{Br}, \text{I}$),⁷ Li_3PS_4 ,⁸ $\text{Li}_7\text{P}_3\text{S}_{11}$,⁹ or $\text{Li}_{9.54}\text{Si}_{1.74}\text{P}_{1.44}\text{S}_{11.7}\text{Cl}_{0.3}$ ¹⁰ to name a few. The latter materials exhibit a high ionic conductivity at room temperature and are mechanically soft, allowing for facile processing by cold pressing.

Despite the individual advantages of Ni-rich NCM CAMs and sulfide SEs, their practical combination in SSBs is faced with many challenges. The stability of NCM decreases with increasing Ni content, while residual lithium species and cation intermixing (Ni^{2+} on lithium site) impair ion transport.¹¹ Apart from that, the charge cutoff voltage of NCM cells surpasses the electrochemical stability window of sulfide SEs.^{12–14} As a result, the NCM/SE interface suffers from degradation, resulting in impedance buildup. In addition, oxygen released

from the CAM (near) surface at high states of charge exacerbates the degradation. It further causes the formation of redox-inactive NiO -like rock salt phases, which accelerates the capacity fading.^{15–17} Notably, recent reports revealed that the performance decay of NCM/sulfide SE battery systems is also due in part to mechanical failure. This includes particle fracture and contact loss caused by “breathing” of the NCM particles during cycling and interfacial side reactions.^{18,19}

A viable approach for solving the aforementioned issues is fabricating a protective coating on the NCM particles, with the objective to prevent physical contact between the bare CAM and the sulfide SE. In recent years, various coating materials have been reported, including binary oxides (e.g., ZrO_2 ,^{20,21} HfO_2 ,^{22,23} Al_2O_3 ,²⁴ $\text{Li}_2\text{O}-\text{ZrO}_2$,^{25,26}) and lithium-based ternary oxides (e.g., LiNbO_3 ,^{27,28} LiAlO_2 ,²⁹ Li_2ZrO_3 ,^{28,30} $\text{Li}_4\text{Ti}_5\text{O}_{12}$,³¹). It should be noted, though, that the coating process inevitably induces the formation of some impurities, especially carbonates, on the CAM surface.^{20,27,30,32} In this regard, Jung *et al.* showed that Li_2CO_3 is detrimental to lithium

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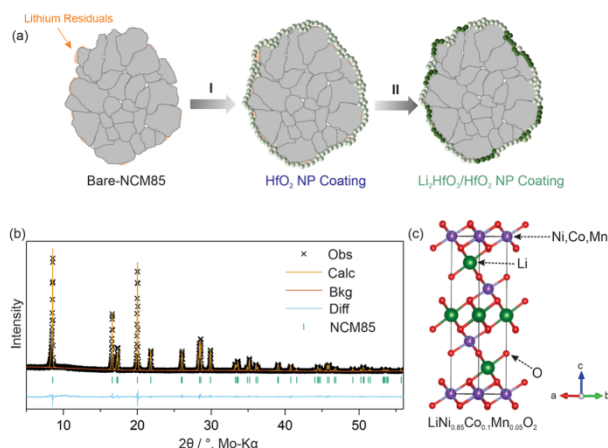


Figure 1. (a) Schematic of the coating procedure. (b) Powder XRD pattern and corresponding Rietveld refinement profile for LHO-NCM85. (c) Structural model of the NCM85.

transport.³³ Furthermore, electrochemical oxidation of carbonates leads to the evolution of oxygen (in addition to CO₂) that can undergo unwanted follow-up reactions with other components in the electrode.^{34,35} The limited stability of sulfide SEs, in general, may have a negative effect on the integrity of the coating structure/morphology (loosening/delamination of the surface layer, etc.). Regardless, producing a conformal coating while preventing major carbonate formation is challenging. Nevertheless, the emerging solution-based nanoparticle (NP) coating technology has been shown to overcome nonuniformity problems, but it does not solve the carbonate formation issue (as demonstrated for ZrO₂ NPs as coating material).²⁰

As a continuation to previous work,^{20,23} here, the original coating strategy was modified to address specifically the latter aspect. To produce well-defined coatings on the CAM primary/secondary particles, the NPs should be ideally monodisperse and present in a nonagglomerated state, i.e., completely dispersed in a solvent, which is challenging to achieve by most methods. HfO₂ was selected as the coating material and precursor due to not only the possibility to readily prepare NP dispersions of good quality but also because of its high stability when in contact with Ni-rich CAMs (irrespective of the degree of lithiation or, in other words, state of charge).^{36,37} After applying the coating to the particles, the CAM, LiNi_{0.85}Co_{0.1}Mn_{0.05}O₂ (NCM85), was subject to annealing to initiate the reaction between HfO₂ and residual lithium. This procedure was meant to decrease the amount of surface carbonates and improve the ionic conductivity of the coating, even though the formed lithium-based ternary oxide is less stable than the parent material. The Li₂HfO₃/HfO₂-coated NCM85 (cathode with high active material content and high areal loading) was eventually tested in bulk-type SSB cells with Li₆PS₄Cl (LPSCI) SE and Li₄Ti₅O₁₂ (LTO) anode and found to show improved cyclability over uncoated CAM.

RESULTS AND DISCUSSION

A schematic of the two-step coating approach employed in the present work is shown in Figure 1a. In short, nonagglomerated

HfO₂ NPs (prepared by solvothermal synthesis) dispersed in solution were combined with the pristine NCM85 (referred to as Bare-NCM85) for surface coating,^{20,23} followed by annealing at 700 °C under oxygen. The second step led to the partial formation of Li₂HfO₃ by solid-state reaction with the residual lithium present on the CAM surface, thereby generating a kind of hybrid coating composed of HfO₂ and Li₂HfO₃ (referred to as LHO-NCM85).

Powder X-ray diffraction (XRD) and subsequent Rietveld refinement analysis (see Figures 1b and S1, Supporting Information) were used to probe the crystal structure before and after coating. The XRD pattern of LHO-NCM85 was found to be very similar to that of Bare-NCM85, suggesting that the layering is well preserved (*R*3*m* space group; see the structural model in Figure 1c). From the refined structural parameters given in Table S1, it can be seen that LHO-NCM85 exhibits slightly larger *a* and *c* lattice parameters than Bare-NCM85, resulting in an increase in cell volume by about 0.05 Å³. However, the degree of cation intermixing (Ni_{Li} defects) remained virtually unaltered, with 3.2% for Bare-NCM85 and 3.5% for LHO-NCM85, indicating that lattice lithium consumption during post-deposition annealing can be largely neglected.

The morphology of the Bare- and LHO-NCM85 CAMs was studied by means of scanning electron microscopy (SEM). The micrometer-sized secondary particles were more or less spherical in shape and consisted of sub-500 nm primary particles, see Figure 2a–d. The surface of the individual primary particles and the grain boundaries in Bare-NCM85 were clean and well defined. In contrast, LHO-NCM85 had rougher surfaces and fuzzy grain boundaries, with traces of NPs clearly covering the material and filling the gaps between the primary particles. In addition to SEM imaging, energy-dispersive X-ray spectroscopy (EDS) mapping was used to characterize the coated CAM (see Figure 2e–i), revealing an even distribution of Hf, Ni, Co, and Mn on the secondary particle level. From this data, it can be concluded that the surface of the NCM85 was uniformly coated, considering the resolution limit of the technique.

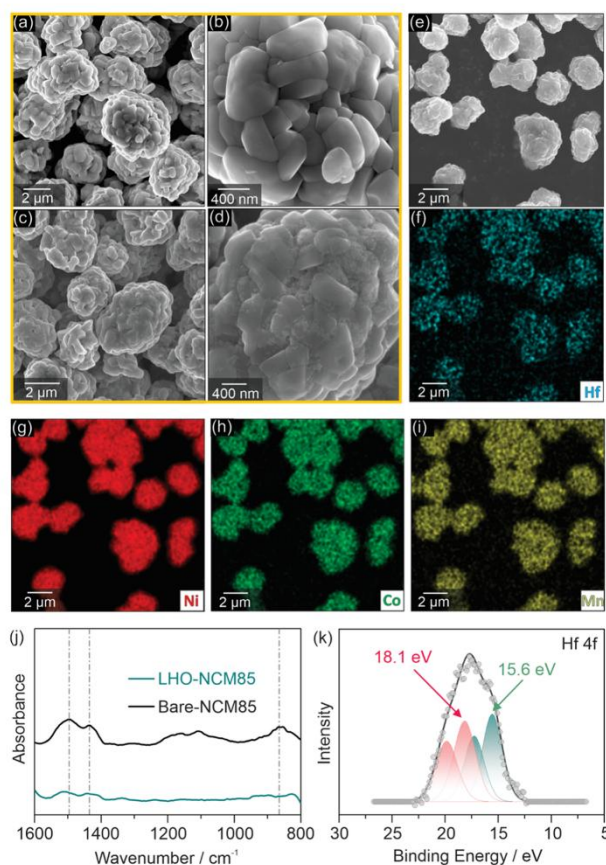


Figure 2. SEM images at different magnifications of (a, b) Bare-NCM85 and (c, d) LHO-NCM85. (e) Low-magnification SEM image of LHO-NCM85 and corresponding EDS mapping results for (f) Hf, (g) Ni, (h) Co, and (i) Mn. (j) ATR-IR data collected from the Bare-NCM85 and LHO-NCM85. Dashed lines denote the carbonate vibrational bands. (k) Hf 4f spectrum of LHO-NCM85.

Attenuated total reflection–infrared (ATR-IR) spectroscopy data collected from the Bare- and LHO-NCM85 samples (see Figure 2j) displayed carbonate vibrational bands at 870, 1430, and 1490 cm^{-1} .^{32,38} The bands observed for LHO-NCM85 were much weaker in intensity than that of Bare-NCM85. This difference implies a possible decomposition of Li_2CO_3 and/or chemical reaction with the HfO_2 NPs on the CAM surface. X-ray photoelectron spectroscopy (XPS) data for the Hf 4f core-level region (see Figure 2k) revealed a total of two doublets after fitting. The doublet at higher binding energy (Hf 4f_{7/2} at 18.1 eV) can be assigned to Hf^{4+} in HfO_2 ,^{39,40} while that at lower binding energy (Hf 4f_{7/2} at 15.6 eV) arises from the change in chemical environment due to lithium incorporation. A similar observation was made for Al_2O_3 coatings on NCM; new peaks appeared upon conversion to the respective lithium-based ternary oxide.^{29,41} Overall, XPS analysis indicated that the coating is a mixture of HfO_2 and Li-Hf-O species.

High-angle annular dark-field scanning transmission electron microscopy (HAADF STEM) measurements were conducted

on a focused ion beam (FIB)-prepared LHO-NCM85 specimen to gain more insights into the coating structure and composition. The low-magnification image in Figure 3a demonstrates that the secondary particles were coated well with a shell-like layer. EDS mapping (see Figure 3b) further confirmed the presence of a conformal coating of thickness $\sim 12\text{ nm}$. The data also indicate that hafnium interdiffusion into the subsurface volume or even the NCM85 bulk can be ruled out (unlike for sol–gel or atomic layer deposition (ALD)-derived zirconia coatings, for example).^{21,22,30,42} This result agrees with the cation intermixing from Rietveld refinement analysis, suggesting minor changes to the nickel on lithium site occupancy factor after post-deposition annealing. The high-resolution TEM (HR TEM) image in Figure 3c, taken from a selected region of the coating, displays lattice fringes, indicating the nanocrystalline nature of the HfO_2 and Li-Hf-O species. The corresponding fast Fourier transform (FFT) pattern shown in Figure 3d can be indexed to the monoclinic phase of HfO_2 ($P2_1/c$ space group, JCPDS card

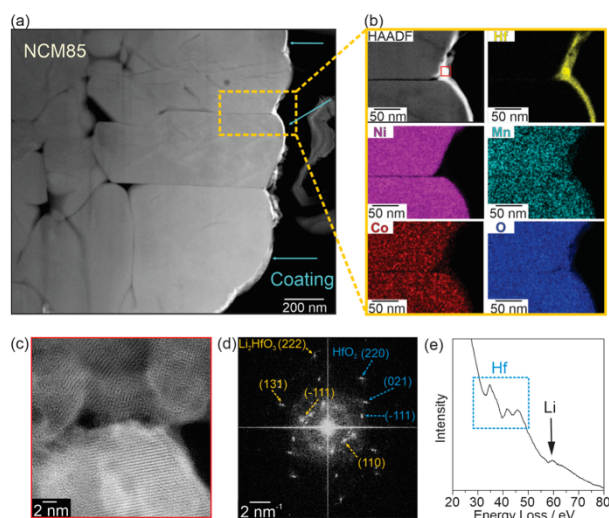


Figure 3. (a) Low-magnification HAADF STEM image of LHO-NCM85. (b) HAADF STEM image of the region denoted by the yellow box in panel (a) and corresponding EDS mapping of Hf, Ni, Mn, Co, and O. (c) HR TEM image of the surface coating denoted by the red box in panel (b), (d) corresponding FFT pattern, and (e) EEL spectrum.

No. 34-0104) and monoclinic Li_2HfO_3 ($C2/m$ space group, mp-756597).⁴³ The electron energy loss (EEL) spectrum in Figure 3e corroborates the presence of lithium in the coating (see Li K-edge peak at ~ 60 eV; note that the peaks in the energy loss range between 30 and 50 eV are characteristic of Hf) and therefore the formation of a $\text{Li}_2\text{HfO}_3/\text{HfO}_2$ hybrid shell on the CAM surface.^{44–46}

Taking into account the above results, quantitative XPS analysis (comparison of peak areas) revealed a ratio of Hf atoms in HfO_2 vs Li_2HfO_3 ratio of 1.02. (see Table S2). Furthermore, inductively coupled plasma-optical emission spectroscopy (ICP-OES, see Table S3) showed a Hf content of 0.84 wt %, which translates into a total coating content of 1.06 with 0.50 wt % HfO_2 and 0.56 wt % Li_2HfO_3 . Because the intensity of the carbonate vibrational bands was strongly diminished for LHO-NCM85 and the degree of cation intermixing barely changed upon surface modification, it appears that Li_2CO_3 served as the major lithium source in the formation of Li_2HfO_3 . Some more discussion on this (involving results from acid titration experiments) is provided in the Supporting Information.

To assess the effectiveness of the CAM coating, the cycling performance of LHO-NCM85 was examined in SSB full cells with a cathode loading of about $11 \text{ mg}_{\text{NCM85}}/\text{cm}^2$ (corresponding to $\sim 3 \text{ mAh}/\text{cm}^2$ for $q_{\text{th}} = 274 \text{ mAh/g}$) and compared to that of the uncoated reference material (Bare-NCM85). Argpyrodite LPSCI was used as SE in the cathode and anode, and Super C65 carbon black served as a conductive additive. The sandwich-type cell structure comprised three layers, namely, CAM/LPSCI/C65/LPSCI/LTO/LPSCI/C65. The electrochemical testing was carried out at 45°C and 81 MPa in the voltage range 1.35–2.75 V vs $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_7\text{Ti}_5\text{O}_{12}$.

Figure 4a shows voltage profiles of the initial cycle at 0.1C rate, revealing significant improvements in specific discharge capacity, with $q_{\text{dis}} = 187$ vs 162 mAh/g , and Coulomb

efficiency, with 82.4 vs 78.6%, for cells using the LHO-NCM85. This is clearly due to the presence of the protective coating (modification/stabilization of the CAMISE interface), which helps to mitigate adverse side reactions and therefore positively affects the charge transfer. The corresponding differential capacity (dq/dV) curves in Figure 4b display the phase transitions (from H1-M over M-H2 to H2-H3, with H: hexagonal and M: monoclinic) that the CAM undergoes during lithium extraction. These transitions are typical of Ni-rich NCM cathodes.⁴⁷ Notably, compared to LHO-NCM85, the H1-M peak of Bare-NCM85 appeared at a higher voltage (by 10 mV, see the inset of Figure 4b) because of sluggish kinetics. This result suggests that coating the secondary particles with an inert material is an effective means to reduce polarization, even at low C-rates.

Figures 4c,d and S2 compare the rate performance of the cells using bare and coated NCM85. Specifically, the C-rate was gradually increased from 0.1 to 1.0C. The LHO-NCM85 CAM delivered specific discharge capacities of 187, 155, 112, and 71 mAh/g at 0.1, 0.2, 0.5, and 1.0C, respectively, i.e., about 83, 60, and 38% of the capacity achieved at 0.1C was retained at higher C-rates (see Figure 4e). By contrast, in the case of Bare-NCM85, the specific discharge capacities were lower by about 25 mAh/g, independent of the C-rate. For example, only 28% (46 mAh/g) of the capacity was retained at 1.0C relative to that at 0.1C (162 mAh/g). This behavior can be explained by the growing overpotential with increasing C-rate (see Figure 4c), which was less pronounced in the LHO-NCM85-based cells due to the coating helping to stabilize the CAMISE interface (see also Figure S3a–c with related discussion).

Figure 4f shows the long-term cyclability of both CAMs at a rate of 0.2C. Bare-NCM85 revealed accelerated capacity fading after around 50 cycles. This is due to (interfacial) impedance buildup during cycling resulting from the SE decomposition and mechanical degradation caused by particle fracture and

3. Results

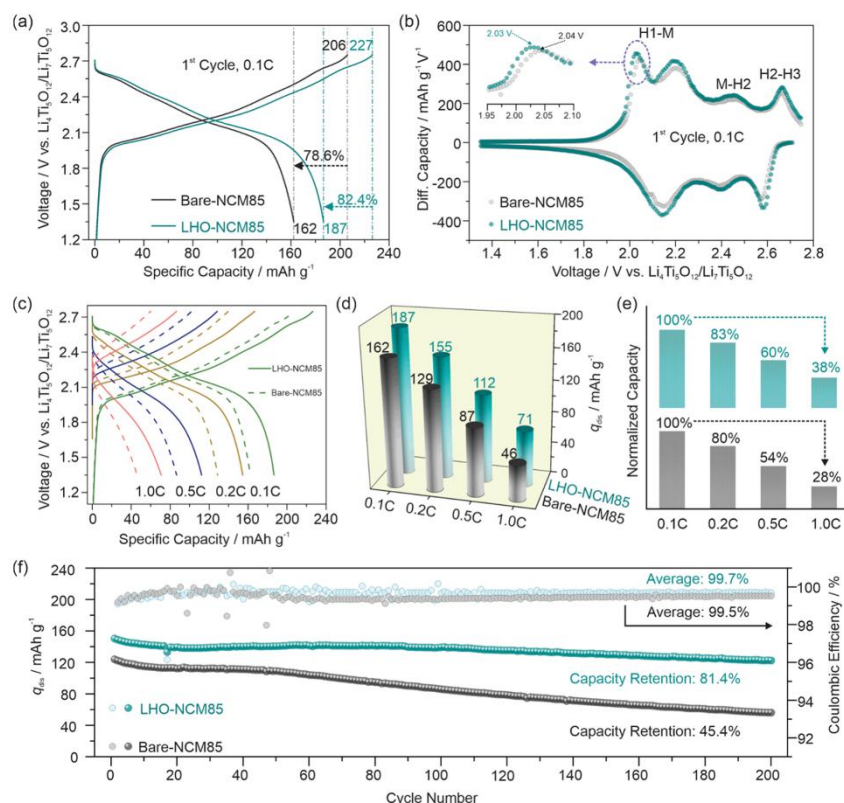


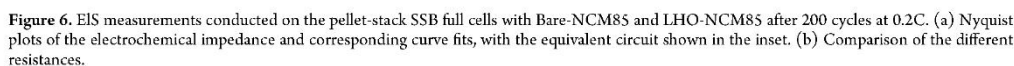
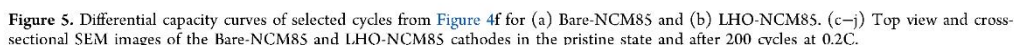
Figure 4. Cyclability of the Bare- and LHO-NCM85 CAMs in pellet-stack SSB full cells at 45 °C. (a) First-cycle voltage profiles and (b) differential capacity curves at 0.1C. (c) Voltage profiles at different C-rates and (d) corresponding specific discharge capacities. (e) Capacity retention with respect to 0.1C cycling (set to 100%). (f) Long-term cycling performance at 0.2C.

void formation.^{18,48} Note that especially the latter exacerbates the deterioration of electronic/ionic percolation through the composite cathode.¹⁹ As a result, the capacity retention after 200 cycles was only 45.4%. Unlike Bare-NCM85, the LHO-NCM85-based cells showed a much more stable performance, with 81.4% of the initial capacity retained after the same number of cycles. The average Coulomb efficiency also improved from about 99.5% for Bare-NCM85 to 99.7% for LHO-NCM85.

The differential capacity plots of selected cycles in Figure 5a,b (from the long-term cycling tests shown in Figure 4f) provide more information about the structural evolution of the NCM85 during cell operation. Characteristic peaks referring to the aforementioned phase transitions were evident for both CAMs in the beginning of cycling. As can be seen from the data, the polarization was much lower for LHO-NCM85 after 200 cycles. In particular, the H1-M peak was shifted to higher voltages by about 60 mV in the case of Bare-NCM85, compared to less than 10 mV for LHO-NCM85 (from the 10th cycle onward). This suggests that the protective coating is somewhat capable of suppressing adverse side reactions in the later cycles, eventually leading to improvements in CAMISE

interface stability.⁴⁹ The decrease in H1-M peak intensity/area for Bare-NCM85 is indicative of severe loss of lithium inventory.⁵⁰ The reason for this is likely a combination of electrochemical and mechanical degradation, including intergranular cracking of the NCM85 secondary particles and contact loss between CAM and SE. The coating, apparently, can not only mitigate degradation at the CAMISE interface but also ensure the structural integrity of the cathode, which is ultimately reflected in enhanced cyclability.

To corroborate the relationship between microstructural evolution and electrochemical performance, the structure/morphology of the Bare- and LHO-NCM85 particles before and after cycling was probed using SEM (see top view and cross-sectional images in Figure 5c–j). In the pristine state, the CAM secondary particles, indicated by yellow arrows in the respective images, were well embedded in the SE matrix at the micrometer level. After 200 cycles, particle fracture was clearly visible for the Bare-NCM85 cathode (see red circles in Figure 5g), while the LHO-NCM85 particles appeared to be largely intact (see Figure 5h). However, some SE cracking and void formation were evident in both cathodes. Furthermore, subtle differences in the cross-sectional SEM images collected from



To confirm the apparent differences in (decomposition) interphase formation among the Bare-NCM85 and LHO-

LHO-NCM85 cathodes, the intensity of the doublet at 163.6 eV ($S_{2p_{3/2}}$) was strongly increased. In addition, new doublets appeared at higher binding energies (>167.1 eV), originating from side reactions between the CAM and SE particles and leading to the formation of oxygenated sulfur species. In general, weaker signals were observed for LHO-NCM85, due to the presence of a protective surface shell and the low amount of remaining residual lithium (see also Figure S4b for relative amounts from quantitative XPS analysis). This corroborates the above results and provides clear evidence that the $\text{Li}_2\text{HfO}_3/\text{HfO}_2$ coating can mitigate but not prevent interfacial degradation, despite good surface coverage. A similar trend was evident from the P 2p data. A new doublet appeared at 133.9 eV ($P_{2p_{3/2}}$) that can be assigned primarily to insulating (meta)phosphates.

Finally, electrochemical impedance spectroscopy (EIS) measurements were conducted at 45 °C on the cells after 200 cycles at the end of discharge, with the objective to quantitatively determine the different contributions to the resistance. Respective Nyquist plots of the electrochemical impedance are shown in Figure 6a. The equivalent circuit, $R_{\text{bulk}}-(R_{\text{GB}}/\text{CPE})-(R_{\text{CAMISE}}/\text{CPE})-\text{CPE}$, used in the fitting of the EIS data, is presented in the inset of Figure 6a. Both bulk (R_{bulk}) and grain-boundary resistance (R_{GB}) in the high-frequency range were found to be similar for the Bare- and LHO-NCM85 (see Figure 6b and fitting results in Table S4). However, as expected, a significant difference in cathode interfacial resistance (R_{CAMISE}) in the medium-to-low frequency range was apparent, with $\sim 50 \Omega \text{ cm}^2$ for LHO-NCM85 and $\sim 850 \Omega \text{ cm}^2$ for Bare-NCM85. This strong impedance rise can only be explained by major differences in the chemo-mechanics and degradation at interfaces within the cathode.

CONCLUSIONS

Using a facile nanoparticle-based coating strategy, this work successfully fabricated a $\text{Li}_2\text{HfO}_3/\text{HfO}_2$ (LHO) protective coating on the secondary particles of a Ni-rich NCM (NCM85) cathode active material by consumption of residual lithium species during post-deposition annealing. TEM investigations indicated that the hybrid coating is relatively uniform (high surface coverage) and dense and has a thickness of ~ 12 nm. In sulfide-based solid-state battery cells, the LHO-coated NCM85 cathode showed superior electrochemical performance in terms of capacity, reversibility, rate capability, and longevity/stability compared to its uncoated counterpart. This improvement results from some stabilization of the interfaces within the cathode, mainly between the cathode active material and the solid electrolyte, and therefore mitigated electro-chemo-mechanical degradation during cycling, as confirmed by various characterization methods such as SEM, XPS, and EIS.

We believe that this work paves the way toward the development of lithium-based protective coatings on layered Ni-rich oxide cathode active materials, which are inherently susceptible to the formation of lithium surface impurities, and may foster the exploration of novel ionically conductive coatings. In this regard, it should be noted that lithium-containing materials are challenging to prepare as nanoscale (high-quality) coatings.

EXPERIMENTAL SECTIONS

Synthesis and Surface Coating. The preparation of HfO_2 NPs and the CAM coating followed previously published procedures.^{20,23}

In short, hafnium(IV) chloride ($\geq 99\%$, Sigma-Aldrich) was combined with anhydrous benzyl alcohol ($\geq 99\%$, VWR), followed by solvothermal reaction in an autoclave at 250 °C for 3 d. The product formed was washed and then transferred into chloroform ($\geq 99\%$, VWR) for surface functionalization with both oleic acid ($\geq 99\%$, Alfa Aesar) and oleylamine ($\geq 99\%$, Alfa Aesar). The resulting (quasi-transparent) dispersion of concentration $\sim 20 \text{ mg}(\text{HfO}_2)/\text{mL}$ (CH_2Cl_2) was used for coating the CAM secondary particles. Prior to coating, the NCM85 (BASF SE) was heated in oxygen at 750 °C for 3 h in order to reduce the amount of residual lithium species. A certain volume of the HfO_2 NP dispersion (plus some extra chloroform) was dropwise added to the CAM powder, targeting a coating content of 1 wt %. Next, the suspension was sonicated for 15 min, followed by heating at 60 °C in an oil bath under magnetic stirring until complete evaporation of the solvent. Finally, the remaining black powder was treated in vacuum overnight and then heated in oxygen at 700 °C for 2 h. After natural cooling, the LHO-coated NCM85 was transferred into an argon glovebox for further use.

Electrode Preparation. LPSCl (NEI Corp.) and Super C65 (TIMCAL Ltd.) were used as the SE and carbon additive, respectively. Ball milling was employed to produce the cathode composite, with the CAM:SE:Super C65 ratio being 69.3:29.7:1.0 by weight. After filling the powder mixture into a 70 mL zirconia jar containing 10 zirconia balls of diameter 10 mm under an argon atmosphere (glovebox conditions with $\text{H}_2\text{O} < 0.1$ ppm and $\text{O}_2 < 0.1$ ppm), it was milled at 140 rpm for 30 min using a FRITZSCH planetary mill. For the anode composite preparation, carbon-coated LTO (NEI Corp.), SE, and Super C65 (30:60:10 by weight) were mixed under the same conditions as described above for the cathode.

Cell Assembly. A customized cell setup with a PEEK ring of inner diameter 10 mm and two stainless steel dies as current collectors was used in the electrochemical testing of pellet-stack SSBs. 100 mg of SE was packed into the PEEK ring and then compressed at 62 MPa to produce the separator layer. Next, 65 and 12 mg of anode and cathode composite, respectively, was spread onto both sides of the separator. Finally, about 435 MPa was applied for 3 min to ensure proper contact between the different components in the electrode. The assembled cells were finally sealed into pouch bags to prevent exposure to the external atmosphere and (harmful) gas release into the environment.

Electrochemical Testing. The electrochemical performance was tested at different C-rates ($1.0\text{C} = 190 \text{ mA/g}$) and at 45 °C and 81 MPa using a MACCOR battery cycler. The voltage range was set to 1.35–2.75 V vs $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_7\text{Ti}_5\text{O}_{12}$, which corresponds to about 2.9–4.3 V vs Li^+/Li . A BioLogic SP-300 potentiostat was used for EIS measurements in the frequency range from 7 MHz to 100 mHz with a voltage amplitude of 7 mV (after a resting period of 1 h at the end of discharge to reach equilibrium).

Physicochemical Characterization. For SEM imaging, a Leo 1530 microscope (Zeiss) equipped with a field emission source was used, and the accelerating voltage was set to 10 kV. EDS was measured using an Oxford X-Max^N detector (Oxford Instruments) at 20 kV.

TEM measurements were performed at an accelerating voltage of 300 kV using a double-corrected Themis-Z microscope (Thermo Fisher Scientific) equipped with a HAADF STEM detector, a Super-X EDS detector, and a Gatan Continuum 970 High-Resolution image filter. The beam current used for STEM EDS mapping was about 200 pA. For TEM lamella preparation, a dual beam focused Ga-ion beam in an FEI Strata 400 at 30 kV was used. The surfaces were protected with carbon coatings by means of ion beam-induced deposition. The samples were subsequently thinned and further cleaned at 5 and 2 kV.

ICP-OES was conducted on samples using an iCAP 7600 DUO (Thermo Fisher Scientific). To this end, CAM powder was digested in a mixture of HCl and H_2SO_4 at 250 °C for 12 h. HfCl_3O (Alfa Aesar) dissolved into 5% HCl was used as the standard for Hf calibration.

ATR-IR was measured from 1800 to 600 cm^{-1} using an ALPHA FT-IR spectrometer (Bruker).

For XRD measurements, samples were packed into 0.5 mm borosilicate capillaries (Hilgenberg), and data were acquired in Debye–Scherrer geometry using a STOE Stadi-P diffractometer equipped with a Mo anode and a DECTRIS MYTHEN 1K strip detector. The instrumental contribution to peak broadening was determined by measuring a NIST Si 640f standard reference material as a line broadening reference. Rietveld refinement was performed using GSAS-II.⁵⁶ For refinement of NCM structural models against the diffraction data, the scale factor, zero shift, and size/strain broadening parameters were allowed to vary. A fixed background was fitted to the data using a Chebyshev polynomial function with 13 terms. In the structural model, the cell parameters, oxygen *z* coordinate, and atomic displacement parameters for each site were refined. Atoms occupying the same site were constrained to have the same atomic parameters, and site occupancy factors were constrained such that each site remained fully occupied.

XPS measurements were performed on a SPECS system with a PHOIBOS 150 energy analyzer using monochromatic Al-*Kα* radiation. Takeoff angle and pass energies for detailed and survey scans were set to 45° and 30/90 eV, respectively. The C 1s peak of adventitious carbon at 284.8 eV was used for binding energy calibration. Curve fits were done with the CasaXPS software using mixed Gaussian–Lorentzian peak functions and Shirley-type backgrounds. The peak area ratio and spin–orbit splitting were set to 4:3 and 1.71 eV for the Hf 4f features, while a 2:1 ratio and splitting of 0.84 and 1.18 eV were used to describe the P 2p and S 2p peak doublets, respectively.⁵⁷

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.chemmater.3c01116>.

XRD pattern and Rietveld refinement profile for Bare-NCM85; rate performance data for the Bare- and LHO-NCM85-based cells; differential capacity curves; S 2p and P 2p XP spectra and relative amounts of sulfur and phosphorus species; tables detailing the refined structural parameters, the relative percentage of Hf species with different chemical environments, the ICP-OES results, and the EIS fitting results; and discussion on the chemical reaction(s) leading to Li₂HfO₃ formation (PDF)

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Notes

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3.2. 3E Measurement Design and Influence of CE in SSBs

In the previous section, a range of physicochemical characterization techniques were employed to investigate the (electro)chemically formed interfaces/interphases between the Ni-rich cathode and SSE, with a particular focus on elucidating interfacial degradation pathways and mechanisms. In parallel, NP coatings were successfully implemented as an interfacial modification strategy, resulting in markedly enhanced stability and associated improvements in electrochemical performance.

EIS, as a powerful, non-destructive technique for probing the interfacial kinetics of energy storage devices, has been widely applied to investigate physicochemical processes in SSBs. When combined with ECM or DRT analysis, targeted interface-related kinetic processes can be effectively identified, and their evolution can be quantitatively tracked. In recent years, EIS-DRT analysis has therefore been extensively adopted to characterize the interfacial kinetics of WEs in the commonly used 2E configuration. However, the polarization of the CE is often not as negligible as assumed. In particular, for frequently used CE materials, such as In/InLi or LTO, their characteristic kinetic processes occur within the same regimes in the time domain comparable to those of the WE. This overlap leads to convoluted kinetic responses from the WE and CE during impedance-assisted interfacial analysis, particularly when the interfacial impedances of both electrodes are non-negligible, making it extremely challenging to decouple their respective contributions. Moreover, the limited thermodynamic stability of SSEs can cause CE polarization during long-term operation or under demanding dynamic conditions, such as high C-rate application, thereby significantly influencing the performance and the objective evaluation of the WE.

An ideal solution to this challenge is the introduction of a RE and the adoption of a 3E setup. However, at the beginning of this doctoral research in 2021, 3E setups for SSBs were rarely reported, primarily due to the intrinsic complexity and practical limitations of solid-state systems. To address this gap, this section presents an in-house-designed 3E setup, together with systematic investigations, which constitute the core research contributions of this PhD work.

First, in **Publication IV**, with a primary focus on RE design, a 3E setup employing an LTO composite as the RE (denoted as LTO-RE) was systematically developed and evaluated. The pronounced overlap of interface-related kinetic processes within similar time-constant regimes was highlighted, underscoring the necessity of 3E configurations for interfacial studies in SSBs. Extending these investigations to more practical operating scenarios, **Publication V** provides a comprehensive and in-depth analysis of the polarization behavior, interface-related kinetic response, and their evolution during long-term cycling for commonly used CEs. When coupled with a Ni-rich cathode as the WE, the influence of the CE on battery performance was systematically examined under various operating conditions. Together, these studies offer multiple perspectives and new analytical approaches for understanding, evaluating, and ultimately improving the performance of SSBs.

3.2.1. Publication IV: Timescale Identification of Electrochemical Processes in All-Solid-State Batteries using an Advanced Three-Electrode Cell Setup

To identify the influence of the CE on the interfacial kinetics of the WE in 2E cells and to separately analyze the response of both WE and CE in a practical SSB, an in-house-designed 3E measurement setup was introduced and evaluated in **Publication IV**. In this study, the primary focus was placed on two commonly used anode materials as CEs in SSBs, namely LTO and In/InLi. Herein, LTO composite and In/InLi were employed as the WE and CE, respectively, for the investigation in both 2E and 3E cells. Nearly identical assembly conditions were enabled for both cell configurations, except for a thicker separator layer in the 3E cells to accommodate the embedded RE.

The RE, as the most critical component in a 3E configuration, its choice of material, geometric form, and placement position constitute key factors governing the reliability of 3E measurements. In this work, an LTO composite in combination with a stainless-steel wire (diameter: 127 μm) was used to fabricate the RE. Importantly, to ensure a stable reference potential, the LTO composite was pre-lithiated in a 2E cell, rather than undergoing *in situ* lithiation in the 3E configuration. Subsequently, the carefully lithiated LTO composite was harvested from the 2E cell in the form of fragmented pieces and further utilized for RE fabrication in the 3E setup (denoted as LTO-RE). As key parameters of the LTO-RE, its pre-lithiation protocol, the composition of the LTO composite (i.e., the weight ratio among LTO, SSE, and Super C65), and the mass loading were systematically optimized.

The stability of the LTO-RE reference potential was evaluated first. The fabricated LTO-RE exhibited a potential drift of only ~ 8 mV over 600 h, demonstrating its suitability as a robust reference electrode. Through *in situ* EIS-DRT analysis on In/InLi|SSE|LTO 2E cells, the SOC-dependent interfacial kinetics of LTO was revisited, and the relationships among potential, SOC, and interfacial kinetics were systematically examined. This analysis provided a basis for objectively assessing the influence of the LTO-RE on measurement outcomes when employed in a 3E setup.

The respective 3E cells exhibited an electrochemical performance virtually identical to their 2E counterparts, confirming the reproducibility of the electrochemical processes in 2E cells enabled by the designed 3E configuration. The 3E measurements further delivered well-separated electrode potentials and high-quality impedance data. EIS-DRT analysis in the 3E configuration clearly revealed overlapping interface-related kinetic processes associated with both electrodes, with pronounced contributions in the charge-transfer regime in the time domain. Moreover, quantitative analysis of the interfacial impedance demonstrated that the contribution of In/InLi as the CE is not as negligible as often assumed and can exert a profound effect on specific interfacial kinetic processes.

3. Results

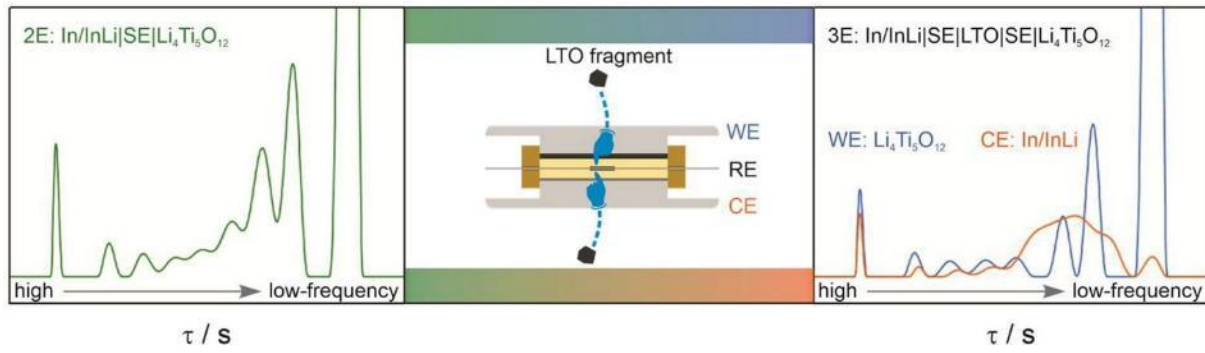


Figure 10. Table of contents graphic of Publication IV. Adapted from reference [47].

The experiments were designed and planned by the first author R. Zhang, under the supervision of A. Kondrakov, J. Janek, and T. Brezesinski. R. Zhang conceptualized the idea, designed the 3E setup, conducted all the involved tests and measurements, including galvanostatic cycling with potential limitation (GCPL), EIS-DRT, XRD, SEM-EDS, and analyzed and interpreted the gathered data. The first draft was written by R. Zhang with further modification by J. Janek and T. Brezesinski. The final paper was edited by all the co-authors.

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Timescale identification of electrochemical processes in all-solid-state batteries using an advanced three-electrode cell setup

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ABSTRACT

Two-electrode (2E) setups commonly employed in solid-state batteries (SSBs) are often not sufficient to deconvolute electrochemical processes of anode/cathode. To address this issue, herein we introduce a three-electrode (3E) cell setup, making use of an electrochemically prelithiated lithium titanate composite as reference electrode (LTO-RE). The potential/state of charge/kinetics relationship of LTO was revisited by conducting both *ex situ* and *in situ* electrochemical impedance spectroscopy measurements and corresponding distribution of relaxation times (DRT) analyses. The proposed LTO-RE maintains a stable reference potential of about 1.57 V vs. Li⁺/Li with minimal drift (by 8 mV over 600 h) and negligible growth in charge-transfer resistance, enabling long-term use in 3E SSB cells. Time constants representing the involved kinetic processes are often quite close and obscure reliable assessment of contributions from different electrodes. By implementing the 3E approach, the overlap of kinetic processes between LTO working electrode and In/InLi counter electrode across a broad range of timescales can be effectively separated and identified. The proposed 3E setup offers a viable approach for thoroughly studying the interfacial kinetics of individual electrodes, thereby enhancing understanding of the underlying degradation processes in SSBs and ensuring stable long-term testing.

1. Introduction

In recent years, solid-state batteries (SSBs) or even all-solid-state batteries (ASSBs), which share a similar configuration with lithium-ion batteries (LIBs) by replacing the liquid electrolyte (LE) with a solid electrolyte (SE), have been regarded as a potential follow-up technology for the electrification process of automobiles [1]. This shift is driven by the increasing demands for safety and driving range in electric vehicles, as well as the approaching physicochemical limits of conventional LIBs [2,3]. The high ionic conductivity observed in superionic (ceramic) conductors, such as sulfide-based SEs, which can even surpass that of LEs, and the potential implementation of lithium metal anodes are paving the way for advanced SSBs to become a reality [4–6]. However, despite the promising general outlook, they still face numerous challenges. For instance, the application of sulfide-based SEs is limited by an intrinsically narrow electrochemical stability window, leading to interface-related issues, especially when coupled with layered Ni-rich oxide cathodes and/or high-capacity anodes [7,8]. Therefore, effective interface engineering of the cathode active material (CAM) and careful

anode selection for electrochemical testing of SSBs at the laboratory scale are imperative [9–14].

In SSB testing, the two-electrode (2E) approach predominates due to its simplicity. Mostly, only one of the electrodes is of primary interest, often the cathode, which can then be considered as working electrode (WE) following conventional notation. Along with this, the counter electrode (CE), simultaneously used as a reference electrode (RE), is expected to provide a stable reference potential with minimal polarization. In cells with liquid electrolytes, this even leads to the rather colloquial notion of “half-cells” when a full cell with a metal anode is studied. Clearly, any conclusion on the properties of a WE in a 2E cell relies on the assumption that the CE does not contribute to the characteristics or that its own contribution can be readily subtracted. However, this assumption often fails, particularly in studies exploring the fast charging capability of the WE [15,16].

The commonly employed alloy-type CEs in SSBs, such as In/InLi, are often presumed to contribute to a minor extent to the overall overpotential and electrochemical degradation, and their effects are typically overlooked. Recent studies have highlighted the stability

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limitations of the In/InLi CE and shown that microstructural deterioration at the In/InLi/SE interface during long-term cycling can lead to unexpected and substantial interfacial resistance [15,17,18]. This emphasizes the necessity of distinguishing and quantitatively analyzing the origin of degradation at the negative and positive electrodes in SSBs. Microscopic and spectroscopic techniques are capable of providing profound insights but are generally destructive. Yet, they may provide detailed information on the chemical and microstructural changes at the interface of individual electrodes, even down to the nanometer level.

In the case of sulfide-based SSBs, the cathode interface and associated degradation mechanisms have been investigated in considerable detail using various techniques, such as X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (TOF-SIMS), and transmission electron microscopy (TEM), as documented in the literature [19–22]. Electrochemical impedance spectroscopy (EIS) is widely used to monitor interfacial kinetics, as well as electrode materials under *operando* conditions in a non-destructive manner. The conventional approach of impedance analysis uses equivalent circuit model (ECM) fitting that often provides a good intuitive understanding of cell components and their behavior but relies on a number of simplifying assumptions. Problems quickly arise from the overlap of impedances with similar time constants in the frequency domain, and the different contributions from the two electrodes can hardly be separated. Therefore, it has recently become more common to first analyze the distribution of relaxation times (DRT), without assumptions on a potential equivalent circuit. Robust numerical routines are available, and DRT has meanwhile been extensively deployed in LIB research [23–26]. The transformation from frequency to time domain reveals and separates the various kinetic processes (through distinct timescales), manifested as peaks of specific shape in the DRT pattern. Any LIB relies on a number of (electro)chemical reactions, with key processes, such as interphase formation, charge transfer, or diffusion, often exhibiting similar time constants ranging from around 10^{-5} to 10^2 s for both the WE and the CE [23]. The 3D character of real electrodes further complicates the impedance analysis, as geometric effects can lead to own impedance signals, well documented for the case of spatial constriction effects [27, 28]. In general, close values of time constants and their spread may lead to misinterpretations in 2E systems.

An effective way to differentiate the contributions of individual electrodes is to employ a three-electrode (3E) measurement system, which is the standard approach in electrochemistry. This method facilitates isolation of effects from the WE and the CE by incorporating a (current-free) RE, which allows tracking the potential and impedance of the electrodes separately during electrochemical testing, provided that the RE is geometrically well defined and positioned [29]. While the implementation of 3E cell setups is widespread in LIBs [30–32], their application in SSBs remains relatively scarce [16,33–36].

Unfortunately, the development of a reliable 3E setup for SSBs faces several challenges. (i) The architecture of SSB testing setups currently lacks standardized designs, even for 2E cells. The introduction of a RE into a solid-state environment introduces rigorous manufacturing demands and spatial constraints, which are more challenging than those in liquid systems. (ii) Various materials or material combinations that can provide a constant RE potential, such as plated lithium, lithium-indium alloy, or lithium-gold alloy, along with insertion-type lithium titanate (LTO), have recently been implemented as REs in 3E cell designs for SSBs [16,29,33,36–39]. Nonetheless, some of these REs require an *in situ* lithiation step post assembly. Such a process, which typically involves connecting the RE to the WE or CE in a circuit, might initiate local volume expansion and SE decomposition near the RE, thus compromising the cell's structural integrity and potentially leading to mechanical failure. Furthermore, the thermal sensitivity of certain RE materials, e.g. lithium-gold alloy, imposes significant spatial and temporal constraints in their practical application. (iii) The integration of a RE, including its current collector (wire, mesh, or point-contact type), significantly complicates the cell design. To ensure stable testing

conditions and mitigate the risk of short circuits, it is required to adopt protective measures. Overall, the logistical and technical challenges associated with constructing 3E cells far exceed those encountered in 2E setups.

Aside from that, a critical question remains whether the introduction of a RE into 3E cell setups accurately mirrors the phenomena observed in 2E cells. Regarding potential tracking, the RE size can strongly affect the outcome, due to local (geometric) blocking effects restricting ion migration [40]. For 3E EIS measurements, artifacts in the high-frequency range are often attributed to factors such as the high-impedance RE, stray capacitance from connected cables, etc. [41, 42]. The shape, placement, and size of RE can also compromise the quality of impedance data, as demonstrated by computational studies [43]. It is thus important to thoroughly evaluate the comparability of 3E measurements to their 2E counterparts.

In view of these constraints, we have developed a robust 3E setup for SSB testing, delivering data that are well comparable to those collected from the corresponding 2E cells. Initially, prelithiation of an optimized LTO composite is performed electrochemically in a 2E cell (here, the LTO is considered as WE). Subsequently, the material, using a stainless steel (SS) wire as current collector, is integrated into the separator layer of a customized 3E cell as RE. Applying *ex situ* rather than *in situ* lithiation for the preparation of the LTO-RE, the reference potential can be predefined and further helps significantly enhance the structural integrity. LTO, serving as the core material in the RE, exhibits excellent chemo-mechanical properties in combination with sulfide-based SEs, which is advantageous for long-term testing in this kind of cell configuration. The LTO-RE contains the same SE employed in the separator, trying to avoid any risks associated with SE heterogeneities. Note that the latter can impede lithium transport and increase constriction resistance [35,44]. Overall, the proposed concept of RE design is facile (lack of complex processing steps), offers chemical flexibility, and can be readily implemented into practical SSB testing.

In the following, we describe all necessary steps in detail. Initially, we conducted a comprehensive investigation into the relationship between potential, state of charge (SOC), and kinetics of LTO in In/InLi/SE|LTO cells by EIS-DRT analysis and examined the stability of the LTO-RE, focusing on potential drift and charge-transfer kinetics. By constructing 3E cells in the form of In/InLi/SE|LTO-RE|SE|LTO, we observed that the DRT patterns from the different electrodes indeed overlap due to similar time constants, emphasizing the challenges in accurately distinguishing individual contributions in 2E cells. These findings underscore the necessity of using 3E configurations for enhancing the understanding of the kinetics of individual electrodes in SSBs.

2. Results and discussion

2.1. Preparation of RE and 3E cell design

Carbon-coated LTO, sourced from NEI Corp., was utilized as active material. Prior to performing any electrochemical investigations, the physical characteristics of the LTO material were assessed by X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS), with the results provided in **Figure S1** and **Table S1** and discussed in some detail in **Supplementary Note 1**.

LTO exhibits a wide voltage plateau during (dc)lithiation owing to a two-phase equilibrium involving spinel-type $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and rock-salt-type $\text{Li}_7\text{Ti}_5\text{O}_{12}$ phases, making it an ideal active material for the preparation of a RE, having a stable potential of about 1.57 V vs. Li^+/Li (equivalent to 0.95 V vs. In/InLi) [38]. First, In/InLi/SE|LTO 2E cells were assembled, as shown in **Fig. 1b**, to tailor the critical parameters, including electrode composition, In/InLi CE, and most importantly, the prelithiation protocol for the LTO-RE. Aiming at minimal potential drift, the most favorable conditions identified during optimization in the 2E cells enabled the expected galvanostatic cycling, as indicated in **Fig. 1c**.

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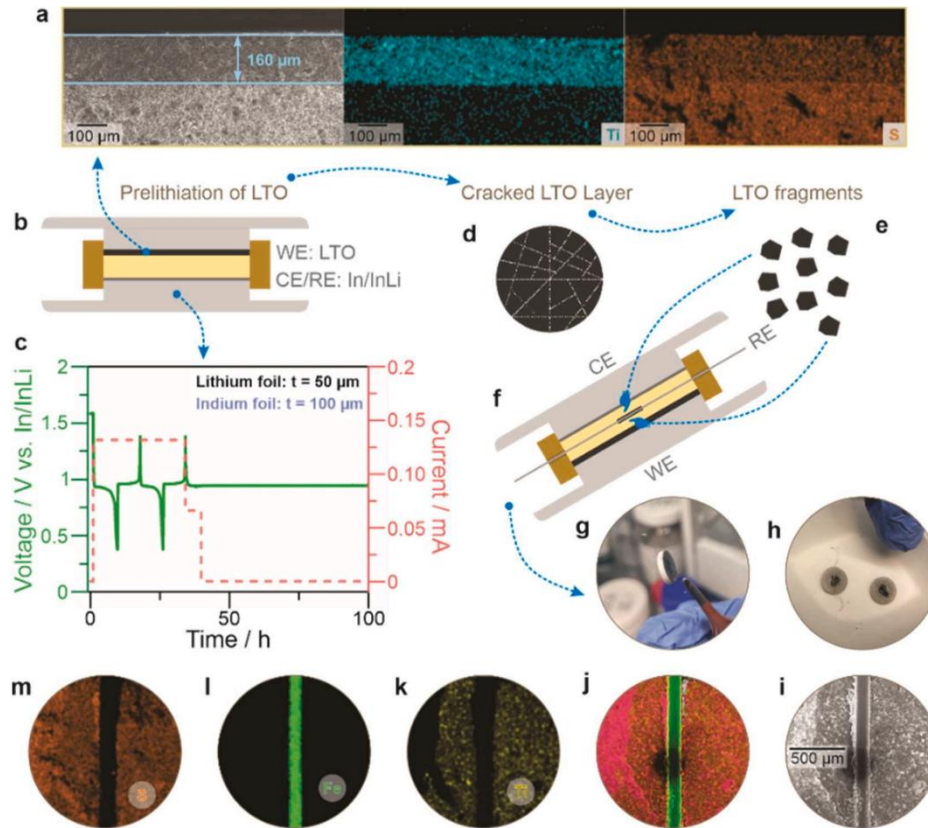


Fig. 1. Preparation of RE and design of 3E SSB cells. (a) Cross-sectional SEM image of the pelletized LTO composite and corresponding EDS mapping of Ti and S. (b) Schematic of 2E cell configuration with LTO as WE and In/InLi as CE/RE. (c) Voltage profile of an In/InLi|SE|LTO cell during prelithiation; the indium and lithium foil thicknesses are indicated. (d) Disassembled pellet after prelithiation. (e) Fragments of the prelithiated LTO composite serve as RE in 3E cells. (f) Schematic of 3E cell configuration featuring a sandwich RE design with two symmetrically embedded LTO fragments in the SE separator and an SS wire as current collector in between. (g) An assembled 3E pellet stack. (h) Inner structure of the embedded RE with corresponding (i) SEM imaging and (j–m) EDS mapping results.

The corresponding parameters are briefly listed in the following. (i) LTO composite with a weight ratio of LTO:Li₆PS₅Cl SE:Super C65 carbon black = 30:65:5 performed best and was used as WE. (ii) 100 μ m thick indium foil-based In/InLi was used as CE. (iii) Initially, two formation cycles at 0.1C were performed, followed by a capacity-limited lithiation of LTO at 0.05C. 50 mAh g_{LTO}⁻¹, corresponding to a capacity of 0.375 mAh (based on the total loading of about 25 mg), was targeted to ensure LTO remains within the two-phase coexistence region during testing (see Fig. 1c). Interestingly, the thickness of indium foil was critical to the success of the prelithiation procedure. Using the same lithium foil of thickness 50 μ m, a thicker indium foil (125 μ m) led to an abnormal lithiation profile of LTO. This may be due to non-uniform alloying near the SE|In interface, resulting in hindrance of ion transport during the initial delithiation. The failure of multiple cells with the thicker indium foil is displayed in Figure S2.

The pelletized LTO composite layer, having a thickness of about 160 μ m, was also probed using cross-sectional SEM combined with EDS mapping, as shown in Fig. 1a, and was then used in the RE preparation. The assembly process of 3E cells is detailed in the experimental section. As illustrated in Fig. 1d and e, after harvesting of the pellet from the 2E

cell, the cracked LTO composite layer (with the SE separator attached) was further thinned, yielding individual fragments (see Fig. 1e). By sandwiching two pieces of LTO fragments between a thin SS wire, a symmetrically structured RE was embedded within the SE separator layer (1.47 mm thickness) of the 3E cell, as depicted in Fig. 1f. A practical 3E cell stack of high structural integrity is shown in Fig. 1g. The dissected pellet, exposing the internal structure of the LTO-RE, is displayed in Fig. 1h. EDS mapping performed in the vicinity of the SS wire confirmed the uniformity of the LTO-RE within the separator, as shown in Fig. 1i–m.

A critical parameter regarding the design of a 3E cell is the size of RE, which could potentially lead to ion-blocking effects [29]. To mitigate hindrance of ion transport, our design incorporates small fragments of the pelletized LTO composite and a wire-type current collector, thereby reducing size and coverage within the 3E cell. About 12.5 to 25% of the surface involved in the lithium transport pathways are covered by the embedded RE. According to the composition (see above), argyrodite Li₆PS₅Cl accounts for 65% of the as-prepared LTO-RE, while the same SE also serves as separator. This approach allows for a high degree of ion percolation through the LTO-RE. Aside from that, the *ex situ*

3. Results

prelithiation of LTO (in 2E cells) ensures in advance the presence of stable interfaces between LTO and SE, thus avoiding unexpected mechanical failure near the RE, which may arise with *in situ* lithiation strategies.

LTO itself exhibits a reasonable ionic conductivity and has recently been applied in sandwich-type, multilayer SE structures for SSBs [45, 46]. Therefore, LTO and composites thereof are less likely to strongly contribute to ion blocking, unlike the current collector of RE. Considering the wire shape of the SS current collector used for the proposed RE, much lower coverage and higher robustness compared to mesh- and point contact-type counterparts can be expected.

2.2. Stability and kinetics of LTO-RE from 2E OCV-EIS analysis

Given that the LTO-RE is embedded within the SE separator throughout the duration of the 3E measurement, it is imperative to evaluate its potential drift and chemo-mechanical stability. To this end, long-term open-circuit voltage (OCV) monitoring, coupled with EIS-DRT analysis, was performed at selected time intervals on an In/InLi|SE|LTO 2E cell, as depicted in Fig. 2a–d. Prelithiated LTO (denoted as

$\text{Li}_{4-x}\text{Ti}_5\text{O}_{12}$) initially displayed a potential of 0.95 V vs. In/InLi, which corresponds to 1.572 V vs. Li^+/Li [13]. A slight shift by about 8 mV toward higher potentials was observed after 600 h (selected point in time: 5), confirming the electrode's capability of sustaining a stable reference potential in a 3E setup.

As the monitoring duration extended, the OCV drift became increasingly evident, exhibiting additional increases by 11 and 46 mV over subsequent periods of 254 h (854 h) and 435 h (1035 h), respectively (selected points in time: 6 and 7). Overall, the trend in OCV drift transitioned from steady (selected points in time: 1 to 5) to accelerated increase (selected points in time: 5 to 7) throughout the monitoring period. Despite the substantial drift from the initial value, a straightforward recalibration protocol, consisting of a full discharge/charge cycle, followed by relithiation to the targeted specific capacity, was effective in correcting for this. The latter recalibration proved successful over extended measurement periods, as illustrated in Figure S3.

The noticeable changes in OCV suggest alterations within the electrode structure. The potential of In/InLi remains stable across a wide range of compositions, as demonstrated by coulometric titration measurements [13]. Therefore, the observed trend is more likely due to

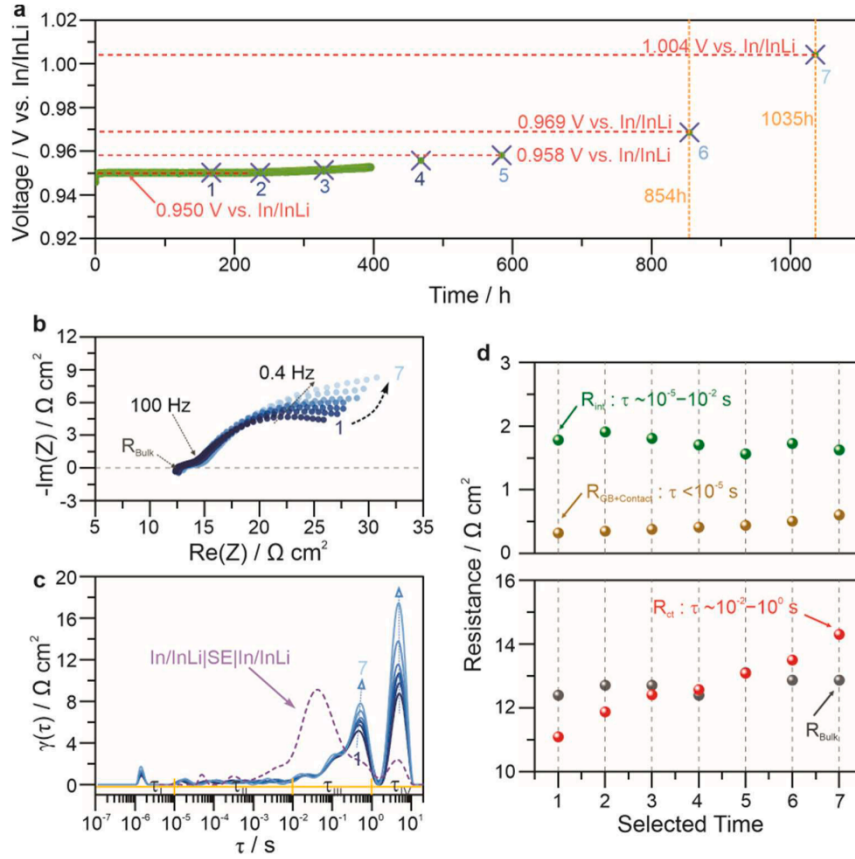


Fig. 2. OCV monitoring with EIS-DRT analysis of the In/InLi|SE|LTO cell. (a) Continuous OCV monitoring after prelithiation; selected points in time, from 1 to 7, for subsequent EIS analysis are indicated. (b) Corresponding Nyquist plots and (c) DRT patterns. The dashed purple line represents the DRT pattern of the In/InLi electrode collected from an In/InLi|SE|In/InLi symmetrical cell. (d) Fitted resistances (SE bulk, SE GB together with the contact resistance, interphase, and charge transfer) are categorized according to their characteristic time constants.

changes in the $\text{Li}_{4-x}\text{Ti}_5\text{O}_{12}$ structure, and hereafter, this discussion will refer to potential drift concerning LTO rather than OCV drift. During the period of OCV monitoring, LTO was maintained in an equilibrium state. Wagemaker *et al.* demonstrated that the lithiated LTO after relaxation exists as a solid-solution phase with nanoscale domains coexisting and exhibiting either 8a Li occupancy (referring to $\text{Li}_4\text{Ti}_5\text{O}_{12}$) or 16c Li occupancy (referring to $\text{Li}_7\text{Ti}_5\text{O}_{12}$) [47,48]. The observed potential shift may correlate with a gradual self-delithiation, from rock-salt $\text{Li}_{4-x}\text{Ti}_5\text{O}_{12}$ toward spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$, indicating a change in SOC via continuous phase transition within these nanodomains. Concurrently, because the argyrodite SE is not stable at the potential of both electrodes, slowly evolving degradation of $\text{Li}_6\text{PS}_5\text{Cl}$ by interfacial reactions could result in microstructural changes to the LTO and/or In/InLi electrode. These would be indicated by variations in charge-transfer resistance. To elucidate the underlying kinetic processes, EIS-DRT analysis was performed.

Fig. 2b illustrates the evolution of impedance across the time intervals indicated in Fig. 2a. As can be seen, the impedance increases with prolonged monitoring, corresponding to the rising potential drift. In the EIS spectra, a barely distinguishable depressed semicircle appears in the medium- to high-frequency range (above 100 Hz), while a prominent and enlarging semicircle is apparent in the medium- to low-frequency range (below 100 Hz). To enhance visualization and quantification of the kinetic processes involved, model-independent DRT analysis was employed. This approach was supplemented by fitting individual peaks derived from the DRT patterns. An example of peak fitting is presented in Figure S4, while the principles of DRT are discussed in Supplementary Note 2, and the general procedure of data processing is depicted in Figure S5. Considering the different timescales of these peaks, we have categorized them into four distinct regimes based on typical kinetic processes in SSBs, as suggested in the literature [23,26].

As shown in Figs. 2c and S4, the single peak within the τ_I regime can be attributed to the grain boundary (GB) response of the $\text{Li}_6\text{PS}_5\text{Cl}$ SE and the potential contact resistance between the electrodes and the current collector. The smaller peaks present in the slower τ_{II} regime are indicative of charge transfer across as-formed interphases, such as $\alpha\text{-Li}_2\text{TiO}_3$ and In_xS_y (e.g., In_2S_3), which are principal decomposition products of LTO and In/InLi, respectively [18,49]. In the τ_{III} regime, more pronounced peaks are observed, reflecting charge-transfer processes of both electrodes. These peaks also reflect microstructural changes at the interface between the electrode active materials and the SE, demonstrating their kinetic response to SOC variations. Finally, the peak in the most sluggish kinetic regime, τ_{IV} , represents diffusive processes and additional interface-related charge-transfer processes, correlated with the respective SOC.

The evolution of the individually fitted peaks and the corresponding changes in resistance during OCV monitoring are presented in Fig. 2c and d and detailed in Tables S2 and S3. The bulk resistance (R_{Bulk}) and the combined grain boundary and contact resistances ($R_{\text{GB+Contact}}$) exhibit slight increases, which may be attributed to microstructural changes either between the current collector and the electrodes or within the electrodes themselves. In contrast, the interphase resistance (R_{int}) reveals a decreasing trend, with an average value of $1.7 \Omega \text{ cm}^2$, indicative of fast charge transport across the interphases formed at both the LTO and In/InLi electrodes. The largest changes are found for the charge-transfer resistance (R_{ct}), which increased linearly from 11.1 to $14.3 \Omega \text{ cm}^2$.

To examine the charge-transfer characteristics of the LTO and In/InLi electrodes, a symmetric cell (In/InLi|SE|In/InLi) was fabricated and cycled galvanostatically to mimic the In/InLi|SE interface in the In/InLi|SE|LTO 2E cell. The respective Nyquist plot and DRT pattern are presented in Figs. 2e and S6. The most significant peak for In/InLi in the DRT pattern, located in the τ_{III} regime, is characterized by a time constant of $4.2 \cdot 10^{-2} \text{ s}$, in agreement with that reported in the literature [50]. This peak corresponds well with peak “P5” (see Figure S4) for the In/InLi|SE|LTO 2E cell, as summarized in Table S2. Throughout the

entire OCV monitoring period (selected points in time: 1 to 7), the “P5” peak remained unaltered at about $1.1 \Omega \text{ cm}^2$. Consequently, it can be inferred that the continuous increase in R_{ct} primarily originates from the LTO side. During OCV monitoring, microstructural changes within the electrode somewhat impede ion transport. However, the rate of increase in R_{ct} over the entire duration (1035 h) was determined to be only $0.003 \Omega \text{ cm}^2 \text{ h}^{-1}$, suggesting that this does not significantly affect charge transport during prolonged operation as RE.

The observed deviation from the flat voltage plateau suggests a gradual phase transition in $\text{Li}_{4-x}\text{Ti}_5\text{O}_{12}$, which correlates with changes in SOC. Given that the lithium diffusivity in LTO depends upon the SOC [51,52], examination of the peak in the τ_{IV} regime revealed a steady, then accelerated increase in peak intensity. This behavior aligns with the observed trend in potential drift. To further explore the relationship between potential, SOC, and kinetics in LTO, *in situ* EIS-DRT analysis was performed, as detailed in the subsequent section.

2.3. In situ 2E EIS-DRT analysis

By applying an ultra-low current (0.05C) for tailoring the degree of (de)lithiation, selected SOC (labeled from 1 to 18, see Fig. 3a) were probed *in situ* using EIS-DRT analysis. The corresponding measured OCVs and specific capacities are given in Table S4. In particular, the interface-related kinetics, which is affected by variations in SOC, was examined, as illustrated in Fig. 3b–g. As the Li^+ ions are inserted/extracted into/from the LTO during discharge and charge, respectively, the composition of the lithium-indium alloy varies reversibly between $\text{Li}_{0.27}\text{In}$ (lithiated state) and $\text{Li}_{0.15}\text{In}$ (delithiated state). For details on the calculation, see Supplementary Note 3 and Table S5. As expected, compared to LTO, the evolution of peaks associated with the In/InLi electrode in the DRT patterns is relatively minor [50]. Consequently, they predominantly reflect the kinetics of LTO with varying SOC. Notably, dominant peaks in the τ_{III} and τ_{IV} regimes indicate major SOC-dependent interfacial charge-transfer processes and solid-state diffusive processes within the LTO particles.

Considering the phase transitions within the nanodomains of LTO, continuous lithiation leads to a transformation from spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ to rock-salt $\text{Li}_7\text{Ti}_5\text{O}_{12}$, progressing from SOC 1 to 9. The differences in the apparent lithium diffusion coefficient between $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ($1.6 \cdot 10^{-11} \text{ cm}^2 \text{ s}^{-1}$) and $\text{Li}_7\text{Ti}_5\text{O}_{12}$ ($1 \cdot 10^{-12} \text{ cm}^2 \text{ s}^{-1}$) result in decreasing ion mobility with increasing rock-salt phase fraction [53]. It is also noteworthy that even minor lithium insertion into $\text{Li}_4\text{Ti}_5\text{O}_{12}$ significantly enhances the electronic conductivity, by four to six orders of magnitude [54]. Thus, the rate-limiting factor is the ionic conductivity rather than the electronic conductivity, which is more pronounced in solid-state systems. As the Li concentration within the LTO particles increases, ion mobility decreases, demonstrating its SOC-dependent nature.

High reversibility is apparent from the subsequent charging process, which involves continuous delithiation of LTO and lithiation of In/InLi, progressing from SOC 10 to 18. As $\text{Li}_7\text{Ti}_5\text{O}_{12}$ is converted back to $\text{Li}_4\text{Ti}_5\text{O}_{12}$, the increasing fraction of the latter phase enhances the overall lithium diffusivity. From SOC 10 to 16, the interface-related kinetic hindrance consistently decreases. From SOC 17 to 18, near the completion of phase transition, a resurgence of peaks in the τ_{III} and τ_{IV} regimes is observed (see Figure S7). This indicates emerging charge-transfer issues at the interface between LTO and SE, as well as an accompanying diffusive or phase transition-induced sluggish process within the particle's interior during the final stages of delithiation. The corresponding changes in resistances are depicted in Fig. 3f and g. The results from peak fitting and the individual resistances, classified by their characteristic time constants, are summarized in Tables S6–S9. Interestingly, the R_{bulk} remained virtually constant throughout both discharge and charge, indicating SOC independence. In contrast, the $R_{\text{GB+Contact}}$ exhibited a slight increase during charge, but maintained a constant value of $0.4 \Omega \text{ cm}^2$ during discharge. The R_{int} and, most notably, the R_{ct} revealed a strong correlation with the SOC. During the

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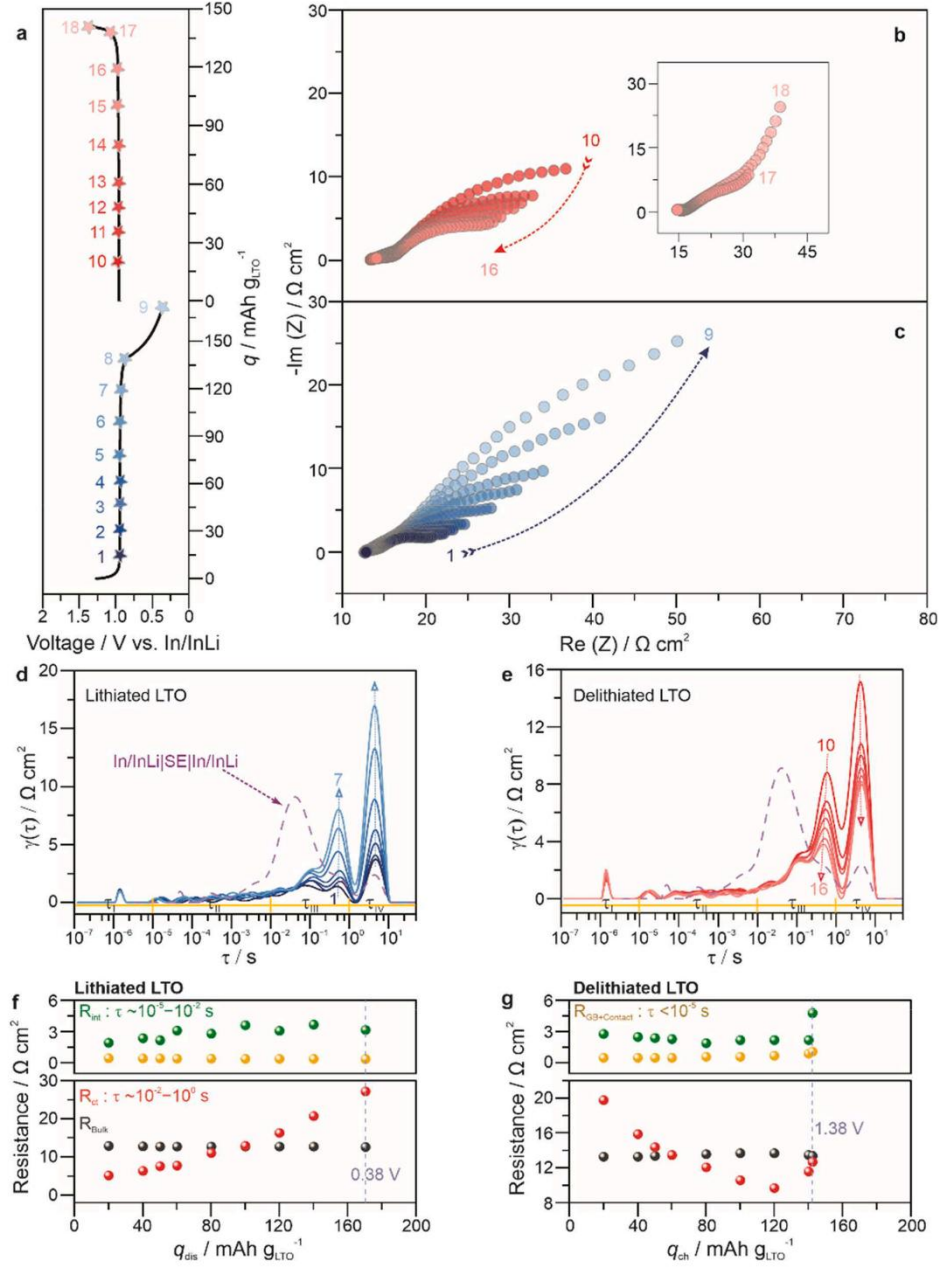


Fig. 3. *In situ* EIS-DRT analysis of the In/InLi|SE|LTO cell. (a) Voltage profile with selected SOC labels from 1 to 18. (b, c) Corresponding Nyquist plots and (d, e) DRT patterns during discharge and charge. Specific time constant regimes are indicated. (f, g) Fitted resistances (SE bulk, SE GB together with the contact resistance, interphase, and charge transfer) are categorized according to their characteristic time constants.

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lithiation of LTO, from SOC 1 to 9, R_{int} shows a subtle and fluctuating increase, whereas R_{ct} undergoes substantial growth (from 5.1 to 27.2 Ω cm²). Conversely, in the subsequent delithiation process, both R_{int} and R_{ct} exhibit V-shaped changes. Importantly, during the major interfacial processes, R_{ct} follows a declining trend in the plateau region (SOC 10 to 16) before increasing again with progressing transition toward the spinel phase (SOC 16 to 18).

As evident from Table S4, the continuous delithiation of LTO during charge leads to a similar trend in potential drift to that observed during OCV monitoring. Given the limited specific capacity for prelithiation (50 mAh g_{LTO}⁻¹), the observed potential drift agrees well with the changes in capacity and OCV seen for SOC 14 to 17, involving a steady increase (from selected points in time 1 to 5, corresponding to SOC 14 to 16) and then an accelerated increase (from selected points in time 5 to 7, corresponding to SOC 16 to 17). Interestingly, the continuous increase in R_{ct} from the selected points in times 1 to 5 contrasts with the change in R_{ct} from SOC 14 to 16 during delithiation. This suggests that microstructural degradation of the LTO electrode contributes more significantly to the increase in charge-transfer resistance than changes in SOC during the period of steady potential drift. Within the accelerated regime, the change from SOC 16 to 17 results in a substantial increase in potential, mirroring the trend observed for the selected points in time 6 to 7. Additional charge-transfer resistance due to transitioning to the final spinel phase further contributes to the overall increase in R_{ct} .

In brief, focusing on the potential drift in the In/InLi|SE|LTO 2E cell, we revisited the kinetics of LTO in SSBs. Specifically, we conducted a comprehensive evaluation of the stability of the proposed LTO-RE considering the potential drift and behavior of the electrode. Notably, under conditions of resting, low currents, or minimal cell utilization, the In/InLi electrode remains stable and largely unaffected, as evidenced by OCV monitoring and *in situ* EIS measurements. However, prolonged cycling leads to changes in microstructure and increases in interfacial resistance [17].

The EIS-DRT analysis of the 2E cell provides important insights into the individual kinetic processes of the electrodes, identified by characteristic time constants. However, overlapping impedances/time constants from coupled electrodes pose challenges in objectively evaluating their (individual) contributions to interfacial degradation, particularly in regimes dominated by charge-transfer processes. Consequently, we

explored the feasibility of decoupling in the designed 3E cell. The analysis emphasizes the value and ultimately the necessity of the 3E approach.

2.4. Comparison between In/InLi|SE|LTO-RE|SE|LTO 3E and In/InLi|SE|LTO 2E cells

As depicted in Fig. 4a, following a 1 h resting period post assembly, the In/InLi|SE|LTO-RE|SE|LTO 3E cell allowed successful deconvolution of potentials of the two individual electrodes. The black, blue, and red curves represent the cell voltage (WE/CE), the WE/RE potential (LTO vs. LTO-RE), and the CE/RE potential (In/InLi vs. LTO-RE), respectively. Because the In/InLi CE has a stable potential of 0.622 V vs. Li⁺/Li under OCV conditions, the initial (reference) potential of the LTO-RE was indirectly determined to be 0.955 V vs. In/InLi, corresponding to 1.577 V vs. Li⁺/Li.

During the formation cycle at 0.1C in a voltage window of 0.38–1.38 V vs. In/InLi (equivalent to about 1.0–2.0 V vs. Li⁺/Li), as shown in Fig. 4b and c, LTO delivered virtually identical capacities to the 2E counterpart, with q_{ch} approaching 139 mAh g_{LTO}⁻¹ (see Fig. 4c). Fig. 4d and e present the individual potentials of the LTO and In/InLi electrodes during discharge and charge, respectively. The overpotential of In/InLi was derived from the difference between the measured CE/RE potential and that determined under OCV conditions, with a constant reference potential in absolute terms. The average overpotential was found to be slightly higher during discharge/delithiation (5 mV) compared to charge/lithiation (2 mV), corroborating findings from coulometric titration tests reported in the literature [13].

2.5. Validation of 3E impedance measurements

The evaluation of the 3E cell setup demonstrates highly reliable performance (similar to that of the 2E counterpart) in terms of capacities and individual potentials. The critical functionality in deconvoluting the impedances of individual electrodes was further validated. From the analysis of the In/InLi|SE|LTO 2E cell, it is apparent that LTO exhibits a SOC-dependent impedance response, as illustrated in Fig. 3. In the proposed combination of LTO and In/InLi, major interface-related charge-transfer processes were observed in the time constant region of

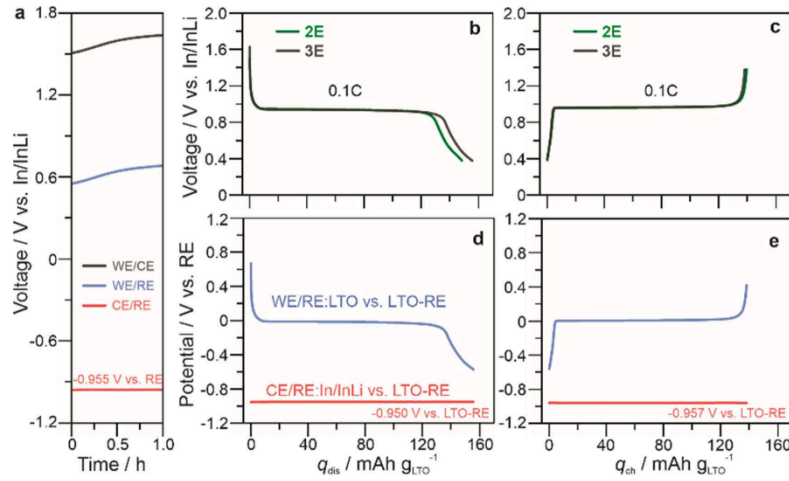


Fig. 4. Comparison of electrochemical performance between In/InLi|SE|LTO-RE|SE|LTO and In/InLi|SE|LTO cells. (a) Potential tracking of WE/RE, WE/CE, and CE/RE during initial OCV resting. (b, c) Voltage profiles of 2E and 3E cells at 0.1C during (b) discharge and (c) charge. (d, e) Potential tracking of WE/RE and CE/RE during (d) discharge and (e) charge.

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τ_{III} (10^{-2} – 10^0 s), revealing severe overlap between the electrodes. Therefore, impedance measurements performed using 2E cell setups cannot accurately differentiate between the contributions of the individual electrodes, potentially leading to misinterpretations.

Following the electrochemical testing, the impedance of the 3E cell was measured at the end of charge, corresponding to the delithiated state of LTO and lithiated state of In/InLi. Three independent measurements were conducted to gather data from the WE/RE, the CE/RE, and the WE/CE, as shown in Fig. 5a. The LTO WE exhibits a semicircle in the medium-frequency range, followed by a Warburg-like capacitive tail, indicative of the diffusive processes occurring in the fully delithiated LTO particles. In contrast, the In/InLi CE displays only depressed semicircles below 1.5 kHz, mainly attributed to the charge-transfer process between the In/InLi and the SE. The sum of the WE and CE impedances closely matches with the 2E results, except for some deviations in the high-frequency region (above 100 kHz).

To further verify and evaluate the discrepancies between the 2E and 3E data, a residuals analysis proposed by Hertle *et al.* was performed [16]. Figs. 5b and c indicate that the real and imaginary parts exhibit residuals within 1.5 and 10% below 100 kHz. It is worth noting that impedance measurements at high frequencies are more vulnerable to the device and circuitry, cell preparation, and testing conditions. Deviations and artifacts in the high-frequency range commonly arise from the connection cables, current collectors, and/or mechanical contact issues.

Improvements could be made by (i) ensuring a more stable environment during the measurement, (ii) limiting cell transportation between different cyclers, and (iii) optimizing the connection between the electrodes and the measurement device. However, the significant overlap of the 3E and 2E data from 100 kHz through the medium- to low-frequency range with low residuals demonstrates the high reliability of resolving individual impedances. The “stable” frequency range is sufficient to cover the interface kinetics of most energy-storage materials [23]. The validity of the gathered impedance data was further confirmed by a Kramers-Kronig (K-K) test, as detailed in Figure S8 and discussed in Supplementary Note 4.

2.6. Interface kinetics of LTO and In/InLi from 3E EIS-DRT analysis

Fig. 6a illustrates the individual DRT patterns for LTO and In/InLi. Surprisingly, the kinetic processes identified by the distinct peaks show significant overlap across the different timescales, with notable variations in peak position and intensity. The primary interfacial contribution, located in the τ_{III} regime, is associated with charge-transfer processes for both LTO and In/InLi. The most sluggish kinetic process, observed in the τ_{IV} regime of LTO, is attributed to diffusive polarization, which is the rate-limiting step in the 3E cell performance. In contrast, lithiated In/InLi exhibits more favorable lithium diffusivity compared to the fully delithiated LTO, as evidenced by the stark contrast in peak

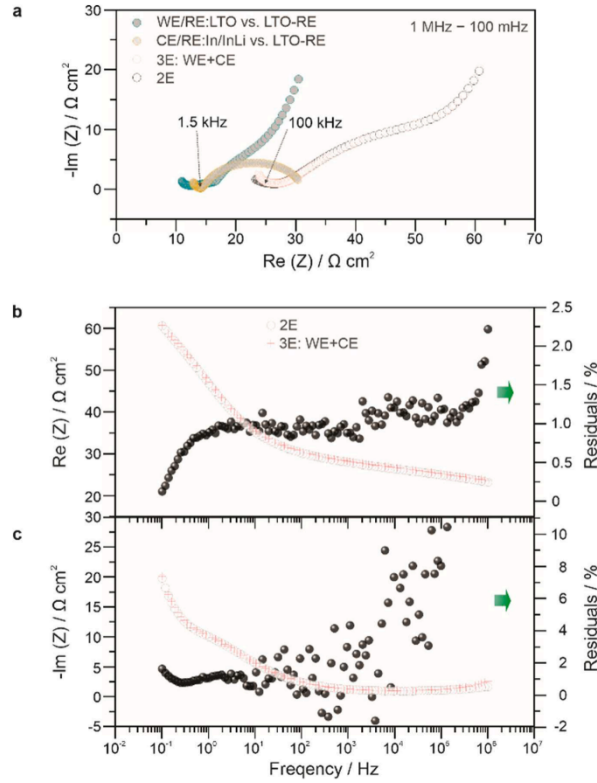


Fig. 5. 3E impedance measurement of the In/InLi|SE|LTO-RE|SE|LTO cell. (a) Nyquist plots for the individual electrodes, with a comparison of overlap between the 2E (WE/CE) and 3E (WE+CE) data. (b, c) Comparisons of impedance results for the real and imaginary parts between the 2E and combined 3E data. Hollow circles represent the 2E results, red crosses the 3E results, and solid circles show the residuals.

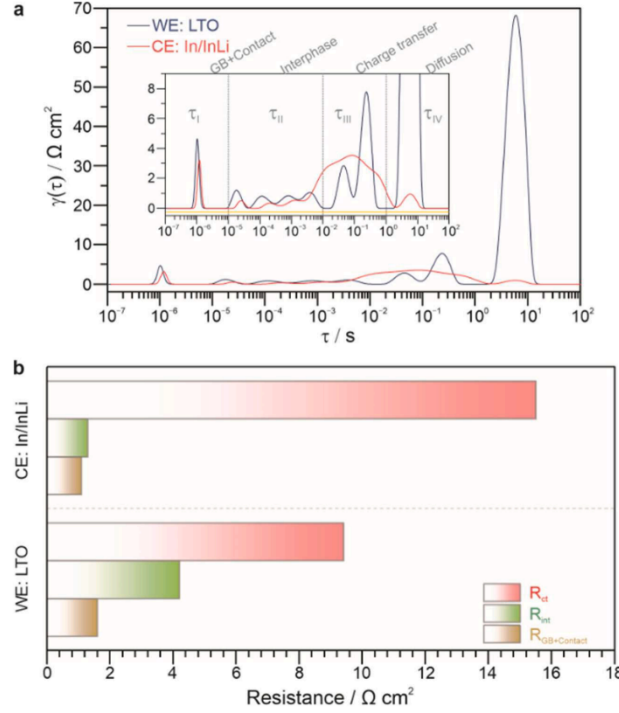


Fig. 6. 3E EIS-DRT analysis of individual electrodes (WE:LTO/CE:In/InLi). (a) DRT patterns. The inset is a zoomed-in view showing peaks reflecting the involved kinetic processes. (b) Fitted resistances (SE GB together with the contact resistance, interphase, and charge transfer) are categorized according to their characteristic time constants.

intensities within the τ_{IV} regime.

Regarding the analysis of interface kinetics, it becomes clear that neither ECM fitting in the frequency domain nor DRT analysis in the time domain can objectively evaluate the contributions of the involved processes for both electrodes in a 2E system due to overlapping time-scales. Furthermore, the traditional separation of frequency ranges, specifically the medium- and low-frequency range, needs to be re-defined. Assignments should focus on attributing contributions to charge transport across the as-formed interphases [cathode electrolyte interphase (CEI) or solid electrolyte interphase (SEI)] and ionic charge transfer between the active electrode material and the SE, respectively, rather than simply categorizing them by cathode and anode.

Quantitatively, the $R_{GB+Contact}$ is similar for both the LTO and In/InLi electrodes, as shown in Fig. 6b. The R_{int} of In/InLi (1.3 $\Omega \text{ cm}^2$) is notably lower than that of LTO (4.2 $\Omega \text{ cm}^2$), yet both with low values suggesting favorable charge transport through the as-formed interphases. The R_{ct} , which is pronounced in the τ_{III} regime, is higher for In/InLi (15.5 $\Omega \text{ cm}^2$) compared to LTO (9.4 $\Omega \text{ cm}^2$), despite the lithiated state of In/InLi, which typically facilitates fast charge transfer. This indicates that charge transfer at the In/InLi|SE interface can be adversely affected, especially after prolonged testing. The DRT peak fits and a summary of the fitted parameters are provided in Figure S9 and Tables S10 and S11.

Unlike the quasi zero-strain behavior of LTO, In/InLi experiences severe volume changes that lead to microstructural degradation and directly affect the pathways for ion and electron transport, resulting in inferior kinetics over time. A suggested improvement in the preparation of In/InLi electrodes by mixing with the SE could facilitate the kinetics of the InLi alloy phase near the interface [15]. Further 3E-assisted

investigations exploring the evolution of different materials during extended cycling will be detailed in subsequent studies.

3. Conclusions

In the present work, we report on a novel strategy for preparing 3E SSB cells by utilizing a LTO-containing composite as RE. A systematic investigation into the potential/SOC/kinetics relationship of LTO was conducted by EIS-DRT analysis to thoroughly evaluate the as-prepared RE. The proposed LTO-RE provides a stable reference potential with minimal drift and low growth rate in charge-transfer resistance (by about 0.003 $\Omega \text{ cm}^2 \text{ h}^{-1}$), offering optimal conditions for practical long-term testing in 3E SSBs, as well as to collect high-quality data for deconvoluting impedance components. Significant overlap across the full timescales of the LTO and In/InLi electrodes is revealed. DRT analysis clearly indicates the challenges of identifying contributions from individual electrodes when examined either in the frequency or time domain using 2E cells. The electrochemically prelithiated LTO composite extends the applicability of the 3E setup to other promising SSB systems while avoiding SE heterogeneities between the RE and the separator layer. LTO, used as active material in the RE, is particularly favorable, facilitating stable performance in low-temperature 3E testing scenarios. We believe that the setup presented herein helps bridge the performance gap between 2E and 3E configurations, providing insights into key issues in SSB research and development.

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4. Experimental section

Materials. Argyrodite $\text{Li}_6\text{PS}_5\text{Cl}$ (NEI Corp.) as SE was used as received. Super C65 carbon additive (TIMCAL Ltd.) and carbon-coated LTO (NEI Corp.) were dried at 300 °C under dynamic vacuum overnight prior to use. For the 2E and 3E SSB testing, In foil (Changsha Santech Materials Co., Ltd.) of 100 or 125 μm thickness was punched into discs of 9 mm diameter. Li foil (Albemarle Germany GmbH) of 50 μm thickness was punched into discs of 6 mm diameter. SS wire (Thermo Scientific) of 127 μm diameter served as current collector in the 3E cell preparation.

Composite preparation and 2E cell assembly. The LTO composite was prepared in an 80 mL zirconia milling jar containing the carbon-coated LTO, SE, and Super C65 in a weight ratio of 30:65:5, along with 10 zirconia balls of diameter 10 mm. After sealing in an argon glovebox [$p(\text{H}_2\text{O})/p < 0.1$ ppm and $p(\text{O}_2)/p < 0.1$ ppm], the composite was milled at 140 rpm for 30 min using a FRITSCH planetary mill. 2E cells, In/InLi|SE|LTO, were assembled using two SS dies as current collectors and a PEEK ring of inner diameter 10 mm. Initially, 100 mg of SE was spread into the PEEK ring and densified at 62.5 MPa. Then, around 20 or 25 mg of LTO composite was placed on one side of the SE separator layer and densified at 440 MPa for 3 min. On the opposite side (without additional pressing), the In/InLi alloy served as CE, with the In foil facing the SE.

Prelithiation of LTO. To prepare the RE for application in 3E cells, carbon-coated LTO as active material was first prelithiated in a 2E cell. The latter cell was assembled as described above, with the potential range set between 0.38 and 1.38 V vs. In/InLi, equivalent to about 1.0–2.0 V vs. Li^+/Li . The optimized protocol involved two formation cycles at 0.1C ($1\text{C} = 175\text{ mA g}_{\text{LTO}}^{-1}$), followed by discharge with a specific capacity limitation of 50 mAh $\text{g}_{\text{LTO}}^{-1}$. After prelithiation, the cell was disassembled, and the pellet stack was harvested in an argon glovebox. The prelithiated LTO composite electrode can be readily broken into pieces and then used as RE in the assembly of 3E cells. The attached SE separator layer was carefully scraped off using sandpaper.

3E cell assembly. The cell setup mirrored the 2E architecture but included two symmetrical holes in the PEEK ring for the SS wire. One of the aforementioned pieces was placed on the SS wire, followed by the addition of 80 mg of SE and densification at 125 MPa. This process was repeated for the second piece, ensuring overlap. A total of 160 mg of SE and the embedded two pieces (fragments) of prelithiated LTO composite completed the RE assembly. The final 3E cell configuration used 20 mg of LTO composite as WE and In/InLi alloy as CE to compare the performance to the 2E counterpart. Both the 2E and 3E cells were sealed into a pouch for electrochemical testing.

Electrochemical testing. The cells were examined at 45 °C and under an external pressure of 81 MPa. Testing was carried out using either a MACCOR battery cycler or a Bio-Logic SP-300 multichannel potentiostat. EIS measurements for both the 2E and 3E configurations were performed across a frequency range from 1 MHz to 100 mHz, with the voltage amplitude set at 7 mV. For the In/InLi|SE|LTO cells with 25 mg LTO composite loading, *in situ* EIS measurements were conducted at selected SOCs, as outlined in Table S4. To ensure thermodynamic equilibrium, a rest period of at least 15 min was implemented prior to each measurement. The 3E impedance was analyzed at the end of charge, corresponding to the completion of LTO delithiation and lithiation of In/InLi. Impedance measurements on individual electrodes, including WE:LTO, CE:In/InLi, and WE/CE (2E configuration), were conducted separately, with each being allowed a rest period of 15 min. DRT analysis was performed using RelaxIS software (rhd instruments). Complex data were used to conduct the DRT transformation with Gaussian radial basis function (RBF)-based discretization. The second derivative of the distribution function was used as the penalty item with a shape factor value of 0.5 and regularization parameter $\lambda = 10^{-5}$ for all patterns in this work. By applying multiple Gaussian peak functions, DRT patterns with multiple peaks were fitted to determine the characteristic time constants and peak areas. More details are provided in the

Supplementary Note 2. The K-K test was performed using the Lin-KK tool (<https://www.iam.kit.edu/et/english/Lin-KK.php>) [55,56].

Physical characterization. SEM imaging was performed using a Leo 1530 microscope (Zeiss) at an accelerating voltage of 10 kV. EDS utilized an Oxford X-MaxN detector at 20 kV. Cross-sectional polishing of pellets was performed using a JEOL IB-19510CP polisher with an Ar-gas source. Powder XRD patterns were recorded on a STOE Stadi-P diffractometer with a Mo anode ($\lambda = 0.70926\text{ \AA}$) and analyzed using GSAS-II for Rietveld refinement [57].

Declaration of generative AI and AI-assisted technologies in the writing process

During the preparation of this work, the author(s) used ChatGPT4.0 (by OpenAI) to polish the writing to improve upon language and readability. The author(s) reviewed and edited the content as needed and take full responsibility for the content of the published article.

CRediT authorship contribution statement

Ruizhuo Zhang: Writing – original draft, Visualization, Validation, Software, Investigation, Formal analysis, Conceptualization. **Aleksandr Kondrakov:** Writing – review & editing, Supervision, Project administration, Funding acquisition. **Jürgen Janek:** Writing – review & editing, Supervision, Funding acquisition. **Torsten Brezesinski:** Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.ensm.2025.104000](https://doi.org/10.1016/j.ensm.2025.104000).

Data availability

Data will be made available on request.

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3.2.2. Publication V: Interfacial Anode Kinetics and Its Influence on Cycling Performance of Sulfide Solid-State Batteries

Building on the results from **Publication IV**, a deeper investigation was carried out in **Publication V**. In this work, 3E-based electrochemical analysis was extensively employed to track the anode/CE contributions in SSBs under various testing scenarios, with particular emphasis on overpotential growth and kinetic response of the In/InLi and LTO electrodes during long-term cycling. Furthermore, when coupled with a Ni-rich cathode, both rate performance and the influence originating from the anode were systematically investigated across multiple cell configurations. Through 3E EIS-DRT analysis, valuable insights into the behavior of both cathode and anode were gained.

In that case, the PC NCM85 CAM was coated with LiNbO_3 via a sol-gel method. The cathode was prepared by slurry casting using 1 wt.% PIB as the binder. LPSCI was employed as the SSE. LTO and In/InLi, as the most commonly used anode materials in laboratory-scale research, were utilized either as WE or as CE under practical testing conditions. The In/InLi electrode was prepared by stacking of metal foils followed by chemo-mechanical alloying. Details of the 3E setup and the LTO-RE are provided in **Publication IV**.

First, in tests using In/InLi as the CE and LTO as the WE, the In/InLi electrode undergoes delithiation at the initial stage of the repetitive charge-discharge process. During long-term cycling at low rates, the polarization of both In/InLi and LTO was continuously tracked and quantitatively analyzed. For the In/InLi CE, a progressive increase in polarization was observed as cycling proceeded, most drastically near the end of the delithiation process, revealing clear signs of electrode aging. During repeated (de)lithiation, lithium transport in the In/InLi electrode became more hindered, especially when delithiation approached completion, and the interfacial region became severely lithium-depleted. *In situ* 3E EIS-DRT analyses performed at different cycling stages further elucidated the evolution of interfacial kinetics at varying SOCs, with a pronounced deterioration of the charge transfer process of In/InLi in the delithiated state. In rate performance tests using PC NCM85 cathodes, the cell-to-cell performance variations observed at high C-rates can be attributed to the inconsistent polarization in the In/InLi CE and the differing polarization responses of the In/InLi and LTO electrodes. Finally, in long-term cycling of cells employing In/InLi as the CE and PC NCM85 as the WE, the impact of CE polarization on capacity fading was clearly revealed, demonstrating that, in 2E cells, the correlated interfacial kinetic hinderance and degraded electrochemical performance can lead to an overestimation of the WE contribution.

3. Results

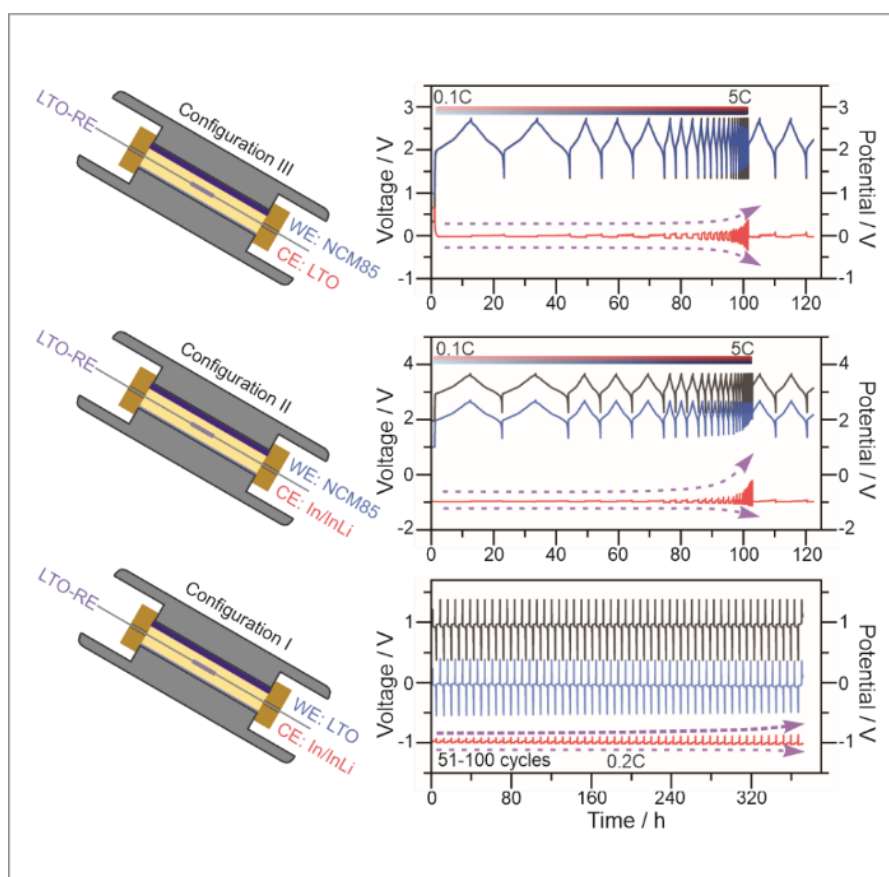


Figure 11. Table of contents graphic of Publication V. Redrawn from reference [42].

The experiments were designed and planned by the first author R. Zhang, under the supervision of A. Kondrakov, J. Janek, and T. Brezesinski. R. Zhang conducted all of the experiments, evaluated the data, and interpreted the results. The first draft was written by the first author with further modification by T. Brezesinski. The final paper was edited by all co-authors.

Interfacial Anode Kinetics and Its Influence on Cycling Performance of Sulfide Solid-State Batteries

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ABSTRACT: Solid-state batteries (SSBs) are primarily tested in two-electrode and/or symmetric cell configurations, which may lead to under- or overestimation of degradation and failure. For long-term cycling and under dynamic conditions, the contribution of the counter electrode (anode) to fading may be substantial but is rarely reported due to lack of suitable characterization techniques. Here, we employed an advanced three-electrode cell setup to elucidate the overpotential growth and interface-related kinetic response for commonly used counter electrodes in lab-scale testing, namely, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and In/InLi , as well as for LiNbO_3 -coated $\text{LiNi}_{0.85}\text{Co}_{0.10}\text{Mn}_{0.05}\text{O}_2$ as the working electrode (cathode) in thiophosphate-based SSB cells. This was achieved through continuous monitoring of individual electrode potentials (>1500 h) and by performing electrochemical impedance spectroscopy measurements in situ in combination with distribution of relaxation times analysis. The results reveal distinct differences in polarization and interfacial kinetics between the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and In/InLi anodes in practical application scenarios and how these affect cyclability and the analysis of capacity fading.

KEYWORDS: three-electrode cell testing, lithium titanate, lithium–indium alloy, overpotential, interfacial kinetics

Inorganic, superionic conductors, such as argyrodite-type thiophosphates, enable competitive ionic conductivities to the commonly used liquid electrolytes at room temperature.^{1–3} By coupling with state-of-the-art, layered Ni-rich oxide cathodes and high-capacity anodes (lithium metal, silicon, etc.), the energy density of solid-state batteries (SSBs) can be potentially increased.^{4,5} Therefore, the development of advanced SSBs and their critical components has emerged as a promising direction in the field of electrochemical energy storage.⁶ The transition from liquid electrolytes to solid electrolytes (SEs) fundamentally alters the interfaces regarding (electro)chemical stability and wetting (solid–solid contact), thus affecting kinetics and cycling performance.⁷

By designing new cathode and/or anode active materials for application in SSBs, standard testing is generally performed using two-electrode (2E) half-cell configurations. The electrochemical characteristics of the synthesized materials, serving as the working electrode (WE), are gathered from multiple testing scenarios. Typically, the data collected from 2E cells closely resemble the practical conditions of the WE, with the assumption that the counter electrode (CE) has no major effect on the overpotential and interfacial resistance (unreasonable for real-world use). Hence, careful selection for electrochemical testing of SSBs is of utmost importance.

Two commonly used materials, namely, lithium–indium alloy (In/InLi) and lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$, LTO), are constrained by the relatively high cost of raw materials and limited energy density, making them unsuitable as SSB anodes in commercial applications. Nevertheless, they are widely seen as CE in lab-scale research.^{8,9} Each exhibits specific characteristics that affect the cell cyclability accordingly.

In/InLi offers a well-defined potential (0.622 V vs Li^+/Li) over a broad range of lithium concentrations.¹⁰ Fast lithium diffusion further allows minimizing polarization, helping to reliably evaluate the kinetics of the WE. However, different scenarios [e.g., sequence of de(lithiation), etc.] may result in a different evolution of interfacial resistance and overpotential growth during battery operation.^{11,12} In addition, the production method used (e.g., stacking of metal foils, etc.) may affect the kinetic response at the CE/SE interface, as reported for In/InLi in the literature.^{13,14} Apart from that,

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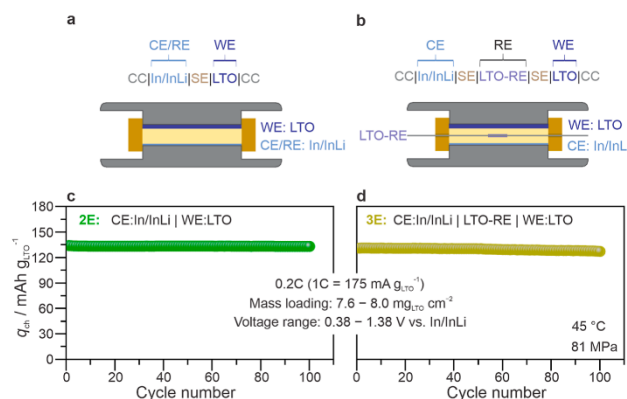


Figure 1. Long-term cycling performance of 2E and 3E SSB cells with LTO and In/InLi as WE and CE, respectively. (a,b) Schematic illustrations of their design and (c,d) cyclability at 0.2C.

volumetric/morphological variations during (de)lithiation may also result in contact loss and, therefore, in increased anode resistance.^{11,15}

LTO, which is recognized for its structural and electrochemical stability, can be readily combined with sulfide (thiophosphate) SEs, such as $\text{Li}_6\text{PS}_5\text{Cl}$ (LPSCl). Dedicated measurements, including in situ pressure monitoring of the WE upon (dis)charge, have been reported for SSBs with LTO as CE.^{16,17} The redox potential of LTO is about 1.55 V vs Li^+/Li , which is relatively high, making it inappropriate for high-energy-density full cell design. Of note, LTO usually exhibits a higher polarization than that of In/InLi, and for both LTO and In/InLi, the charge-transfer kinetics is sensitive to the state of charge (SOC),^{18,19} thus interfering with the evaluation of the WE in 2E cells.²⁰

In a conventional 2E configuration, determining the kinetics of the individual electrodes is challenging. This complexity necessitates adopting three-electrode (3E) cell designs, where electrode-specific overpotentials and kinetics can be examined independently. Nevertheless, studies of 3E measurements on SSBs are relatively scarce, particularly regarding practical application scenarios.^{11,13,21–23} In our previous work, by developing robust 3E cells, we highlighted the overlapping of characteristic interface-related kinetic responses between different electrodes, emphasizing the interference from the CE and the potential overestimation of degradation at the WE in typical 2E cell configurations. To the best of our knowledge, there are no literature reports available yet that address the evolution of overpotentials and interface-related kinetics upon long-term cycling and uncover the “hidden” polarization behavior of the CE and its effect on the WE under realistic operational conditions, such as fast (dis)charge, leaving significant knowledge gaps for future SSB R&D and reliable testing.

In this work, we applied 3E cells for SSB testing in different configurations and scenarios. By configuring In/InLi and LTO as CE and WE, respectively, the individual electrode potentials were simultaneously and continuously recorded during galvanostatic cycling (100 cycles at 0.2C; >1500 h operation). Valuable information from aged In/InLi and LTO electrodes regarding overpotential growth and interface-related kinetic

response as a function of SOC or, in other words, degree of (de)lithiation were obtained by electrochemical impedance spectroscopy using distribution of relaxation times (EIS-DRT) analysis. Notably, In/InLi in the “delithiation first” scenario (see Experimental Section for details) showed progressively exacerbated charge transfer at the anode interface during cycling. Furthermore, practical applications with a Ni-rich cathode were also assessed by pairing LiNbO_3 -coated $\text{LiNi}_{0.85}\text{Co}_{0.10}\text{Mn}_{0.05}\text{O}_2$ (NCM85) with either In/InLi (“lithiation first” scenario) or LTO in 3E cells, enabling us to examine the effect that different CEs have on the cycling performance and stability. Ultimately, the electrochemical behavior of In/InLi relative to that of NCM85 was unraveled.

RESULTS AND DISCUSSION

In this study, we employed 3E SSB cells to investigate their electrochemical behavior across various configurations. Details on the 3E design are reported elsewhere.¹⁸ Both the preparation of the reference electrode (RE) and the cell assembly are described in the Experimental Section. Specifically, a prelithiated LTO composite was used. The advantages of employing LTO as RE (LTO-RE) include (i) the high (electro)chemical stability of LTO against LPSCl, (ii) the use of the same SE in both the LTO-RE and the separator, which mitigates charge-transport limitations due to heterogeneities, (iii) the quasi-zero-strain nature of LTO during (de)lithiation, enabling excellent mechanical stability even after prolonged cycling, and (iv) the feasibility of ex situ rather than in situ prelithiation, which helps reduce degradation in the vicinity of the current collector of the LTO-RE. Collectively, these attributes ensure high structural integrity and robustness of the as-prepared LTO-RE.¹⁸ Schematic illustrations of both the 2E and 3E cell configurations are presented in Figure 1a,b.

Cycling Performance of the In/InLi and LTO Electrodes in 3E SSB Cells. To examine the cyclability of the In/InLi and LTO electrodes independently, 3E cells were assembled, and their behavior was compared to that of 2E counterparts. In this configuration, In/InLi was designated as “delithiation first” CE, with the chemomechanically formed alloy undergoing delithiation, while the LTO WE is simultaneously lithiated in the initial discharge cycle, followed by the reverse electro-

chemical reactions upon charging. The performance of these cells was evaluated first (see Figures 1c,d and S1, Supporting Information).

After assembly, the 3E cells were allowed to rest for 1 h. In their pristine state, the cell voltage (between WE and CE), along with the individual electrode potentials, was monitored, as shown in Figure S2 (Supporting Information). The as-formed In/InLi of composition $\text{Li}_{0.27}\text{In}$ revealed a stable potential over a broad range of lithium concentrations.¹⁰ The initial equilibrium potential of the LTO-RE was indirectly calculated to be 1.575 V vs Li^+/Li , based on a recorded potential of -0.953 V between the In/InLi CE (0.622 V vs Li^+/Li) and the RE.

In the two formation cycles at a current density of 0.14 mA cm^{-2} (0.1C), as shown in Figure S1 (Supporting Information), the 3E cells delivered capacities similar to those of the 2E counterparts, with first-cycle $q_{\text{ch}} \approx 142 \text{ mAh g}_{\text{LTO}}^{-1}$ compared to $147 \text{ mAh g}_{\text{LTO}}^{-1}$ (delithiation capacity). As expected, the In/InLi CE exhibited a flat voltage plateau during (de)lithiation, with the virtually identical voltage/potential profiles of the WE/CE and WE/RE indicating stable behavior with negligible polarization. The absolute value of overpotential upon (de)lithiation, with respect to the equilibrium potential, remained small at about 4 mV (without excluding Ohmic polarization), thus indicating the insignificant effect of the In/InLi CE on cell performance.

Furthermore, both the 2E and 3E cells underwent cycling at 0.28 mA cm^{-2} (0.2C) for 100 cycles. As evident from Figure 1c,d, the 3E cells demonstrated a capacity retention of $\sim 97\%$, with q_{ch} decreasing from about 131 to $127 \text{ mAh g}_{\text{LTO}}^{-1}$, closely resembling that of the 2E cells ($\sim 99\%$, with $q_{\text{ch}} \approx 133 \text{ mAh g}_{\text{LTO}}^{-1}$ after 100 cycles). The minor deviations between the performance data validate and support the robustness and reliability of the 3E setup employed in the present work.

As summarized in Table 1 and depicted in Figure 2a,d, the 3E cell testing comprised three major phases, aiming at monitoring the polarization and interfacial kinetic response throughout cycling.

Table 1. Experimental Procedure Followed in the Testing of In/InLi/SE/LTO-RE/SE/LTO 3E SSB Cells

phase	type of measurement
1	formation cycles at 0.1C rate after 1 h resting period
2, 4, 6	in situ 3E-EIS measurements after cell formation as well as after 50 and 100 cycles
3, 5	galvanostatic cycling at 0.2C rate for cycles 1–50 and 51–100

The individual electrode potentials (WE/RE, CE/RE) and the cell voltage (WE/CE) are shown for the 1st to 50th and 51st to 100th cycles at 0.2C in Figure 2b,c, respectively, enabling facile exploration of overpotential growth during the course of cycling. The overpotential was derived from potential differences between the electrodes in their initial (equilibrium) and operational states, measured against the LTO-RE. Therefore, it is crucial to assess the stability of the RE and its potential drift upon cycling, which is rarely reported in the application of 3E cells.

As shown in Figure S2 (Supporting Information), the 3E cells were allowed to rest for 1 h under open circuit voltage (OCV) conditions in the pristine state, after 50 cycles, and after 100 cycles while monitoring the electrode potentials and the cell voltage. The as-prepared LTO-RE exhibited a potential

drift from stable to accelerating, consistent with previous observations.¹⁸ However, the drift remained modest during the first 600 h, with an increase by only about 7 mV , followed by an additional 46 mV over the next 680 h (after 100 cycles). Overall, the potential drift was monitored and found to remain low, ensuring a reliable reference potential during electrochemical measurements, such as EIS, at selected states. To minimize possible deviations caused by potential drift of the RE, an accumulated algorithm was applied, aiming at quantifying the growth of overpotential, as detailed in the following section, ultimately allowing for objective analysis of the polarization behavior of the In/InLi and LTO electrodes.

In the cell voltage profiles, the step-like (dis)charge plateaus were more pronounced than those observed for the LTO WE, primarily due to polarization of the In/InLi CE. Initially, the potential profiles of In/InLi during (de)lithiation remained fairly flat (0.2C), as can be seen from Figure S3 (Supporting Information). However, with prolonged cycling, a steady increase in potential was observed toward the end of delithiation, leading to a continuous increase in lower cutoff potential for LTO (see Figures 2c and S3, Supporting Information). Obviously, the polarization of the In/InLi electrode is dependent upon its state of delithiation. Consequently, an additional driving force (overpotential) seems to be required to extract more lithium from the CE.

A recent work probing lithium–indium alloys in SSBs has reported on an experimental design study to overcome lithium deficiency near the interface by facilitating transport in the bulk phase.¹² Hence, it can be inferred that the lithium concentration near the In/InLi/LPSCl interface plays a critical role in altering the overpotential and kinetics. Regardless, sudden increases in overpotential are common in studies on lithium alloys, such as Li–In, Li–Mg, or Li–Sn, in solid-state environments, especially when approaching the accessible capacity or when charge transfer is inhibited during delithiation.^{11,13,24,25} Here, our study presents a more practical scenario.

The reversible capacity was initially determined by the LTO. Given the geometric parameters of the as-prepared In/InLi, excess capacity was ensured, with a theoretically calculated CE:WE (n/p) ratio of 3.6 (defined as the ratio of areal capacities), providing sufficient lithium for the electrochemical reactions. Accordingly, under these conditions, no notable deviations from the expected cell behavior were observed during the first tens of cycles (Figure 2b). Nevertheless, with prolonged cycling, the delithiation of In/InLi became less seamless, indicating hindrance of charge transport or reduced effective lithium diffusion within the electrode.

To gain a better understanding of overpotential and its evolution during battery operation, a quantitative analysis was performed for the individual electrodes at various states of (de)lithiation. Instead of directly tracking the potential of the In/InLi electrode at the end of (de)lithiation in each cycle, we aimed at keeping the effect that potential drift of the RE has on quantification at a minimum. Based on the assumption that the drift evolves gradually, the increase in overpotential was determined from the incremental changes between adjacent cycles. Specifically, an accumulated algorithm was developed to minimize the overestimation of the overpotential growth during cycling. Details are provided in Supporting Information Note S1 and Figure S4 (Supporting Information).

Quantitative Analysis of Overpotentials. Considering that both the In/InLi and LTO electrodes exhibit distinct

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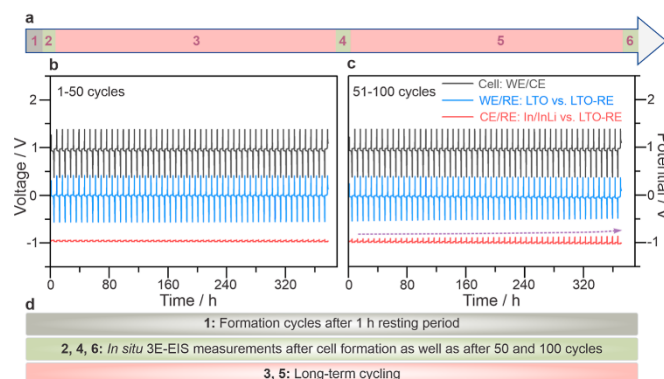


Figure 2. Experimental procedure and continuous monitoring of electrode potential during long-term cycling of 3E SSB cells with LTO and In/InLi as WE and CE, respectively. (a,d) Electrochemical measurements categorized into six groups: (1) Two formation cycles after 1 h resting at OCV [not shown in panels (b) and (c)]. (2, 4, 6) In situ EIS measurements after cell formation and after 50 and 100 cycles. (3, 5) Galvanostatic cycling with (b) and (c) showing cycle nos. 1–50 and 51–100, respectively. Both cell voltage (WE/CE, black) and deconvoluted potentials of the WE/RE (blue) and CE/RE (red) are shown.

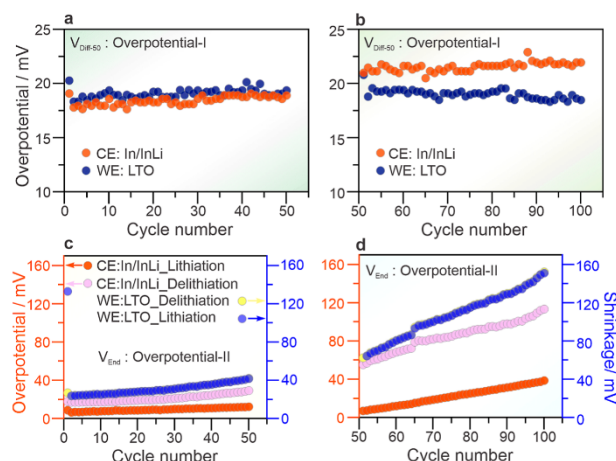


Figure 3. Continuous monitoring of overpotential during long-term cycling of 3E SSB cells with LTO and In/InLi as WE and CE, respectively. (a,b) Overpotential-I for the In/InLi and LTO electrodes in the plateau regions ($50 \text{ mAh g}_{\text{LTO}}^{-1}$) for cycle nos. 1–50 and 51–100. (c,d) Corresponding overpotential-II at the end of (de)lithiation. For LTO, overpotential-II is defined as the change (reduction) in the operating potential window (of note, LTO was to be cycled between about 1.0 and 2.0 V vs Li^+/Li).

(de)lithiation plateaus, where the majority of the accessible capacity is extracted, overpotential analysis was performed on these voltage plateaus. For this purpose, the potential difference at $50 \text{ mAh g}_{\text{LTO}}^{-1}$ during charge and discharge ($V_{\text{Diff-50}}$) was selected as an indicator of overpotential, hereafter termed overpotential-I. In calculating it, Ohmic polarization was found to be virtually identical due to the sandwich-type structure of the LTO-RE [with similar amounts of SE between WE/CE and RE], ensuring that overpotential-I reflects the intrinsic polarization of the electrodes.

The LTO WE was found to display a stable overpotential-I, with an average value of 19 mV (Figure 3a,b). In contrast, the In/InLi CE revealed a lower polarization during the first tens

of cycles (18 mV on average over the first 50 cycles), with a slight increase observed in the subsequent cycles ($\sim 22 \text{ mV}$). Overall, both the LTO and In/InLi electrodes demonstrated minor and relatively stable polarization on the plateaus, benefiting from reasonable (electro)chemical stabilities against LPSCI.

Focusing on the end of (de)lithiation, a different situation emerged from that observed for overpotential-I. For these states, a second indicator, denoted as overpotential-II, was defined. It should be noted that for In/InLi, the potentials at the end of (de)lithiation (V_{End}) relative to the equilibrium state included the Ohmic polarization. For the LTO WE, which is affected by the polarization of the In/InLi CE during cycling,

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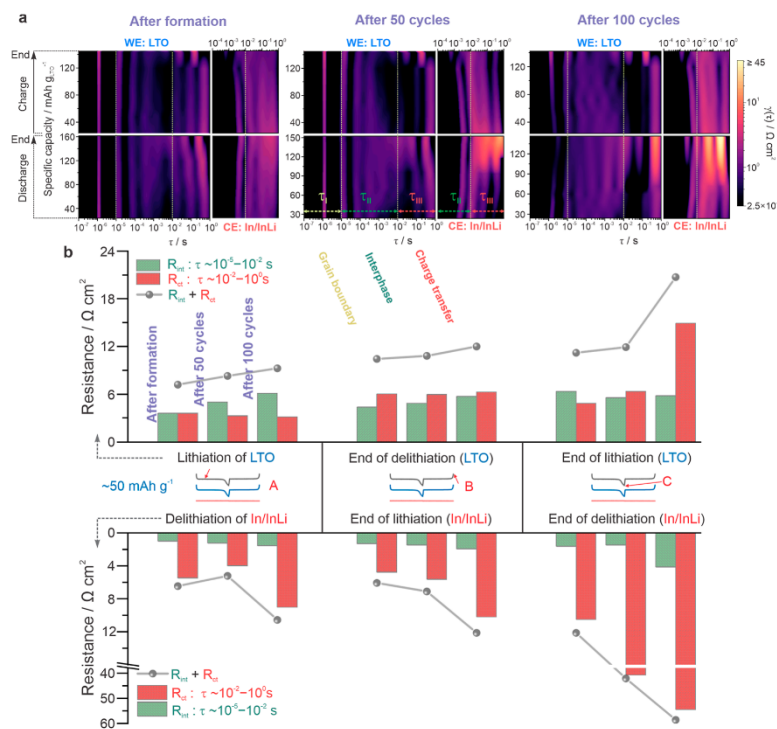


Figure 4. Monitoring of interface-related resistance during long-term cycling of 3E SSB cells with LTO and In/InLi as WE and CE, respectively. (a) Contour plots of DRT patterns for the In/InLi and LTO electrodes upon (de)lithiation after cell formation as well as after 50 and 100 cycles. (b) Corresponding quantitative analysis of the evolution of interfacial resistance [R_{int} : as-formed interphase(s), R_{ct} : charge transfer, A: discharge to 50 mAh g_{LTO}⁻¹, B: end of charge, and C: end of discharge].

overpotential-II was defined as the decrease (reduction) in the potential window. As shown in Figure 3c, during the first 50 cycles, overpotential-II for In/InLi at the end of lithiation increased linearly but remained at a relatively low level. A similar trend was apparent for overpotential-II at the end of delithiation. However, steadily accelerating growth was observed after 30 cycles. In the last 50 cycles, as illustrated in Figure 3d, the increase in overpotential-II for both states was much more pronounced, with a steeper slope at the end of lithiation and severe growth at the end of delithiation. Note that EIS measurements were performed between the 50th and 51st cycles, introducing some discontinuity in the overpotential growth.

With continuous (de)alloying of the In/InLi electrode during battery operation, the lithium deficiency near the interface grows. Locally inhibited lithium transport requires progressively greater overpotentials to facilitate lithium movement from the bulk to the CE/SE interface at the end of delithiation, with the deterioration of charge transfer ultimately manifesting in the form of overpotential growth. By combining overpotential-II at the lithiated and delithiated states (see Figure S5, Supporting Information), the overall effect within a single cycle can be quantitatively determined (referred to as overpotential-III for the In/InLi electrode; also corresponding to the decrease in the potential window of the LTO WE).

Even under relatively moderate cycling conditions in lab-scale testing (here, 45 °C, 81 MPa, 0.28 mA cm⁻², high n/p ratio), the overpotential near the end of delithiation gradually increased, although no sudden failure of the In/InLi CE occurred. Both the In/InLi and LTO electrodes initially exhibited a low overpotential-I (with limited growth), demonstrating their ability to maintaining relatively stable kinetics. However, the gradual degradation of the In/InLi microstructure (including phase distribution) negatively affects interfacial kinetics, thus contributing to capacity fading. Crucially, the performance is highly dependent on the specifics of electrode preparation, as reported in the literature.^{13,14} If the cycling conditions become more practical, e.g., due to lower operating temperature and/or reduced external pressure, the overpotential and its rate of increase in the In/InLi electrode could be more pronounced, as both temperature and pressure have a decisive influence on the interfacial kinetics.^{11,26,27} Therefore, more systematic investigations under various conditions are needed to fully understand the kinetic limitations.

Additional cells (denoted as cell-2 and cell-3) were independently tested (Figure S6, Supporting Information). Both exhibited a similar overpotential-I for the In/InLi and LTO electrodes throughout the entire testing process. However, clear differences were seen in overpotential-III,

directly affecting performance (Figures 1d and S6, Supporting Information). It can be deduced from this that, in addition to the already known factors that influence the polarization of In/InLi, even minor deviations occurring during assembly can have an impact on the extent of overpotential growth, leading to a certain degree of unpredictability that ultimately results in deviations in performance indicators.

Overall, the overpotential growth for the In/InLi CE upon long-term cycling may become an important constraint and unfortunately is difficult to discern in 2E cell testing. Therefore, with the deconvoluted electrode potentials and the continuously monitored overpotentials from the 3E cell testing, we have reason to believe that not only the quality of the as-prepared In/InLi but also the evolution of overpotential during electrochemical cycling may yield major inconsistencies in performance, even with the same WE, as also reported in a study on benchmarking of In/InLi-based (2E) SSB cells.⁹

SOC-Dependent Interfacial Kinetics. To further elucidate the interface-related kinetics of the In/InLi and LTO electrodes and their evolution upon cycling, in situ EIS measurements were conducted on the 3E cells, following specific cycles, as outlined in Table 1. Overlapping processes were deconvoluted by means of DRT analysis. However, it is important to note that even with DRT analysis, LTO and other types of WEs exhibit significantly overlapping responses with the In/InLi CE, thereby emphasizing the necessity of utilizing 3E cell configurations for probing individual electrodes.^{18,22,28,29}

Nyquist plots of the electrochemical impedance for the In/InLi and LTO electrodes upon (dis)charge after cell formation and after 50 and 100 cycles are presented in Figure S7 (Supporting Information). Notably, the Ohmic resistance of the CE remained relatively stable across all SOC, with values ranging from 18 to 20 $\Omega \text{ cm}^2$, indicating intimate contact between In/InLi and SE. The characteristic kinetic processes are reflected in the form of peaks in the DRT patterns (see the contour plots in Figure 4a). Within the measured frequency range from 1 MHz to 100 mHz, the time scales of peaks were divided into four major regimes, with corresponding physical meanings suggested by the literature.^{18,19,30} The τ_1 regime, with time constants smaller than 10^{-5} s, can be attributed to the bulk properties of SE (ion transport in the bulk, across grain boundaries, etc.) as well as to the contact resistance between the electrodes and the current collector. The peaks in the 10^{-5} to 10^{-2} s range, denoted as the τ_{II} regime, are assigned to charge transfer across the as-formed (decomposition) interphase(s). The response in the 10^{-2} to 1 s range (τ_{III} regime) signifies the major interfacial processes for the In/InLi and LTO electrodes. The most sluggish process originates from the lithium diffusion within the electrodes, with characteristic time constants larger than 1 s (not included in Figure 4a but evident as capacitive tails at low frequencies in the Nyquist plots).

Focusing on the peaks within the τ_{II} and τ_{III} regimes, which cover the interface-related kinetic response of interest, τ_{III} revealed a significant increase in charge-transfer resistance with prolonged cycling. Growth was clearly evident upon approaching the end of lithiation of the LTO WE after 100 cycles, whereas for the In/InLi CE, substantial growth occurred at the end of delithiation, even after 50 cycles. To better compare the evolution of kinetics for different SOC [i.e., (de)lithiation states] during electrochemical cycling, three distinct states, denoted as A, B, and C, were selected. State A

represents the 3E cells after discharging to 50 mAh g_{LTO}^{-1} , state B the end of charge (delithiation of LTO, lithiation of In/InLi), and state C the end of discharge (lithiation of LTO, delithiation of In/InLi), as illustrated in Figure 4b. The respective peaks in the DRT patterns were fitted for the quantitative analysis of evolving interfacial resistances related to interphase formation (R_{int}) and charge transfer (R_{ct}).¹⁸ Details are provided in Supporting Information Note S2 (Supporting Information). A representative DRT pattern with individual peak fits is shown in Figure S8 (Supporting Information), and summaries of the fitting results are given in Tables S1–S4 (Supporting Information).

The R_{int} of LTO was relatively low without major SOC dependencies throughout cycling, and the same trend was observed for In/InLi, however, at a much smaller value, demonstrating the good electrochemical stability of both electrodes when coupled with LPSCl. However, a distinct difference was found in the R_{ct} , especially at certain SOC. For LTO, compared to states A and B, the charge transfer with approaching full lithiation (state C) was impeded, particularly after long-term cycling. About a 3-fold increase in R_{ct} (from 4.9 to 14.9 $\Omega \text{ cm}^2$) occurred from cell formation to after 100 cycles. Nevertheless, the overall increase in interfacial resistance ($R_{int} + R_{ct}$), irrespective of SOC, was relatively small, emphasizing the stability of LTO in LPSCl-based SSBs.

By contrast, charge-transfer hindrance during cycling was severe at the CE side. For states A and B, where the lithium concentration at the In/InLi interface was sufficiently high, R_{ct} increased by a factor of about two from cell formation (5.5 $\Omega \text{ cm}^2$ for A and 4.8 $\Omega \text{ cm}^2$ for B) to after 100 cycles (9.0 $\Omega \text{ cm}^2$ for A and 10.2 $\Omega \text{ cm}^2$ for B). Notably, state A exhibited a reduction in R_{ct} after 50 cycles, presumably due to the improved interfacial conditions in the early stages of cycling. Overall, the R_{ct} remained relatively low due to well-maintained percolation pathways, with the bulk phase possessing a high apparent lithium diffusion coefficient.^{11,19} However, for state C, where the In/InLi was present in a highly delithiated state, the R_{ct} after cell formation (10.5 $\Omega \text{ cm}^2$) was even higher than that in states A and B after 100 cycles. Already after 50 cycles, an almost 4-fold increase in R_{ct} was observed, with a slower increase over the last 50 cycles, resulting in a final value of 54.5 $\Omega \text{ cm}^2$. The increase in R_{ct} can be clearly correlated with the worsening of lithium deficiency in the vicinity of the In/InLi/LPSCl interface. During continuous (de)alloying, microstructural changes occur, ultimately leading to the formation of some kind of lithium concentration gradient from the bulk to the interface. Nonuniform indium precipitation accompanied by void formation during delithiation of the In/InLi electrode can strongly impede ion transport. As a consequence, some lithium is likely trapped, meaning that it cannot properly diffuse through the indium phase to the interface. In the Nyquist plots in Figure S7 (Supporting Information), substantial growth of the capacitive tail is evident upon approaching the end of delithiation of the CE, which is indicative of reduced effective lithium diffusion and agrees well with the behavior of R_{ct} . The pronounced increase in R_{ct} can also be seen from the contour plots in Figure 4a, with an earlier onset during discharge (τ_{III} regime) in the later cycles.

Interestingly, despite the significant increase in R_{ct} , the 3E cells in Figure 1 still demonstrated a good stability with about 97% capacity retention after 100 cycles at 0.2C. This discrepancy between electrochemical performance and impedance build-up, particularly at the end of delithiation of In/

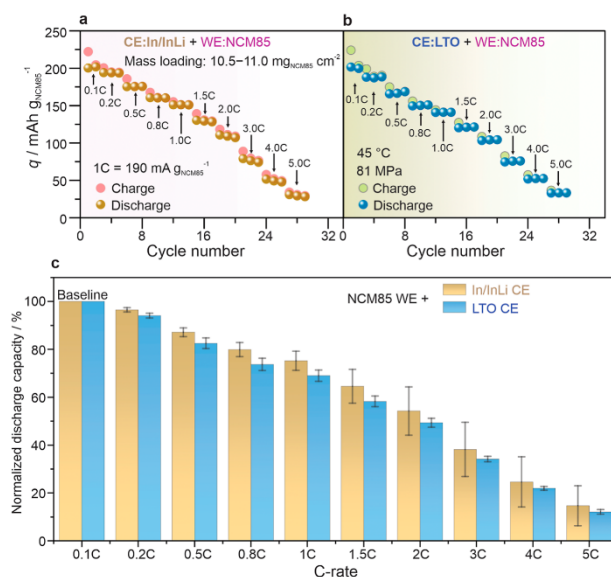


Figure 5. Rate capability testing of the LiNbO_3 -coated NCM85 cathode paired with either LTO or In/InLi anode. Specific charge/discharge capacities at C-rates ranging from 0.1C to 5.0C (equivalent to current densities of about 0.2 to 10 mA cm^{-2}) averaged from 4 to 5 independent cells with (a) In/InLi and (b) LTO as CE. (c) Corresponding normalized discharge capacities. Error bars represent the standard deviation.

InLi, warrants further analysis. Initially, the CE exhibits favorable interfacial kinetics. Thus, LTO can be effectively lithiated with limited capacity loss resulting from the In/InLi electrode. The concurrent high overpotential and R_{ct} at the end of discharge seem to represent a unique circumstance, reflecting a state with sluggish charge transfer at the In/InLi/LPSCI interface rather than a solid indicator to quantitatively evaluate the capacity fading during battery operation. Notably, it likely includes a sluggish diffusive response, evident from the low-frequency range in the Nyquist plots and coinciding with the high R_{ct} . Overall, it is reasonable to consider a “pitfall” with regard to correlating interfacial kinetics with electrochemical performance when In/InLi-based 2E cells are examined at the end of delithiation of the CE, owing to overlapping of WE and CE in terms of characteristic response and overpotential.

In summary, we found that in the “delithiation first” scenario, at certain SOC, charge-transfer hindrance at the CE/SE interface cannot be neglected, even though the cells were tested under moderate conditions in this study. Varying overpotential growth among different cells eventually causes a deviating electrochemical performance. Compared with In/InLi, LTO apparently shows more favorable interface-related kinetics. Aside from that, the unique chemo-mechanical behavior of LTO renders it promising for investigating industrially relevant cathodes, such as NCMs, in thiophosphate-based SSB environments.

To further explore the effect that In/InLi and LTO anodes have on the rate and long-term performance when paired with a layered Ni-rich cathode, 3E cells of configuration In/InLi or LTO/SE/LTO-REISE/NCM85 were assembled and electrochemically tested.

Cycling Performance of the In/InLi and LTO Anodes Paired with NCM85 Cathode.

As mentioned above, LiNbO_3 -coated NCM85 was employed as the cathode active material. The LPSCI-based composite cathode, denoted as NCM85 WE, was prepared by slurry casting with 1 wt % polyisobutylene binder, ensuring good chemo-mechanical stability, as evidenced in previous studies.^{16,31} Further details on the protective surface coating and electrode preparation can be found in the Experimental Section. Identical NCM85 WEs were tested in 2E and 3E cells, coupled with either In/InLi or LTO as CE, across four configurations. Each configuration was evaluated by using several independent cells. The voltage range was set from 2.28 to 3.68 V vs In/InLi or from 1.35 to 2.75 V vs $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_7\text{Ti}_5\text{O}_{12}$, aiming at cycling the NCM85 in a potential window of about 2.9–4.3 V vs Li^+/Li . Importantly, the focus was not on exploring the electrochemical performance of NCM85 but rather on understanding the influence of different CEs on overpotential and rate capability. The testing protocol was designed in a typical constant current mode, ranging from 0.1C to 5C (~ 0.2 to 10 mA cm^{-2}), without constant voltage or resting steps during (dis)charge.

As can be seen from Figure 5a,b (data averaged from 4 to 5 independent experiments), the cells with either In/InLi or LTO CE delivered specific discharge capacities of $q_{\text{dis}} > 200 \text{ mAh g}_{\text{NCM85}}^{-1}$ at 0.1C and exhibited a high initial Coulomb efficiency ($\varphi > 90\%$), indicating effective coverage of the NCM85 secondary particles by the LiNbO_3 coating. With increasing C-rate, from 0.2 to 2C, discrepancies in discharge capacity between the In/InLi and LTO cells became relatively pronounced. The largest one was observed around 1C, with $q_{\text{dis}} \approx 151$ and 141 $\text{mAh g}_{\text{NCM85}}^{-1}$ for the In/InLi and LTO cells, respectively. However, for C-rates higher than 3C, the

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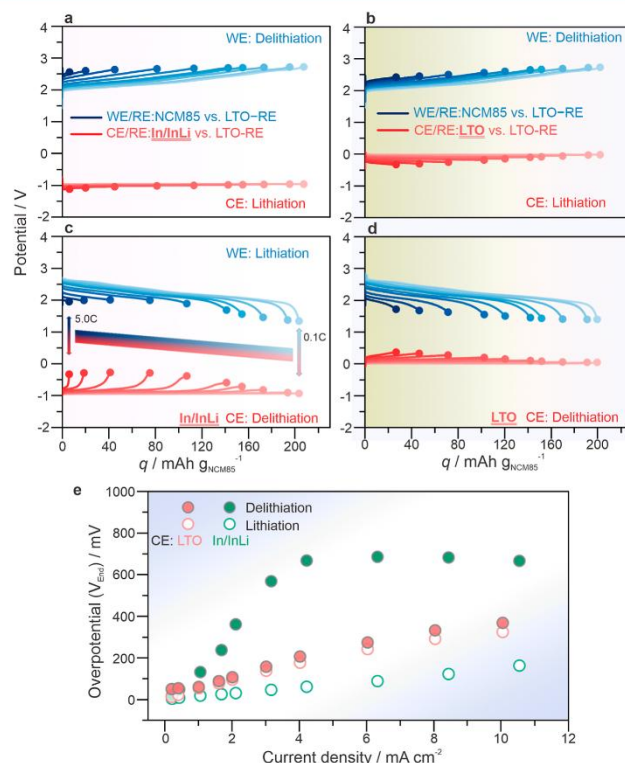


Figure 6. Potential profiles of 3E SSB cells with the LiNbO_3 -coated NCM85 cathode and either LTO or In/InLi anode and overpotential for the CEs at the end of (de)lithiation. (a–d) Deconvoluted potentials of the WE/RE (blue) and CE/RE (red) at various C-rates. The representative cell shown is denoted as cell-1. (e) Corresponding overpotential for the LTO and In/InLi electrodes at the end of (de)lithiation as a function of current density.

differences in discharge capacity were relatively minor. In general, the In/InLi-based cells were found to exhibit a superior rate performance over the LTO-based counterparts. This can be attributed to the fast lithium diffusion in In/InLi and the additional Ohmic polarization introduced by the LTO CE (thicker electrode due to high active mass loading). To further and more objectively examine the extent to which the choice of CE affects the rate capability, as well as to elucidate the underlying principles, the specific discharge capacities were normalized relative to that achieved at 0.1C, with the mean of the capacity retention as a function of C-rate and corresponding standard deviations (SDs) presented in Figure 5c.

In line with the discussion on the capacities above, the performance was better with the In/InLi-based cells, particularly in the range from 0.2 to 2C. Overall, based on the averaged results, the NCM85 WE exhibited a comparable rate capability when paired with the different CEs. However, when focusing on the SDs, the differences between the In/InLi- and LTO-based cells become much more apparent. As shown in Figure 5c, the performance of cells using LTO was very stable, with SDs remaining below 3% across all tested C-rates. In contrast, the In/InLi-based cells displayed substan-

tially larger SDs, especially at C-rates $\geq 1\text{C}$, reaching a maximum of about 11% at 3C, despite identical initial states of the as-prepared NCM85 and In/InLi electrodes. The electrochemical data are summarized in Table S5 (Supporting Information). A similar trend was also observed across different cell configurations (Figure S9, Supporting Information), confirming that the effect is independent of whether the measurements are conducted on 2E or 3E cells. Notably, the mean values for the 2E cells with an In/InLi CE exceeded those of their 3E counterparts, particularly at medium-to-high C-rates, which can be attributed to the lack of potential ion-blocking effects when the RE is embedded in the separator in the 3E configuration.

In a recently reported benchmarking study on SSBs, substantial variations among cells from different testing groups were observed, with one contributing factor being the lithium–indium alloy anode.⁹ Alt et al. and Yanev et al. demonstrated that different preparation procedures for the In/InLi electrode can result in major kinetic differences.^{13,14} Herein, focusing on the widely applied chemo-mechanical formation by stacking metal foils, the results from multiple cells revealed that the extent to which the kinetics of the In/InLi CE varies becomes particularly evident at medium-to-high C-rates, indicating that

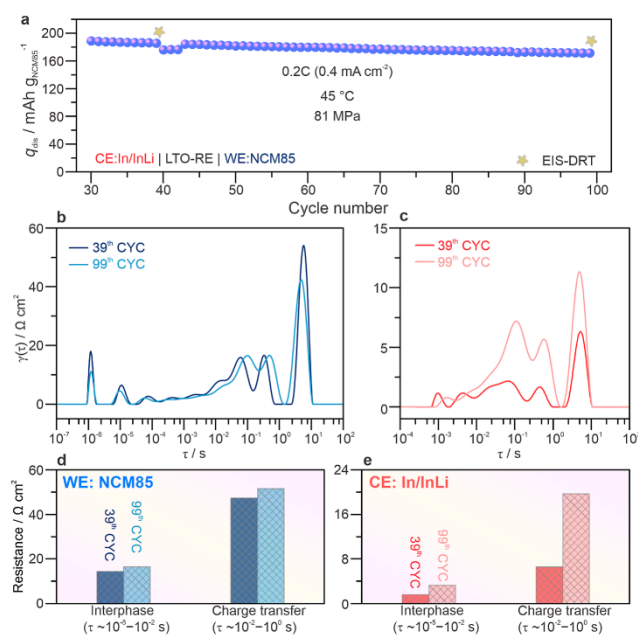


Figure 7. Long-term cycling performance of 3E SSB cells with the LiNbO_3 -coated NCM85 cathode and In/InLi anode and results from EIS-DRT analysis. (a) Cyclability at 0.2C after rate capability testing. (b,c) DRT patterns for the LiNbO_3 -coated NCM85 cathode and In/InLi anode after 39 and 99 cycles at the end of discharge and (d,e) corresponding interface-related resistances.

the overall conditions alter during extended electrochemical cycling.

To unravel the origin of the deviations in cells with In/InLi and to examine the overpotentials for the LTO and In/InLi anodes during rate-performance testing, the individual electrode potentials extracted from representative 3E cells (denoted as cell-1) are shown in Figure 6. Note that in the case of LTO, the lithium that can be shuttled back and forth only originates from the NCM85. This means that, unlike for In/InLi, there is no excess lithium available in the cells. As shown in Figure 6b,d, the LTO electrode potential exhibited the expected plateau on (dis)charge. The overpotential gradually increased with increasing C-rate, primarily due to Ohmic polarization. The NCM85 potential was correspondingly affected by the polarization of the CE, eventually resulting in early termination of the lithiation (discharge). Overall, LTO showed symmetric polarization behavior upon (de)lithiation, maintaining a high Coulomb efficiency during C-rate testing.

For the In/InLi CE, a stable lithiation plateau was observed but with a much smaller Ohmic polarization compared to that of LTO (see Figure 6a,c). However, upon approaching the end of delithiation (discharge), an abrupt increase in electrode potential was noticed for C-rates $\geq 0.5\text{C}$ ($\sim 1\text{ mA cm}^{-2}$), similar to the “delithiation first” scenario discussed previously. Again, this is due to overpotential and suggests sluggish charge-transfer and lithium diffusion kinetics at the In/InLi/LPSCI interface at high current densities. Accordingly, NCM85 was strongly affected by the asymmetric polarization behavior of CE (reflected in incomplete lithiation during discharge at higher C-rates). This indicates that for In/InLi, even in a

“lithiation first” scenario, kinetic hindrance is apparent and significant. High loading, symmetric In/InLi cells have been reported in the literature but with the extractable capacity at similar current densities not being much higher.^{11,32} Hence, the interfacial kinetics seems to be primarily related to both the quality (production method) of the In/InLi electrode and the (delithiation) current density.

The overpotential increase at the end of (de)lithiation of the In/InLi and LTO electrodes was further quantitatively analyzed as a function of current density (Figure 6e). In agreement with the symmetric polarization behavior of the LTO CE, a linear overpotential growth was observed with a maximum around 370 mV at 10 mA cm^{-2} . For the In/InLi CE, the growth during lithiation was also rather linear in nature but with a smaller slope. However, a strong increase in overpotential with increasing current density occurred upon delithiation, leveling off at 680 mV at about 4 mA cm^{-2} . The overpotential growth observed for another independent cell (denoted as cell-2, see Figures S10 and S11, Supporting Information) followed the same trend as that of cell-1. Interestingly, the asymmetric polarization of the In/InLi CE was lacking for the cell denoted as cell-3. In that case, a linear relationship was found between the overpotential and current density for both lithiation and delithiation, clearly accompanied by a better rate performance.

By continuously tracking the individual electrode potentials, the distinct evolution of overpotential among the In/InLi-based 3E cells became readily apparent (Figure S10, Supporting Information). Minor and quasi-symmetric polarization was observed for cell-3 across the tested C-rates,

indicating a kinetically favorable CE. In contrast, cell-1 and cell-2 exhibited pronounced asymmetric polarization behavior with substantially higher overpotentials, reflecting strong kinetic hindrance. Based on the cells studied in this work, the discrepancy in overpotential during delithiation can be as high as several hundreds of mV at current densities $\geq 3 \text{ mA cm}^{-2}$, providing an explanation for the relatively large SDs in Figure 5c.

The extent of the increasing overpotential in 2E cells with In/InLi is difficult to identify experimentally. As a result, the evaluation of the WE can become considerably more complex, being strongly influenced by the CE. For both “delithiation first” and “lithiation first” scenarios, the kinetics of In/InLi may be strongly affected by the microstructure and phase distribution near the interface. While the optimization of the In/InLi electrode is beyond the scope of this work, high-quality anodes with favorable kinetics for application in practical SSBs are in high demand. Obviously, the (de)lithiation current density is critical for the long-term stability, especially when paired with high energy density cathodes, such as layered Ni-rich oxides or sulfur.^{33,34} The commonly applied method for the preparation of In/InLi electrodes is sequential stacking and pressing of indium and lithium foils. Accordingly, the foil thickness and diameter, temperature, pressure, stacking order, etc., determine the overall behavior to different degrees.

A summary of reported design parameters for In/InLi paired with different WEs is given in Table S6 (Supporting Information). As can be seen from these data, the (successfully) applied delithiation current density varied from 2 to 26 mA cm^{-2} . Of note, the effect that the In/InLi has on cell performance is less dependent on quality at low current densities. However, when testing is performed at high current densities or on thick electrodes, the delithiation capacity of the CE becomes much more critical. Since that of In/InLi is dependent on current density, yet virtually independent of loading, tailoring of the WE rather than the CE seems important. For examining cells with Ni-rich cathodes under dynamic conditions, such as fast (dis)charge, the influence of CE polarization plays a significant role and must be considered separately. During rate capability testing, reversible lithium insertion/extraction can be limited by the polarization of In/InLi, particularly when it is asymmetric and nonlinear with regard to current density. In such cases, the observed performance is much lower than what would be expected from the intrinsic lithium diffusivity of the cathode. Therefore, for SSB testing, the selection of CE in terms of suitability, kinetics, etc., should be paid more attention to in future studies. Of course, for deconvoluting the polarization associated with interfacial effects, a reliable and robust 3E setup is required.

Finally, to unravel the evolution of interfacial kinetics in the In/InLi and NCM85 electrodes upon extended battery operation, after rate-performance testing, the cell was cycled for another 70 cycles at 0.2C (0.4 mA cm^{-2}), and the anode/cathode impedance build-up was investigated by 3E EIS-DRT analysis (see Figure 7a–e). As evident from Figure S12 (Supporting Information), the (de)lithiation plateau of In/InLi remained flat, without a significant increase in overpotential by the 99th cycle. The initial specific discharge capacity was about $189 \text{ mAh g}_{\text{NCM85}}^{-1}$ (Figure 7a), close to that achieved at 0.2C in Figure 5a, underscoring the electro-chemo-mechanical stability of the NCM85 WE, even after extensive testing at

high C-rates. The capacity retention was $\sim 91\%$ upon completion of the 70 cycles.

EIS measurements were conducted on the 3E cells in the 39th and 99th cycles at the end of discharge. Corresponding Nyquist plots of the electrochemical impedance for the WE + CE, WE, and CE are presented in Figure S13 (Supporting Information). Note that the overlapping charge-transfer resistance of the NCM85 and In/InLi electrodes (second semicircle) is indistinguishable from the 2E data due to similar characteristic frequencies. Deconvoluted by the 3E cell configuration, two semicircles were found for NCM85 (lithiated state) and one for In/InLi (delithiated state).

To study the evolution of interface-related kinetics individually, DRT analysis was performed, the results of which are presented in Figure 7b,c. The most significant processes took place in the 10^{-2} to 1 s range. Much lower peaks were seen for the WE in the 10^{-5} to 10^{-2} s range, corresponding to charge transfer across the as-formed interphase(s) and the protective coating. Quantitative analysis via peak fitting revealed that NCM85 contributes most to the prevailing interfacial resistance ($R_{\text{int}} + R_{\text{ct}}$), with limited growth upon cycling. In contrast, the evolution in the CE was rather pronounced, with a 3-fold increase in R_{ct} from about 6.6 to $19.7 \Omega \text{ cm}^2$. Summaries of the fitting results are given in Tables S7 and S8 (Supporting Information). In general, the R_{ct} contributed strongly to the impedance build-up, with the growth being more pronounced for In/InLi during the course of cycling at 0.2C. In the Nyquist plots (see Figure S13, Supporting Information), no distinct capacitive tail was observed for the CE at the end of delithiation, not even after 70 cycles. Since there was no significant increase in overpotential upon approaching the end of delithiation, the “pitfall” mentioned above is not present here. Hence, the R_{ct} for In/InLi directly correlates with capacity degradation.

The dilemma inherent in 2E EIS analysis stems from the overlapping electrochemical processes between WE and CE, particularly in the medium-to-low frequency range, which is associated with interfacial charge transfer. Misidentification of semicircles may lead to under- or overestimation of aging (failure). As seen from Table S8 (Supporting Information), about 75% of the total interfacial resistance ($R_{\text{int}} + R_{\text{ct}}$) can be associated with NCM85, with 28% of the R_{ct} originating from In/InLi at the end of discharge in the 99th cycle.

The interface-related kinetics at the end of charge was also examined by performing an additional cycle. It was anticipated that for the CE in the lithiated state, the resistance would be significantly lower than that at the end of delithiation. However, the R_{ct} of the WE is also strongly dependent upon the SOC. As shown in Figure S14 and summarized in Tables S7 and S8 (Supporting Information), the R_{int} for both electrodes did not change much from that observed at the end of discharge. However, R_{ct} decreased considerably. Similar to the discharged state, about 73% of the total interfacial resistance can be attributed to the WE, yet the CE contribution to R_{ct} increased to 39%. In this scenario, the estimation of charge-transfer resistance in the NCM85 would be still significantly skewed due to superimposed contributions from the CE in 2E cell configurations. Aside from that, it remains challenging to predict whether the charge-transfer resistance of In/InLi will continue to increase, potentially leading to accelerated capacity fading, as documented in the literature, or whether the interfacial resistance/overpotential growth will level off in the subsequent cycles.²⁰ Hence, to better assess the

electrochemical performance of the WE, a robust (kinetically favorable) CE should be employed. In addition, as discussed in the present work, a reliable 3E cell setup is in high demand to explore the characteristic interface-related kinetics of individual electrodes, especially those that show a strong SOC dependency.

CONCLUSION

This study focused on the impact of typical anode materials on the cycling performance of SSBs, probed by using a recently developed 3E cell setup. For examining LTO with In/InLi as CE in a “delithiation first” scenario, the parameters of the lab-scale testing conditions were chosen to be relatively moderate, namely, 45 °C, 81 MPa, and 0.28 mA cm⁻², with a high n/p ratio. The development of overpotential was found to be significant for the CE, particularly in its delithiated state. In addition, variations in the growth of the overpotential led to deviations in performance among the cells tested. From a kinetics perspective, there was a substantial increase in charge-transfer resistance at the end of delithiation of In/InLi, marked by the appearance of distinct blocking tails in the Nyquist plots and large overpotentials. This is likely due to sluggish ion transport, resulting in a localized lithium deficiency near the In/InLi/LPSCl interface. However, a “pitfall” was identified when analyzing the cell degradation. The high charge-transfer resistance observed at the end of delithiation did not correlate well with capacity fading upon cycling. Instead, it rather reflects the state-specific phase distribution within the In/InLi electrode. Evidently, overlapping interfacial processes between WE and CE may lead to an overestimation of cathode degradation in 2E cells under these conditions.

In SSB tests involving a slurry-cast NCM85 cathode, distinct appearances of overpotential were noticed for cells with LTO or In/InLi as the CE. Cells using LTO revealed symmetric polarization states and a linear increase with increasing current density. In contrast, cells with In/InLi (“lithiation first” scenario) showed unstable and nonuniform behavior, with asymmetric polarization upon (de)lithiation. Notably, for medium-to-high C-rates, the standard deviation of normalized capacities was much larger for cells with In/InLi than for those with LTO, indicating a deviating rate performance in 2E and 3E cells with In/InLi as CE. Lessons learned from cells with better rate capability suggest that linear overpotential growth plays a critical role, underscoring the need for tailored (kinetically favorable) In/InLi anodes for use in SSB testing.

Interestingly, upon extended cycling at moderate C-rates, the growth of interfacial resistance in the NCM85 WE was much more limited than that in the In/InLi CE at the end of discharge, despite the dominant cathode contribution. SOC-dependent charge-transfer resistance was observed for both the NCM85 and In/InLi electrodes. In fact, the charge-transfer resistance of the CE at the end of charge in the 100th cycle was significantly lower compared to the delithiated state, with the overall differences between NCM85 and In/InLi being less substantial. Therefore (for cycles of interest), in 2E cells, the effect that the cathode has on electro-chemo-mechanical degradation may be overestimated due to the anode contribution. The hidden overpotential growth and overlapping interfacial kinetic response in the frequency and time domains among the cathode and anode highlight the necessity of 3E cell testing to objectively evaluate the performance of the WE.

In summary, our work elucidates the characteristic interface-related kinetic evolution in CEs in practical application scenarios. The results contribute to the rational design of electrochemical testing protocols for the SSBs. Furthermore, this study provides valuable information on resistance build-up in In/InLi, LTO, and NCM85 electrodes, offering insights into effects of cell configuration and testing conditions.

EXPERIMENTAL SECTION

All materials/composites prepared and used in this study were handled in Ar-filled closed systems, either in sealed jars or a glovebox [LABmaster SP from MBraun, with $p(\text{H}_2\text{O})/p < 0.1$ ppm and $p(\text{O}_2)/p < 0.1$ ppm]. Assembled cells were sealed in pouch bags for electrochemical testing.

Materials. In this study, argyrodite Li₆PS₄Cl (LPSCl, NEI Corp.) was employed as a solid electrolyte (SE). Both the Super C65 (TIMCAL Ltd.) carbon additive and carbon-coated Li₄Ti₅O₁₂ (LTO, NEI Corp.) were preheated at 300 °C under vacuum overnight before usage. The pristine LiNi_{0.85}Co_{0.10}Mn_{0.05}O₂ (NCM85, BASF SE) was heated at 750 °C for 3 h under an O₂ flow to remove residual lithium species present on the surface of the secondary particles. Indium (Changsha Santech Materials Co., Ltd.) and lithium (Albemarle Germany GmbH) foils of thickness 100 and 50 μm, respectively, were used to prepare the In/InLi counter electrode (CE). To this end, 9 and 6 mm diameter discs were punched out from the indium and lithium foils, respectively, followed by stacking to produce the CE with an initial composition of Li_{0.37}In. A stainless steel wire (Thermo Fisher Scientific) of diameter 127 μm served as a current collector in the fabrication of the reference electrode (RE).

Coating of Cathode Particles. A detailed description of the preparation of LiNbO₃-coated NCM85 is provided elsewhere.³⁵ In brief (for 1 wt % coating content), 1.0 M lithium ethoxide (410 μL) and 0.5 M niobium ethoxide (820 μL) in absolute ethanol were combined with 6 g of NCM85 and sonicated for 30 min. Afterward, the mixture was dried under vacuum, and the resulting LiNbO₃-coated NCM85 was subjected to heating at 350 °C for 2 h under O₂ flow.

Preparation of Anode/Cathode Composites. The different components were blended by ball milling at 140 rpm for 30 min. Specifically, carbon-coated LTO, LPSCl, and Super C65 with a weight ratio of 30:65:5 and LiNbO₃-coated NCM85, LPSCl, and Super C65 with a weight ratio of 69.3:29.7:1 were used for the anode and cathode, respectively.

Preparation of Slurry-Cast Cathodes. The as-prepared cathode composite was combined with 1 wt % polyisobutylene (Oppanol N150, BASF SE) as polymer binder and anhydrous o-xylene (97%, Sigma-Aldrich) following a procedure described in previous studies.^{31,36} Finally, 9 mm diameter discs were punched out of the electrode tape for further usage.

Preparation of LTO-RE. Detailed instructions on the preparation of the LTO-RE are provided elsewhere.¹⁸ About 25 mg of LTO composite and In/InLi were used as WE and CE, respectively, in a 2E cell to prelithiate the LTO to a specific capacity of 50 mAh g_{LTO}⁻¹. The cell was then transferred to an Ar-filled glovebox, and the pellet stack was harvested. After the pellet was carefully fractured, the separator and In/InLi anode were worn off using sandpaper. The resulting LTO composite fragments were used to produce the RE.

For facile introduction of the stainless steel current collector into the cell stack (for 3E cells), two symmetric holes were drilled into a PEEK ring (see also section on the assembly of 2E and 3E cells below). First, a piece of the LTO composite fragment was placed on the stainless steel wire, followed by 80 mg of LPSCl. Subsequently, 125 MPa was applied for 1 min to densify the components. Following the same procedure, another LTO composite fragment and LPSCl were used on the other side, thereby producing a sandwich-type RE.

Assembly of 2E and 3E Cells. For 2E cells, a customized SSB setup was used including two stainless steel current collectors and a 10 mm diameter PEEK ring. Initially, 160 mg of LPSCl was densified at 62.5 MPa for 1 min. Next, either 20 mg of the LTO composite or a

LiNbO₃-coated NCM85 cathode disc was placed on one side of the separator and densified at 440 MPa for 3 min. Finally, the In/InLi CE was attached to the other side, with the indium facing the separator.

When using LTO as the CE, about 65 mg of anode composite was placed on one side of the separator. In this case, both the LiNbO₃-coated NCM85 cathode disc and the anode composite were densified together at 440 MPa for 3 min. For the 3E cells, the assembly steps were the same as those described for the 2E cells.

(De)lithiation Scenarios of In/InLi. During galvanostatic cycling, with In/InLi serving as the CE, the sequence of initial (de)lithiation varies depending on the WE used. To distinguish between different cell configurations, we refer to the In/InLi as either “delithiation first” or “lithiation first” when combined with LTO or LiNbO₃-coated NCM85, respectively.

Electrochemical Measurements. For 2E and 3E cells, the electrochemical performance was tested in constant current mode at 45 °C and 81 MPa by using both a MACCOR battery cycler and a Biologic SP-300 multichannel potentiostat. For LTO as WE, the voltage window was set to 0.38–1.38 V vs In/InLi (equivalent to about 1.0–2.0 V vs Li⁺/Li). The specific current was calculated based on $1C = 175 \text{ mA g}_{\text{LTO}}^{-1}$. The voltage window for cells containing the LiNbO₃-coated NCM85 cathode was either 2.28–3.68 V vs In/InLi or 1.35–2.75 V vs Li₄Ti₅O₁₂/Li₄Ti₅O₁₂ (equivalent to about 2.9–4.3 V vs Li⁺/Li). The specific current was calculated based on $1C = 190 \text{ mA g}_{\text{NCM85}}^{-1}$.

In situ electrochemical impedance spectroscopy (EIS) measurements were conducted on 3E cells of configuration In/InLi/SE/LTO-RE/SE/LTO, with the frequency ranging from 1 MHz to 100 mHz and with a voltage amplitude of 7 mV. State of charge tailoring was realized by cycling at 0.05C with limited capacity (0.075 or 0.15 mAh per step). Corresponding distribution of relaxation times (DRT) analysis was performed using the RelaxIS software (rhd instruments GmbH & Co. KG). The transformation from frequency to time domain was accomplished by applying complex data with a regularization parameter of $\lambda = 10^{-5}$. By utilizing multiple Gaussian functions, peaks appearing in the DRT patterns were fitted to determine the characteristic time constants and resistances for quantitatively evaluating the evolution of interface-related kinetics.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsnano.5c17276>.

For cells with LTO WE and In/InLi CE: voltage/potential profiles of 2E/3E cells during formation, potential drift of the LTO-RE upon long-term cycling, voltage/potential profiles for selected cycles, details on the quantitative overpotential analysis, long-term cycling performance and overpotential tracking, Nyquist plots of the electrochemical impedance from in situ EIS measurements, details on the quantitative analysis of DRT data, and summaries of the fitting results; for cells with LiNbO₃-coated NCM85 WE and LTO or In/InLi CE: normalized discharge capacities for different cell configurations, summary of specific and normalized discharge capacities during rate performance testing, voltage/potential profiles and overpotential tracking as a function of current density, design parameters used for the In/InLi CE and corresponding current densities enabling “stable” cycling over more than 500 cycles, voltage/potential profiles for selected cycles, and Nyquist plots and DRT analysis, with results from peak fitting for selected cycles and SOC (PDF)

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Notes

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3.3. Enhancing the Electrochemical Performance of Slurry-Cast Cathodes through Systematic Optimization

Enhancing the electrochemical performance of SSBs is a multidimensional and system-level challenge. For the cathode, one of the most promising configurations is the combination of Ni-rich cathodes with SSEs. The moderate incorporation of additional inactive components, such as conductive additives and/or binders, together with particle size engineering of the core components, not only expands charge transport pathways within the electrode and improves structural stability, but also enables up-scaling based on wet- or dry-processing routes.

Beyond optimizing cathode performance and stability, attention was further extended to the anode side. In **Publication VI**, the regulation of the laboratory-scale anode material led to a significant enhancement in electrochemical performance of the investigated system. This approach further broadens the available strategies for mitigating mechanical failure at the cathode side.

3.3.1. Publication VI: Compromise Between Energy Density and Stability: Proper Capacity Balancing Enables High-Performance Solid-State Batteries

In the previous publications, a variety of characterization techniques were employed to systematically investigate interfacial issues in SSBs, with particular emphasis placed on the (electro)chemical degradation. In **Publication VI**, the focus was shifted toward mechanical failure, specifically at the cathode side. For the applied PC Ni-rich cathode, a strategy was proposed, in which regulation of the anode was used to enhance cathode stability, resulting in a marked improvement in cycling stability and enabling a favorable balance between attainable capacity and capacity retention.

In this work, PC NCM85 was again selected as a representative CAM and paired with LPSCI as the SSE, forming the core components of the cathode. To minimize the interference of (electro)chemical degradation arising from interfacial side reactions on the analysis of mechanical failure, LiNbO₃ was applied as a coating material. In addition, a polymer binder was introduced, and the cathode was fabricated by slurry casting, thus further increasing mechanical stability of the system. The central concept of this study lies in the rational regulation of the n/p ratio by employing LTO as the anode/CE, thereby enabling a dynamic process that provides adaptive compensation for capacity fading induced by polarization.

More specifically, it was noted that even after deviating from the two-phase region, LTO retains a considerable amount of accessible capacity. Based on this characteristic, we exploited this tail region by adopting a low n/p ratio, such that during the charging step, the initial upper cut-off potential (IUP) remains lower than the desired upper cut-off potential (DUP). This design embodies the first advantage of the strategy: by intentionally lowering the upper cut-off potential of the NCM85 initially, the extent of volume changes experienced in the highly delithiated state is significantly reduced. Although this comes at the cost of some initial capacity, the overall mechanical stability of the

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electrode is substantially improved. As cycling proceeds, electro-chemo-mechanical degradation remains inevitable and manifests as increasing polarization and subsequent performance decay. This, in turn, activates the second advantage of the strategy: the low n/p design provides an adaptive capacity-compensation window. Starting from an initial state with $IUP < DUP$, the upper cut-off potential of NCM85 can progressively shift toward higher potentials in subsequent cycles, eventually releasing additional capacity to compensate for loss caused by polarization growth and leading to superior electrochemical performance.

LTO was employed here as a model anode/CE, actually not for considerations of energy density, but rather due to its highly stable electrochemical behavior and well-defined, controllable potential profile. The underlying design concept demonstrated in this work can be extended to emerging alloy-type anodes. As such, this study provides clear design principles for the development of high-energy-density SSBs, spanning material selection, electrode design, and cell-level engineering.

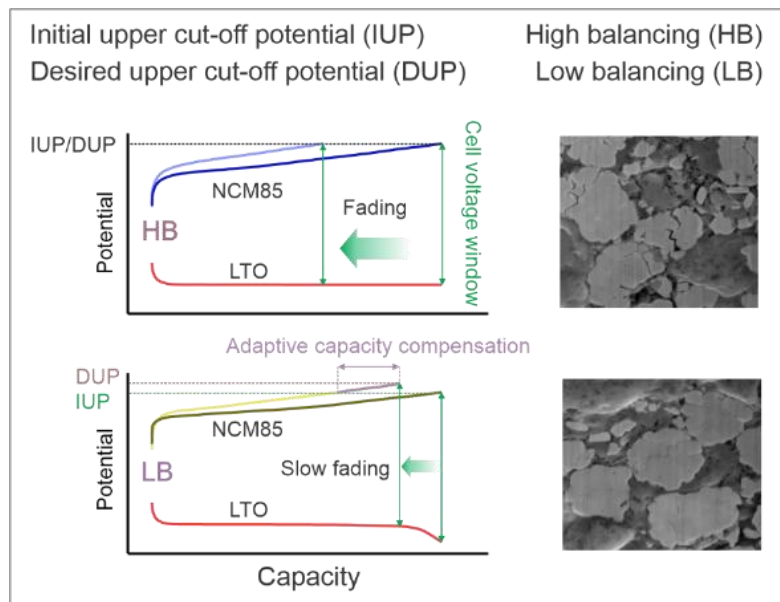
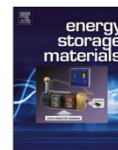


Figure 12. Table of contents graphic of publication VI. Redrawn from reference [48].

The experiments were designed and planned by the first author R. Zhang, under the supervision of A. Kondrakov, J. Janek, and T. Brezesinski. The initial idea was conceptualized by R. Zhang, S. Payandeh, and T. Brezesinski. R. Zhang performed the CAM coating, prepared the cathode tape, conducted the electrochemical tests, carried out XRD, SEM-EDS, *in situ* pressure measurements, analyzed the data, and elucidated the core mechanism. D. Goonetilleke refined and analyzed the XRD data. Y. Tang performed the FIB measurements. The first draft was written by the first author. The final paper was edited by all co-authors.



Compromise between energy density and stability: Proper capacity balancing enables high-performance solid-state batteries

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ABSTRACT

Controlling electro-chemo-mechanical effects remains a key challenge in advancing the development of solid-state batteries (SSBs) with layered Ni-rich cathode and sulfide solid electrolyte. While surface coatings suppress parasitic side reactions, mechanical failure can still be severe, and there is a relative lack of effective strategies to counteract it. To improve the integrity of the cathode, herein we propose a capacity balancing approach with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) as a model anode in thiophosphate-based SSBs. By leveraging the tip-shaped lithiation tail of LTO with a low negative-to-positive balancing (LB), this strategy enables a reduced upper cut-off potential of the $\text{LiNi}_{0.85}\text{Co}_{0.10}\text{Mn}_{0.05}\text{O}_2$ (NCM85) cathode used, thereby mitigating mechanical stress/strain induced by the H2-H3 phase transition. As polarization increases during cycling, the potential is gradually increased, compensating for the loss of capacity without external voltage adjustment. Three-electrode measurements validate the proposed mechanism across several C-rates and corroborate this self-regulating process. Unlike high negative-to-positive balancing (HB), the LB configuration achieves improved structural integrity, reduced charge-transfer resistance, and prolonged cycle life, retaining 80 % capacity after about 1300 cycles at 1C (compared to 400 cycles in HB cells). Overall, this work offers a simple, yet effective strategy for extending the longevity of cathodes for the development of high-performance SSBs.

1. Introduction

Solid-state batteries (SSBs) have been established as a next-generation electrochemical energy storage technology, promising higher energy densities and safety compared to conventional lithium-ion batteries (LIBs) [1,2]. Replacing the flammable liquid electrolyte in LIBs with a superionic solid electrolyte (SE) eliminates the risk of leakage and combustion while also making the use of lithium metal anodes for further energy density improvements feasible. Among the different classes of SEs, sulfides (thiophosphates) stand out due to their superior room-temperature ionic conductivity (up to $10^{-2} \text{ S cm}^{-1}$) and favorable mechanical softness, ultimately enabling close contact with the other (active/inactive) electrode components [3–5]. In parallel, the development of layered Ni-rich oxide cathode active materials (CAMs), such as polycrystalline $\text{LiNi}_{0.85}\text{Co}_{0.10}\text{Mn}_{0.05}\text{O}_2$ (NCM85) or even single crystal

counterparts, offers high energy density and renders them attractive candidates for coupling with sulfide SEs in SSBs [6–8].

In general, the combination of Ni-rich cathodes and sulfide SEs is a promising route toward realizing high-performance (practical) SSBs. However, this configuration presents substantial challenges, particularly at the interface between CAM and SE [9–11]. Electrochemical side reactions can lead to the formation of resistive interphases and microstructural degradation of the CAM particles. To address this, protective coatings, such as LiNbO_3 , have been widely employed for passivating the cathode surface and suppress the decomposition of SE [6,12–14]. While coating strategies have generally proven effective in improving (electro) chemical stability, particularly in terms of increasing initial capacity and reversibility, mechanical degradation, including intergranular particle cracking and/or contact loss, remains a major obstacle to the longevity of SSBs [14–17].

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To mitigate adverse mechanical effects, the optimization of components within the cathode, for example, using glassy SEs and/or tailored polymer binders, has been intensively investigated [18–21]. It should be noted that, in the preparation of scalable cathodes, binder-containing electrodes are usually produced either by slurry casting (wet processing) or by dry processing [18,22,23]. Compared with (rigid) pelletized electrodes, slurry-cast tapes not only improve mechanical cohesion within the electrode, but also help accommodate volume variations of the CAM, thereby increasing stability and enhancing cyclability.

Despite these advances, it is the CAM itself that plays a decisive role in determining the performance and energy density of SSBs. Consequently, a fundamental trade-off exists between maximizing the specific capacity of Ni-rich cathodes and ensuring long-term stability, which is regulated by their proper use. While operation at a high upper cut-off potential (UP) enables better utilization of the lithium inventory, it inevitably exacerbates structural degradation arising from intrinsic phase transitions. Lowering the UP mitigates mechanical stress/strain and improves interfacial stability, but this benefit is accompanied by a sacrifice in capacity. In addition, prolonged operation leads to electrochemical degradation, as interphases continuously grow and microstructural damage occurs, eventually resulting in cell polarization and capacity fading.

To overcome this, in the present work, we propose an adaptive compensation strategy through the rational design of capacity balancing. Using polycrystalline NCM85 coated with amorphous LiNbO_3 (LiNbO_3 -NCM85) and processed into slurry-cast electrodes, we paired the cathode (working electrode, WE) with carbon-coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) as a model anode (counter electrode, CE). Under low balancing (LB) conditions with a negative-to-positive (n/p) capacity ratio of 1.1, the tip-shaped lithiation tail of LTO is used to lower the initial upper cut-off potential (IUP) of the WE, thereby mitigating the H2-H3-induced volume change and associated mechanical degradation of the Ni-rich cathode. Over the course of cycling, electro-chemo-mechanical degradation gradually leads to polarization, which ultimately increases the UP to the desired UP (DUP) and helps compensate for the loss of capacity without requiring active control of the voltage window. This LB design greatly improves cycling stability by increasing the mechanical integrity of the cathode.

Taken together, our findings establish capacity balancing as a powerful strategy to reconcile high energy output and long-term cycling stability in sulfide-based SSBs with a Ni-rich cathode. In particular, the LB approach offers new design/mechanistic perspectives under realistic manufacturing conditions.

2. Results and discussion

To improve the (electro)chemical stability at the interface between CAM and SE, LiNbO_3 was applied to the surface of the NCM85 particles using a sol-gel process [13]. Powder X-ray diffraction (XRD) patterns of both pristine NCM85 and LiNbO_3 -NCM85 are presented in Figure S1. As can be seen, the reflections before and after coating matched, indicating a well-preserved layered structure ($R\bar{3}m$ space group) without new peaks due to the low content (1 wt. %) and amorphous nature of LiNbO_3 . Scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDS) revealed that LiNbO_3 forms a continuous shell around the secondary particles (see Figure S2a–g) without noticeable inhomogeneities. The average size of the LiNbO_3 -NCM85 particles was about 4 μm , and they had a nearly spherical shape. The as-made LiNbO_3 -NCM85 and argyrodite $\text{Li}_6\text{PS}_5\text{Cl}$ (LPSCl) were then used as main components for the assembly and testing of SSBs.

2.1. Cathode microstructure and ionic/electronic partial conductivities

As a well-recognized approach for improving the mechanical stability of electrodes, a binder-containing cathode was produced by wet processing for electrochemical testing. To investigate the effects of the

added polymer binder and the slurry casting process on the cathode in terms of effective ionic/electronic partial conductivities and microstructure, a pelletized cathode was also produced and measured in parallel. Ball milling was used to produce the cathode composite by dry mixing LiNbO_3 -NCM85 CAM, LPSCl SE, and Super C65 carbon additive, as shown in Fig. 1a. The composite obtained can be compacted directly and used as a cathode in SSBs, which is often implemented in laboratory-scale research. To produce the slurry-cast cathode, a polyisobutylene (PIB) binder and *o*-xylene as nonpolar solvent were added to the aforementioned composite (see Fig. 1e), after which the mixture was coated onto Al foil. Further details can be found in the Experimental section.

A cathode with a smooth surface was achieved using 1 wt. % binder (see Fig. 1f). In the pristine state (without compaction), the morphology of the CAM and SE particles and their distribution were first examined through top-view SEM-EDS imaging. As is evident from Fig. 1b, agglomerated SE particles were closely surrounded by the CAM. To evaluate the microstructure after densification, both the pelletized and slurry-cast cathodes were subject to compaction at 435 MPa. As shown in Fig. 1c and d, the slurry-cast cathode was much denser than its pelletized counterpart, due to better elimination of macroscopic pores/voids. Interestingly, most of the pores/voids in the pelletized cathode were concentrated in areas where the CAM tends to agglomerate, creating relatively large gaps between the rigid CAM "clusters" and the deformable SE particles. In contrast, the improved dispersion of particles achieved by slurry casting ensures a more uniform embedding of the CAM. Specifically, the insulating PIB binder, which appears to be evenly distributed across the cathode, formed an adhesive film that holds the composite together and reduces porosity. After compaction, the "island-like" SE domains observed in the pelletized cathode were clearly smaller and better distributed, resulting in improved ionic percolation through the slurry-cast cathode.

To quantify how the microstructural differences affect the charge-transport properties, ion- and electron-blocking cell configurations were used, as shown in Figure S3a and b. To mimic the conditions of the actual SSBs, the same assembling/operating pressures and temperature were used for AC polarization measurements. The effective ionic/electronic partial conductivities were eventually extracted by fitting impedance data using specific transmission line models (see Figure S3c–f). As shown in Fig. 1g and Table S1, the pelletized cathode exhibited an ionic conductivity (σ_{ion}) that was about 2.6 times higher than that of the slurry-cast cathode (0.37 versus 0.14 mS cm^{-1}). A similar observation was made for the electronic conductivity (σ_{el}), but to a much greater extent (1.3×10^{-1} versus 4.8×10^{-2} mS cm^{-1}). It should be noted that, in addition to the volume ratio of CAM to SE and the carbon content, the nature/properties of the selected binder also strongly determine the percolation paths for ion and electron transport. Regardless, the binder impairs charge transport, at least to some degree, especially when it is finely distributed in the cathode. Nevertheless, the slurry-cast cathode preserved relatively high ionic and electronic partial conductivities while offering greater mechanical stability than the pelletized counterpart, which is required for stable SSB operation.

2.2. Capacity balancing and cell cyclability

As mentioned above, LTO was employed as a model anode in the present work. To determine the specific capacity that can be achieved with the individual electrodes, SSBs were assembled with indium-lithium alloy (In/InLi) as CE (0.62 V vs. Li^+/Li). The In/InLi|LPSCl|LTO and In/InLi|LPSCl| LiNbO_3 -NCM85 cells were cycled between 0.38 and 1.38 V vs. In/InLi (equivalent to approx. 1.0–2.0 V vs. Li^+/Li) and between 2.28 and 3.68 V vs. In/InLi (equivalent to approx. 2.9–4.3 V vs. Li^+/Li), respectively. Cells of configuration LTO|LPSCl|NCM85 were also operated within a 1.4 V window, namely from 1.35 to 2.75 V vs. $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_7\text{Ti}_5\text{O}_{12}$. All electrochemical measurements were performed at 45 °C and under a constant external pressure of 81 MPa. As shown in

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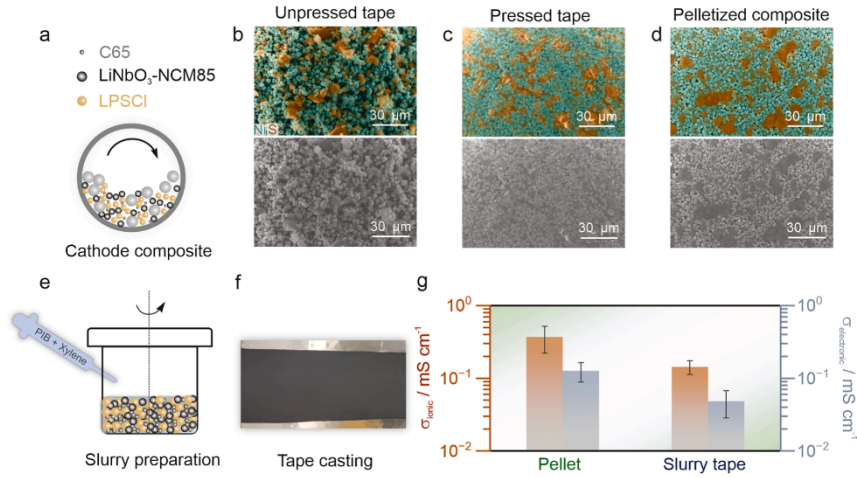


Fig. 1. Microstructure and transport properties of slurry-cast and pelletized cathodes. Schematic representation (a) of the dry mixing of cathode composite by ball milling and (e) of the subsequent slurry preparation with PIB binder and *o*-xylene as solvent. Top-view SEM images in conjunction with EDS mapping of nickel and sulfur for the slurry-cast cathode (b) before and (c) after compaction at 435 MPa, as well as (d) for the pelletized cathode. (f) Photograph of the slurry-cast cathode. (g) Effective ionic and electronic partial conductivities from three independent cells determined by AC polarization at 81 MPa and 45 °C.

Figure S4a, the In/Li-based cells underwent two formation cycles at 0.1C, followed by two cycles at 0.2C. The LiNbO₃-NCM85 cathode exhibited an initial Coulomb efficiency of 90.4 %, indicating good interfacial stability due to the presence of a protective LiNbO₃ coating. LTO, known for its high mechanical robustness and compatibility with sulfide SEs, is widely used in SSB systems as a zero-strain anode. As shown in Figure S5, the material employed retained about 97 % of its initial capacity after 200 cycles at 0.2C (~131 mAh g_{LTO}⁻¹), suggesting negligible capacity fading from LTO. From the fourth-cycle lithiation/delithiation profiles in Figure S4b and c, it can be seen that both LiNbO₃-NCM85 and LTO exhibit high reversibility (Coulomb efficiency).

When LTO is used as an anode (CE) in the electrochemical testing of SSBs, a relatively high n/p capacity ratio is typically sought to maintain the plateau at 1.55 V vs. Li⁺/Li as a reliable reference potential. Notably, the discharge profile showed a gradual potential drop upon approaching the cut-off potential during lithiation (see Figure S4c), where LTO transitions from a two-phase coexistence region to the rock-salt Li₇Ti₅O₁₂ phase. As can be seen, this tip-shaped lithiation tail contributes significant capacity at low potentials. Therefore, using the fourth-cycle specific capacities, $q_{ch} = 202 \text{ mAh g}^{-1}$ for LiNbO₃-NCM85 and $q_{dis} = 132 \text{ mAh g}^{-1}$ for LTO, we focused on two capacity balancing conditions, namely high balancing (HB, n/p = 1.5) and low balancing (LB, n/p = 1.1), as shown in Fig. 2a. The core difference lies in the way the LTO lithiation profile is used. In HB cells, the LTO anode operates entirely within the voltage plateau region, whereas in LB cells, due to the constrained voltage window, the potential of the LTO anode falls below the plateau toward the end of the charging process. This leads to a lower upper cut-off potential (UP, ~4.2 V vs. Li⁺/Li) for the LiNbO₃-NCM85 cathode in the LB cells. As a result, the LB design deliberately reduces the initial upper cut-off potential (IUP) at the expense of some capacity to mitigate the H2-H3 phase transition that typically occurs above 4.2 V vs. Li⁺/Li in Ni-rich cathodes (thereby indirectly affecting mechanical integrity). For practical implementation, the capacity balancing was controlled by tailoring the mass of the LTO composite (see Experimental section).

The first-cycle voltage profiles of the HB and LB cells at 0.2C in Fig. 2b confirm the expected differences in achievable specific charge/discharge capacities with 227/198 mAh g_{NCM85}⁻¹ and 210/185 mAh

g_{NCM85}⁻¹, respectively. With the same charge capacity as in the LB case, the cut-off voltage of the HB cell would be about 2.65 V vs. Li₄Ti₅O₁₂/Li₇Ti₅O₁₂ (corresponding to ~4.2 V vs. Li⁺/Li), which is consistent with the reduction in IUP in the LB cells.

Differential capacity (dq/dV) curves of the initial cycle (see Figure S6a) show clear H1-M-H2-H3 phase transitions for both configurations. However, the H2-H3 peak is significantly weaker in the LB cells. Since this high-voltage transition causes large volume changes and irreversible structural damage to Ni-rich cathodes, the LB condition apparently helps reduce the formation of mechanical stresses and thus improves stability.

As shown in Fig. 2c and d, the HB and LB cells exhibit distinct differences in capacity retention at 0.2C. Considering the cell-to-cell variations frequently observed in the testing of SSBs and the need for repeated measurements and statistical averaging for an objective evaluation of the proposed strategies, the long-term cycle data presented here represent the average of two independent cells [24]. The HB configuration started with a higher initial specific discharge capacity of $q_{dis} = 199 \text{ mAh g}_{\text{NCM85}}^{-1}$, but retained only ~85 % (169 mAh g_{NCM85}⁻¹) after 120 cycles. In contrast, despite a lower starting value of $q_{dis} = 185 \text{ mAh g}_{\text{NCM85}}^{-1}$, the LB configuration achieved a higher capacity retention of ~94 %, corresponding to 173 mAh g_{NCM85}⁻¹, demonstrating the beneficial effect of the capacity balancing strategy. Regardless, both exhibited average Coulomb efficiencies of $\eta = 99.6 \%$ (HB) and 99.8 % (LB), confirming the high reversibility. The superior capacity retention of the LB cells is based on two synergistic effects: (i) improved structural integrity of the cathode due to a lower IUP and (ii) gradual increase in UP during cycling, which adaptively compensates for polarization-related capacity fading.

Evidence of the latter can be found in the 2D and 3D contour plots of the differential capacity for the charging process in Fig. 2e and f and Figure S7a and b, respectively. Focusing on the evolution of the H2-H3 transition (~2.65 V vs. Li₄Ti₅O₁₂/Li₇Ti₅O₁₂), the peak intensity in the HB cells clearly decreased with cycling, indicating a loss of reversible capacity in this potential range, likely due to structural degradation of the CAM. By contrast, in the LB case, the peak intensity increased, pointing toward a gradual rise in UP that counteracts the capacity decay caused by degradation. After 120 cycles (see Figure S6b), the peaks

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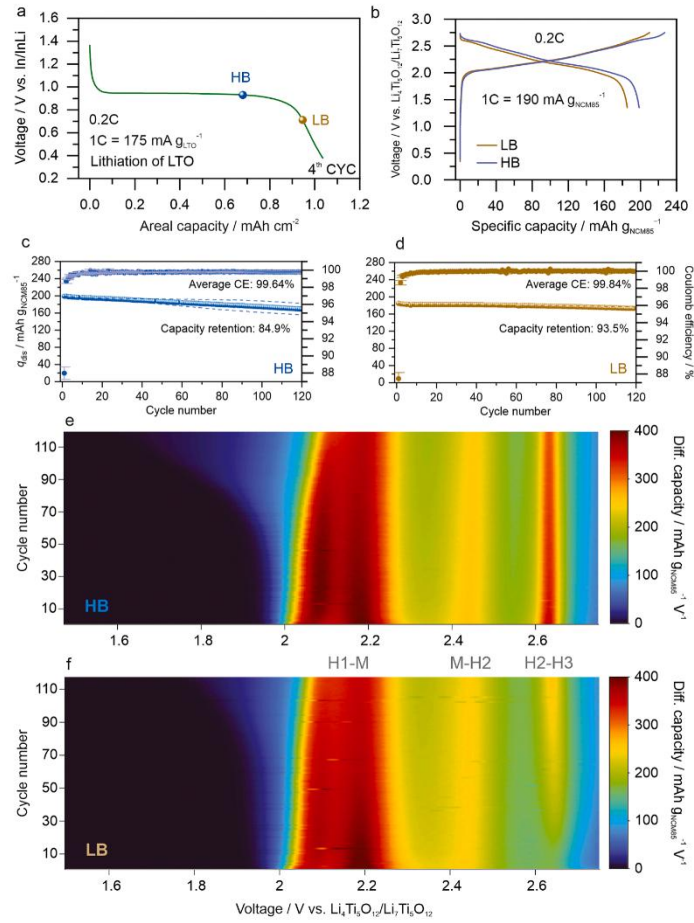


Fig. 2. Capacity balancing and electrochemical performance. (a) Fourth-cycle lithiation profile of LTO in an In/InLi|LPSCl|LTO cell at 0.2C (0.38–1.38 V vs. In/InLi). Based on Fig. 1 (see Experimental section), two n/p ratios were selected, referring to high balancing (HB, 1.5) and low balancing (LB, 1.1), as indicated by the blue and yellow dots, respectively. (b) First-cycle voltage profiles of LTO|LPSCl|LiNbO₃-NCM85 HB and LB cells at 0.2C (1.35–2.75 V vs. Li_{0.5}Ti_{0.5}O₂/Li_{0.5}Ti_{0.5}O₂). (c, d) Corresponding long-term cyclability, shown as average specific discharge capacity and Coulomb efficiency from two independent cells. The standard deviations vary from 0.9 to 13.5 mAh g_{NCM85}⁻¹ (first to 120th cycle) for the HB and LB cells, respectively. (e, f) 2D contour plots of differential capacity during charging. The characteristic phase transition ranges are specified.

representing the H1-M and M-H2 transitions overlapped well in terms of intensity and position for the HB and LB cells, while in the case of the H2-H3 peak, the intensity of the LB cells was still somewhat lower than that of the HB cells. Overall, these results confirm the effectiveness of the LB strategy in achieving stable performance of SSBs with Ni-rich cathode and sulfide SE. In the following section, the improvement in mechanical integrity is discussed in some more detail.

2.3. Cathode breathing

To find out how capacity balancing affects the mechanical stability, *operando* pressure measurements were conducted on the HB and LB cells, aiming at tracking the cathode breathing during battery operation. Given that LTO was used as CE, any pressure changes are primarily due to the mechanical response of the cathode. The respective cells were

again cycled under an external pressure of 81 MPa, and a force sensor was used to monitor the pressure evolution *in situ*.

After 12 h rest at open circuit voltage (OCV), the cells reached thermodynamic equilibrium, and the corresponding pressure baseline was established for calibration of the signals recorded at 0.1C in the following five cycles. For layered Ni-rich oxide cathodes, it is well known that the lattice parameter *a* decreases upon delithiation (charge), while *c* initially increases and then drops sharply in the H2-H3 region [25–27]. This anisotropic behavior eventually results in a volume contraction that is responsible for the pressure evolution observed for the HB and LB cells (see Fig. 3a and b). As can be seen, both configurations exhibit reversible, negative net pressure changes. Interestingly, the overall pressure evolution was almost identical for the different cells over the first two cycles. This similarity could be due to initial microstructural changes within the cathode, which appear to mask the

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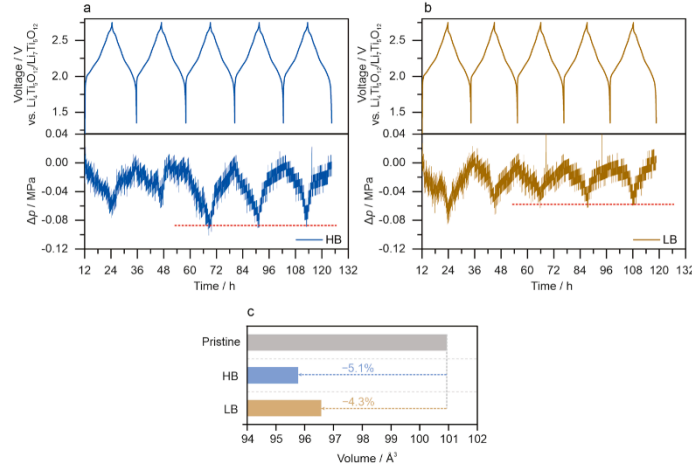


Fig. 3. Mechanical behavior of LTO|LPSCl|LiNbO₃-NCM85 HB and LB cells. (a, b) *Coperando* pressure measurements. The cells were cycled at 0.1C (1.35–2.75 V vs. $\text{Li}_4\text{TisO}_{12}/\text{Li}_7\text{TisO}_{12}$) for five cycles, following a 12 h rest under OCV conditions. The corresponding voltage profiles and pressure responses are shown in the upper and lower panels, respectively. Red dotted lines indicate the extent of pressure change during cycling. (c) Unit-cell volume of LiNbO₃-NCM85 in the pristine state and after first charging at 0.2C. The volume contraction is indicated by dotted lines.

intrinsic volume variations of the CAM, at least to some extent.

To quantify the structural evolution of NCM85, *ex situ* XRD measurements combined with Rietveld refinement analysis were performed on harvested cathodes from the HB and LB cells after the first charge cycle and compared to their pristine state (see Figure S8). As shown in Fig. 3c and Table S2, the crystallographic volume shrinkage in the LB cells is 4.3 %, much smaller than the 5.1 % shrinkage in the HB cells. This result confirms both the successful realization of a lower UP under LB conditions and the effective suppression of lattice contraction, even during the initial formation cycles. As cycling progressed, the mechanical breathing behavior became more pronounced. From the third to fifth cycle, the LB cells exhibited a smaller negative net pressure change compared to the HB cells. This response supports the conclusion that a low n/p ratio helps improve stability, particularly within the cathode. Moreover, it correlates well with the superior capacity retention observed for the LB cells during long-term cycling, emphasizing the critical role of mitigating mechanical stresses through targeted capacity balancing.

2.4. Rate performance and post-mortem characterization

To evaluate the effects of capacity balancing on the electrochemical performance and microstructural evolution of the cathode during long-term cycling, rate capability and post-mortem analyses were performed. Specifically, the HB and LB cells were subject to sequential C-rate testing from 0.1C/0.2C to 5C for two rounds (see Fig. 4a). The corresponding specific discharge capacities are summarized in Table S3. For all C-rates, the HB cells delivered higher capacities than the LB counterpart. This is due to the lower IUP in the LB configuration, which resulted in a slightly lower specific discharge capacity from the very beginning at 0.1C (199 versus 204 mAh g_{NCM85}⁻¹). The difference in capacity was most pronounced between 0.5C and 2C, suggesting that the LB strategy with larger Ohmic polarization effectively reduces the UP across various C-rates. Nevertheless, the LB cells exhibited good rate performance. For instance, the specific discharge capacities at 1C, 2C, and 5C were found to be 164/147, 141/125, and 96/85 mAh g_{NCM85}⁻¹ for HB/LB, respectively. As shown in Fig. 4f, both exhibit nearly identical normalized capacities, irrespective of the C-rate. This result shows that, despite the

different n/p ratios, the use of LTO as an anode ensures consistent performance within the same cell system.

After testing the rate capability, the HB and LB cells were subject to a further 200 cycles at 0.2C (see Fig. 4b). After 90 cycles, the specific discharge capacities were similar, with $q_{\text{dis}} = 191$ and 189 mAh g_{NCM85}⁻¹ for HB and LB, respectively. After 290 cycles, the LB cells achieved a capacity retention of ~83 %, which is higher than the ~75 % observed for the HB cells, confirming the importance of capacity balancing for long-term stability.

To determine whether there are any changes in interfacial kinetics across the cells after long-term cycling, electrochemical impedance spectroscopy (EIS) and distribution of relaxation times (DRT) analysis were performed at the end of discharge to ensure similar states of charge (SOCs) for the LiNbO₃-NCM85 cathode and the LTO anode (avoiding UP-induced deviations). As can be seen from the Nyquist plots (frequency domain) in Fig. 4c, both the HB and LB cells showed poorly resolved semicircles and a distinct Warburg diffusion tail at low frequencies. By converting the impedance data from frequency to time domain for DRT analysis (see Fig. 4d), six distinct peaks (P1–P6) were identified and divided into three characteristic regimes, namely, (i) high-frequency region ($\tau < 10^{-5}$ s; attributed to SE grain boundaries and particle contact), (ii) intermediate-frequency region (10^{-5} s $< \tau < 10^{-2}$ s; attributed to as-formed interphases [R_{int}], including cathode electrolyte interphase [CEI] and solid electrolyte interphase (SEI) at the anode), and (iii) medium-to-low frequency region (10^{-2} s $< \tau < 1$ s; attributed to charge-transfer processes [R_{ct}] [28,29]). It is important to note that the inductive and diffusive parts in the impedance data were discarded during pre-processing. Considering the overall cell configuration, the resistance contribution in the R_{int} regime is largely due to the cathode, while the R_{ct} regime encompasses contributions from both cathode and anode [6,28,29]. Given the electrochemical stability of LTO against sulfide SEs and the fact that the HB and LB cells were analyzed at a similar SOC, the differences observed in the R_{ct} regime can be attributed primarily to the cathode side.

The interface-related resistance was quantitatively evaluated by fitting the individual peaks in the DRT patterns. Without assigning them to specific physical processes, the peak areas within the defined characteristic regimes (i.e., R_{int} and R_{ct}) were examined instead for

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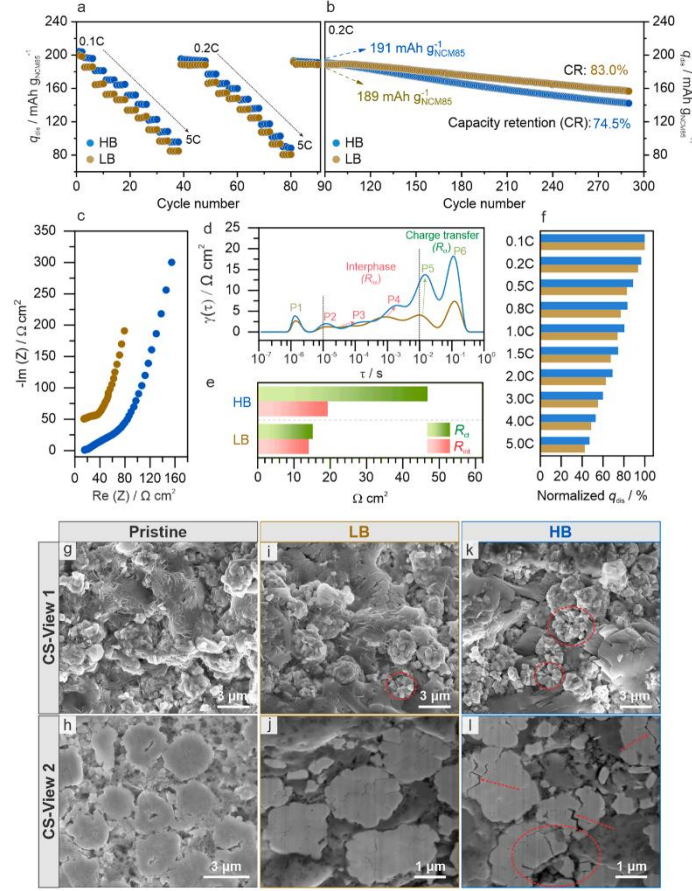


Fig. 4. Electrochemical performance of LTO|LPSCI|LiNbO₃-NCM85 HB and LB cells and post-mortem characterization. (a) Rate capability tested in two rounds from 0.1C/0.2C to 5C (1.35–2.75 V vs. Li₄Ti₅O₁₂/Li₇Ti₅O₁₂) and (b) subsequent long-term cycling at 0.2C. (c) Nyquist plots of the electrochemical impedance measured from 1 MHz to 100 mHz at the end of discharge after long-term cycling. The LB data is offset along the imaginary axis for clarity. (d) Corresponding DRT patterns with segmented kinetic time constants in the time domain for the as-formed interphases (R_{int} , with $\tau = 10^{-5}$ to 10^{-2} s) and charge-transfer processes (R_{ct} , with $\tau = 10^{-2}$ to 1 s) regimes. The inductive and diffusive parts at high and low frequencies were discarded. (e) Comparison of R_{int} and R_{ct} . (f) Normalized discharge capacities from rate-performance testing. (g–l) Cross-sectional SEM images collected from the cathode in the pristine state and after long-term cycling (discharged state). CS-View 1 and CS-View 2 refer to mechanically exposed and polished/FIB-cut areas. The dotted red circles/ellipses and arrows indicate the mechanical degradation.

determining cumulative resistance contributions, as presented in Fig. 4e and Tables S4 and S5. The results indicate that, due to the LiNbO₃ coating being present on the NCM85 particles, the R_{int} values are relatively low and comparable between the cells (19.3/14.1 $\Omega \text{ cm}^2$). However, there is a significant difference in the R_{ct} ; it is more than three times larger for the HB cells (46.8 versus 15.2 $\Omega \text{ cm}^2$). We attribute this difference to microstructural degradation, such as particle fracture and/or void formation, which strongly impedes charge transfer. From the data, it appears that the LB cells are capable of retaining better structural integrity, thus effectively mitigating the growth of charge-transfer resistance during battery operation. This means the preserved microstructure enables more stable electrochemical behavior and contributes to the superior cycling performance observed under LB conditions.

To corroborate the above results, cross-sectional SEM analysis was performed (see Fig. 4g–l). Specifically, two types of imaging techniques

were used, namely, (i) mechanical fracturing to expose the bulk cathode (CS-View 1) and (ii) focused-ion beam (FIB) cutting or Ar-ion polishing to reveal the internal structure of the CAM particles (CS-View 2). In their pristine state (see Fig. 4g and h), the LiNbO₃-NCM85 particles were structurally intact (i.e., showing no obvious cracking) and tightly embedded in the cathode matrix. Only a few voids in the interior were observed, which originate from the synthesis process [30]. After cycling, a clear difference between the HB and LB cathodes was noticeable. In the LB cells (see Fig. 4i and j), the structural integrity of the secondary particles remained largely intact. Although some fractured particles were observed, the grains (primary particles) remained well connected, and no signs of pulverization and/or interfacial delamination were found. Note that intimate CAM/SE contact facilitates lithium and electron transport, which is consistent with the lower R_{ct} discussed previously. In the HB cells (see Fig. 4k and l), on the other hand, severe

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mechanical degradation was apparent. As expected, larger volume changes and local stress concentrations lead to mechanical failure, which ultimately results in a strongly deteriorated microstructure. The low-magnification SEM images in Figure S9 confirm this observation.

To further evaluate the longevity and performance limitations of the sulfide-based SSBs, long-term cycling tests were performed at 1C, as shown in Fig. 5. For this purpose, both the HB and LB cells with similar areal loadings of $8\text{--}9\text{ mg}_{\text{NCM85}}\text{ cm}^{-2}$ were first subject to a short C-rate sequence at 0.1, 0.2, 0.5, 1, and 2C, followed by continuous cycling at 1C. The resulting specific discharge capacities for the HB (203, 195, 178, 160, and 134 $\text{mAh g}_{\text{NCM85}}^{-1}$) and LB cells (201, 189, 167, 148, and 124 $\text{mAh g}_{\text{NCM85}}^{-1}$) were consistent with the above results (see Fig. 4a and Table S3), confirming the reproducibility of the electrochemical behavior. During the subsequent cycling at 1C, the HB and LB cells initially delivered specific discharge capacities of $q_{\text{dis}} = 161$ and 149 $\text{mAh g}_{\text{NCM85}}^{-1}$, respectively. However, with prolonged cycling, a noticeable difference in stability became apparent. The HB cells maintained 80 % of their initial capacity after 414 cycles and delivered 111 $\text{mAh g}_{\text{NCM85}}^{-1}$ after 718 cycles, corresponding to a capacity retention of $\sim 69\%$. In contrast, the LB cells achieved around 80 % capacity retention over 1318 cycles, which corresponds to a 3.2-fold increase in cycle life, and still retained 111 $\text{mAh g}_{\text{NCM85}}^{-1}$ after 1575 cycles (equivalent to 75 % retention). This improvement is solely attributable to the LB strategy. Notably, both cells exhibited high Coulomb efficiencies throughout cycling, averaging 99.9 % for HB and 100 % for LB.

In summary, the LB condition leads to increased cathode stability, which is associated with improved capacity retention. The lower IUP mitigates (early-stage) lattice contraction and stress-induced cracking of the $\text{LiNbO}_3\text{-NCM85}$ secondary particles. Over the course of cycling, polarization—due to electro-chemo-mechanical effects—leads to an increase in UP, which in turn provides additional capacity to compensate for losses caused by adverse side reactions and degradation. The gradually increasing volume changes apparently create more spatial and temporal tolerance for the adaptation of the electrode components to each other, thereby increasing the effectiveness of the LB strategy in terms of enhancing electrochemical and mechanical robustness in SSB systems.

2.5. Mechanistic considerations

To verify the functionality of the tip-shaped lithiation tail of LTO under LB conditions and for various C-rates, a three-electrode (3E) analysis is essential. The strategy is based on exploiting the region near the end of lithiation to enable a lower IUP instead of the DUP. However, this subtle deviation from the voltage plateau cannot be captured in

conventional two-electrode (2E) cell setups. Instead, 3E measurements are required to deconvolute the contributions of individual electrodes to the voltage profile and determine whether the proposed mechanism actually occurs. We have therefore developed an advanced 3E setup for SSBs using prelithiated LTO as the RE, which provides a stable and well-defined reference potential of 1.55 V vs. Li^+/Li . Details on the cell design are provided in the Experimental section and in previous work [29].

As shown in Figure S10, a rate capability test from 0.2C to 5C was conducted on the 3E LB cells using a protocol similar to that of the 2E cells (see Fig. 4a). In fact, their electrochemical performance showed strong consistency with the 2E counterpart across all C-rates, as summarized in Table S6, confirming the accuracy and robustness of the measurement setup. The deconvoluted potential profiles of the $\text{LiNbO}_3\text{-NCM85}$ WE and LTO CE are presented in Fig. 6a. As highlighted by the green dotted circles, the LTO potential did indeed show a distinct tip-shaped behavior toward the end of charging, even after several cycles at different C-rates. This confirms that the lithiation tail persists and remains active in the compensation mechanism. In parallel, by examining the end-of-charge potential of the $\text{LiNbO}_3\text{-NCM85}$ WE (see red dotted circles), a gradual increase in UP throughout cycling was observed, from 4.1919 V vs. Li^+/Li in the initial cycle to 4.1931 V in the second cycle, and up to 4.2237 V after returning back to 0.2C in the 24th cycle. This trend strongly supports our hypothesis that polarization causes a gradual increase in UP, enabling capacity compensation during SSB operation. Of note, with respect to the corresponding lower cut-off potential of the LTO CE, the cell voltage calculated from the WE/CE remained essentially unaltered (relative to the pre-defined window of 1.35 to 2.75 V vs. $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_7\text{Ti}_5\text{O}_{12}$). A summary of the cut-off potentials of WE and CE, together with the resulting cell voltage at the end of charge and discharge during rate performance testing of the LB cells, is provided in Table S7. Individual potential profiles for selected C-rates are presented in Fig. 6b–c. As is evident, the tip-shaped lithiation tail of LTO was consistently observed across all C-rates, further validating the robustness of the proposed LB strategy and making the approach highly relevant for practical SSB applications.

In general, the performance of Ni-rich cathodes paired with sulfide SEs strongly depends on the mechanical stability given that detrimental side reactions are effectively suppressed by interface engineering. Therefore, the key to balancing between capacity and stability lies in regulating the mechanical behavior of the electrode active materials, particularly the CAM. The excellent long-term performance achieved here is based on an adaptive compensation process that is maintained throughout cycling. To provide a better understanding of this mechanism under different capacity balancing conditions, Fig. 7 shows schematic representations summarizing the principles underlying it.

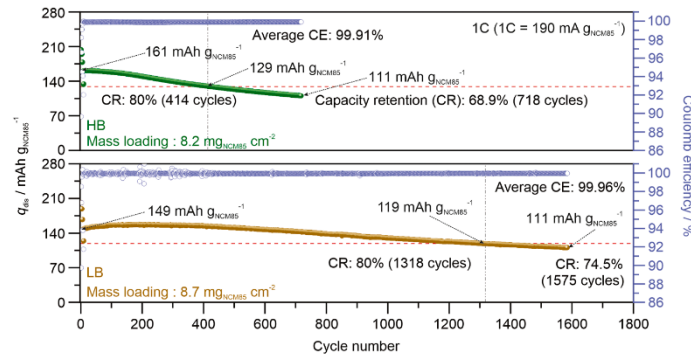


Fig. 5. Long-term cycling performance of $\text{LTO}|\text{LPSCl}|\text{LiNbO}_3\text{-NCM85}$ HB and LB cells at 1C (1.35–2.75 V vs. $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_7\text{Ti}_5\text{O}_{12}$). At the beginning, a C-rate test from 0.1C to 2C was performed.

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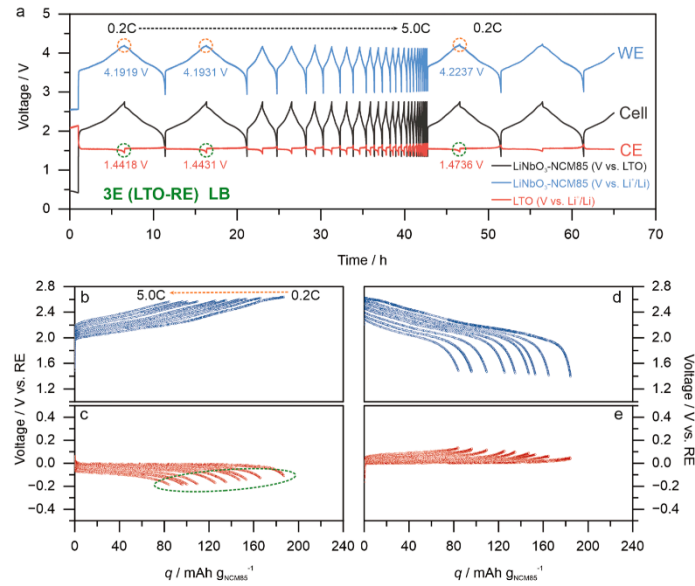


Fig. 6. Three-electrode analysis of an LB cell during rate capability testing from 0.2C to 5C. (a) Deconvoluted potential profiles of the $\text{LiNbO}_3\text{-NCM85}$ WE and LTO CE and cell voltage (WE/CE) shown in blue, red, and black, respectively. The potential of the WE and CE is referenced to Li^+/Li using an LTO reference electrode (LTO-RE, 1.55 V vs. Li^+/Li). The red and green dotted circles indicate the behavior upon approaching end of charge/discharge of the $\text{LiNbO}_3\text{-NCM85/LTO}$. Selected potential profiles (b) of the NCM85 WE (delithiation) and (c) LTO CE (lithiation) at various C-rates referenced to the LTO-RE. The green dotted ellipse indicates the deviation of the LTO potential from its plateau near the end of the charging process. Corresponding potential profiles (d) of the NCM85 WE (lithiation) and (e) LTO CE (delithiation).

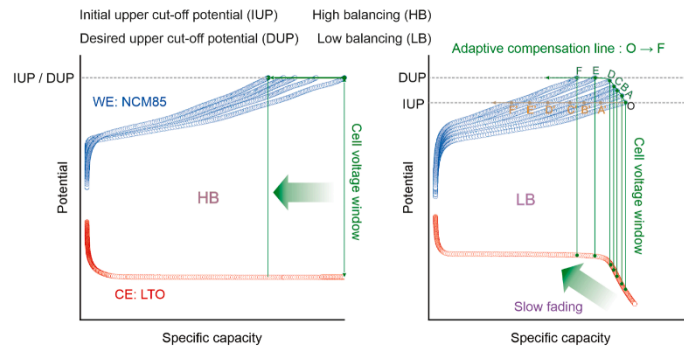


Fig. 7. Schematic representation of the proposed adaptive compensation through capacity balancing. For HB cells, the IUP of the WE corresponds to the DUP. For LB cells, there is a discrepancy between IUP and DUP, which is limited by the pre-defined voltage window. Upon cycling, due to capacity loss caused by polarization, the UP increases along the compensation line from O to F. With the IIB design, faster capacity degradation is observed along the line from O to F'.

Under HB conditions, the LTO CE was found to operate entirely within the 1.55 V plateau, enabling the NCM85 WE to reach the DUP of 4.3 V vs. Li^+/Li in each cycle [31]. However, electro-chemo-mechanical degradation inevitably occurs, causing increasing polarization, which ultimately leads to capacity fading and poor stability. In the HB case, the system clearly lacks flexibility, as the IUP and DUP are the same, meaning that it cannot respond to changes in polarization unless the voltage window is adjusted manually. Consequently, there is no intrinsic mechanism that can compensate for capacity decay.

Under LB conditions, the cathode initially terminates the delithiation

at a lower upper cut-off potential of ~ 4.2 V vs. Li^+/Li . This is due to the tip-shaped lithiation tail of LTO, with the CE deviating from the 1.55 V plateau as the cell approaches the charge cut-off. Overall, the LB configuration offers two distinct advantages: (i) it somewhat lowers the (initial) degree of cathode delithiation, thereby mitigating mechanical degradation by alleviating the H2-H3 phase transition and also reducing side reactions at the CAM|SE interface, and (ii) it creates a discrepancy between IUP and DUP, resulting in a kind of capacity reservoir/buffer that is gradually exploited to compensate for polarization-related capacity losses and thus extends longevity. The decoupling of IUP and DUP

distinguishes LB from HB, where such compensation is not possible. During cycling, the cathode's UP increases gradually and eventually approaches the DUP, as indicated by the compensation line (from O to F) in Fig. 7. The latter not only ensures dynamic capacity recovery, but also prevents severe volume changes. Apparently, this self-regulated voltage evolution gives the cathode sufficient time to adapt structurally and electrochemically, which in turn positively affects stability and cyclability. However, it does not completely prevent mechanical degradation, as the effect eventually reaches its limits when the LTO potential returns to the plateau region. Nevertheless, the LB strategy offers an effective means of delaying the onset of instability.

3. Conclusions

In this work, which aimed to develop high-performance SSBs with Ni-rich cathode and thiophosphate SE, we propose a capacity balancing strategy using LTO as anode for achieving an optimal compromise between capacity (energy density) and stability. Under low balancing conditions, the effective initial upper cut-off potential of the cathode was found to be lower than the targeted one, resulting in a partially suppressed H2-H3 phase transition, thereby reducing the net volume change of the active material during (de)lithiation and mitigating the mechanical stresses that normally lead to particle fracture and/or interfacial delamination. Over the course of electrochemical cycling, the polarization caused by electro-chemo-mechanical degradation gradually increased the cut-off potential, as also confirmed by 3E measurements, ultimately enabling adaptive compensation for capacity loss. This mechanism significantly extended the longevity without requiring active control of the voltage window. In fact, the low balancing cells had a cycle life (80 % capacity retention) at 1C rate more than three times longer than that of the high balancing cells.

Taken together, this study demonstrates that capacity balancing is a simple, yet powerful approach to improving the stability of Ni-rich cathodes in sulfide SSBs. LTO served not only as a model electrode, but can also be considered a conceptual bridge for the development/use of newly developed alloy-type (energy-dense) anodes that are compatible with adaptive compensation schemes.

4. Experimental section

All preparation steps, including those for the materials, composites, electrodes, and cell assembly, were performed in Ar environments, involving among others sealed ball-milling jars and gloveboxes with $p(\text{H}_2\text{O})/p < 0.1$ ppm and $p(\text{O}_2)/p < 0.1$ ppm.

4.1. LiNbO₃ coating

Prior to coating, polycrystalline NCM85 ($d_{50} \approx 4$ μm, BASF SE) was heated at 750 °C for 3 h under an O₂ atmosphere to remove surface impurities. The procedure for LiNbO₃ sol-gel-type coating followed our previous work [13]. To achieve a nominal coating content of 1 wt. %, 410 μL lithium (1.0 M) and 820 μL niobium ethoxide solutions (0.5 M) were added to 5.94 g of NCM85, along with 1 mL of absolute ethanol. The resulting mixture was ultrasonicated for 15 min and subsequently dried under vacuum. The obtained powder was then calcined at 350 °C for 2 h under an O₂ atmosphere, yielding LiNbO₃-NCM85.

4.2. Preparation of cathode and anode composites

Li₆PS₅Cl (LPSCl, NEI Corp.) and Super C65 (TIMCAL Ltd.) were used as SE and conductive carbon additive, respectively. The weight ratios of the components were 69.3:29.7:1.0 for LiNbO₃-NCM85:LPSCl:Super C65 (cathode composite) and 30:65:5 for LTO:LPSCl:Super C65 (anode composite). For 1 g of composite, 10 ZrO₂ balls (10 mm in diameter) were added, and the mixture was ball-milled at 140 rpm for 30 min using an 80 mL jar.

4.3. Preparation of slurry-cast cathodes

The as-prepared composite was used to fabricate slurry-cast cathode tapes. Anhydrous *o*-xylene (97 %, Sigma-Aldrich) and polyisobutylene (Oppanol N150, BASF SE) served as solvent and polymer binder, respectively. The cathode composite was first pre-wetted and subsequently mixed with 1 wt. % binder. The weight ratio of the components was 68.6:29.4:1.0:1.0 for LiNbO₃-NCM85:LPSCl:Super C65:Oppanol N150. After thorough mixing, the slurry was cast onto Al foil, followed by drying. Circular electrodes with a diameter of 9 mm were punched out for electrochemical measurements. Further details of the procedure can be found elsewhere [19,22].

4.4. Capacity balancing

In this work, the balancing between the LiNbO₃-NCM85 cathode and the LTO anode was realized by adjusting the mass of the LTO composite. Specifically, the capacities achieved in the fourth cycle at 0.2C rate (after cell formation) were used as initial values in the calculations, namely, a specific charge (delithiation) capacity of 202 mAh g⁻¹ for LiNbO₃-NCM85 and a specific discharge (lithiation) capacity of 132 mAh g⁻¹ for LTO, as shown in Figure S4. The balancing factor *B* was defined, and the mass of LiNbO₃-NCM85 (m_{CAM} , in grams) was used to determine the corresponding LTO mass (m_{LTO}) via the following equation:

$$m_{\text{LTO}} = B \cdot m_{\text{CAM}} \cdot \frac{202 \text{ mAh g}^{-1}}{132 \text{ mAh g}^{-1}} \quad (1)$$

The required mass of LTO composite was then calculated based on the ratio of components mentioned above.

4.5. SSB assembly

In-house designed setups for two-electrode (2E) and three-electrode (3E) cells were used for SSB testing. Each cell consisted of a PEEK ring (10 mm in diameter; for 3E, two symmetrical holes were drilled) and two stainless steel current collectors. For 2E cells, 100 mg of SE was first pre-pressed at 63 MPa to form the separator layer. The punched cathode tape, with CAM loadings of 8–9 mg cm⁻², was placed on one side of the separator layer, while a certain amount of LTO composite (based on the balancing strategy) was added to the opposite side. The cells were then pressed at 435 MPa for 3 min. For cells with an In/InLi counter electrode (CE), the working electrode (WE), either the cathode tape or the LTO composite, was placed onto the separator layer, followed by pressing at 435 MPa for 3 min. Indium (9 mm in diameter, 100 μm thick, Changsha Santech Materials Co., Ltd.) and lithium foil discs (6 mm in diameter, 50 μm thick, Albemarle Germany GmbH) were stacked in sequence on the opposite side. For 3E cells, the preparation of the reference electrode (RE) and the assembly procedure followed previous work [29]. The LTO composite was used as LTO-RE, with a stainless steel wire (0.127 mm in diameter, Thermo Fisher Scientific) serving as current collector. The LTO-RE was embedded in the center of a thickened separator layer (160 mg). The subsequent assembly of WE and CE followed the same procedure as that for the 2E cells.

4.6. Galvanostatic cycling

The SSB cells were cycled using a MACCOR battery cycler. When LiNbO₃-NCM85 served as cathode (WE), the potential was set between 2.9 and 4.3 V vs. Li⁺/Li. Depending on the choice of CE, the cell voltage was adjusted accordingly: with LTO (1.55 V vs. Li⁺/Li), the window was set to 1.35–2.75 V vs. Li₄Ti₅O₁₂/Li₇Ti₅O₁₂, and with In/InLi (0.62 V vs. Li⁺/Li), it was set to 2.28–3.68 V vs. In/InLi. When LTO was used as WE, the potential range was approx. 1.0–2.0 V vs. Li⁺/Li, corresponding to 0.38–1.38 V vs. In/InLi. The current was defined based on the specific C-

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rate, with $1C = 190 \text{ mA g}_{\text{NCM85}}^{-1}$ for $\text{LiNbO}_3\text{-NCM85}$ and $1C = 175 \text{ mA g}_{\text{LTO}}^{-1}$ for LTO. 3E cells were sealed in a pouch bag and cycled at 45°C and under an external pressure of 81 MPa based on the voltage between WE and CE.

4.7. Powder X-ray diffraction (XRD)

CAM (pristine NCM85 or $\text{LiNbO}_3\text{-NCM85}$) was loaded into 0.3 mm borosilicate capillaries (Hilgenberg), while 0.5 mm capillaries were used for the cathode composite. Diffraction data was collected in Debye–Scherrer geometry using a STOE Stadi-P diffractometer equipped with a Mo anode ($\lambda = 0.7093 \text{ \AA}$) and a DECTRIS MYTHEN 1 K strip detector. LaB_6 standard reference material was used to evaluate the instrumental peak broadening. GSAS-II software was used for Rietveld refinement [32]. For determining the crystallographic parameters of NCM85, the scale factor, zero shift, and size/strain broadening parameters were refined. A fixed background function using a 13-term Chebyshev polynomial was applied. The lattice parameters, oxygen z-coordinate, and atomic displacement parameters for each site were refined. Atoms occupying the same site were constrained to have the same atomic parameters, and site occupancy factors were constrained such that each site remained fully occupied.

4.8. Scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDS)

Morphological and elemental analyses were performed using a Leo 1530 microscope (Zeiss) equipped with a field-emission gun. For elemental mapping via EDS, an Oxford X-Max^N detector (Oxford Instruments) was used.

4.9. Cross-sectional imaging

The pristine cathode tape was polished by Ar-ion milling using an IB19510CP cross-section polisher (JEOL). Cycled samples were sectioned using a dual-beam focused ion beam (FIB) system (FEI Strata 400) with Ga^+ ion source operated at 30 kV. To minimize potential impact from air exposure during characterization, the samples were mounted onto a stage within an Ar-filled glovebox and immediately transferred to the FIB chamber using a sealed packaging bag. Throughout this process, the samples were exposed to air for less than 20 s.

4.10. Electrochemical impedance spectroscopy coupled with distribution of relaxation times analysis (EIS-DRT)

Potentiostatic EIS (PEIS) measurements were performed using a Bio-Logic SP-300 multichannel potentiostat. The cells were rested for 1 h at the end of either charge or discharge prior to the impedance measurements. Spectra were recorded over a frequency range from 1 MHz to 100 mHz, with a perturbation amplitude of 10 mV. DRT analysis was performed by processing the complex impedance data after subtracting the inductive (high-frequency) and capacitive (low-frequency) contributions. A Gaussian radial basis function (RBF)-based discretization method was applied, using a shape factor of 0.5 and a regularization parameter of $\lambda = 10^{-4}$ for all spectra. Multiple Gaussian functions were used to fit the peaks in the DRT patterns, enabling quantitative analysis of interfacial kinetics within the relaxation time constant between 10^{-5} and 1 s [29].

4.11. Operando pressure measurements

A force sensor (KM26 10 kN, ME-Meßsysteme GmbH) was mounted on top of a sealed cell and clamped in a rigid frame, applying an initial load of 6.35 kN (equivalent to 81 MPa). The dynamic force, due to volume changes of the $\text{LiNbO}_3\text{-NCM85}$ cathode during cycling, was

recorded continuously. An initial 12 h resting period at 45°C allowed for mechanical relaxation, and the stabilized force value served as baseline for the subsequent galvanostatic measurements. The cells were cycled for five cycles at 0.1C rate within the voltage window defined for the $\text{LiNbO}_3\text{-NCM85}$ cathode and LTO anode using a Bio-Logic VMP-3 multichannel potentiostat.

CRediT authorship contribution statement

Ruizhuo Zhang: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Seyedhosein Payandeh:** Writing – review & editing, Validation, Conceptualization. **Yuan Ma:** Writing – review & editing. **Damian Goonetilleke:** Writing – review & editing, Validation, Formal analysis. **Yushu Tang:** Writing – review & editing, Validation, Investigation, Formal analysis. **Aleksandr Kondrakov:** Writing – review & editing, Supervision, Project administration, Funding acquisition. **Jürgen Janek:** Writing – review & editing, Supervision. **Torsten Brezesinski:** Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.ensm.2026.105045](https://doi.org/10.1016/j.ensm.2026.105045).

Data availability

Data will be made available on request.

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4. Conclusions and Perspectives

With the aim of advancing the design of SSBs and facilitating their further commercialization, layered Ni-rich oxides combined with SSEs are regarded as one of the most promising cathode configurations, offering both high performance and compatibility with existing battery manufacturing processes. The optimization of SSBs is inherently a system-level endeavor. From the cathode perspective, it is crucial to investigate and identify (potential) failure mechanisms and to objectively assess their impact while simultaneously developing effective strategies and methodologies to mitigate structural degradation induced by electro-chemo-mechanical effects.

PC NCM85 coupled with argyrodite LPSCI, as a representative combination for the cathode discussed above, was fabricated via a slurry-casting approach and investigated throughout this doctoral thesis. Overall, three interrelated research directions were pursued: (1) investigation and mitigation of kinetically driven interfacial degradation, with a particular emphasis on identifying new failure mechanisms and their underlying pathways; (2) identification and in-depth analysis of polarization originating from the anode/CE, its interference with the interfacial kinetic analysis of cathode/WE, and its impact on performance decay; and (3) development of an effective strategy to enhance mechanical stability in the cathode, in which mutual constraints between the potential of anode and cathode were exploited, thus a favorable balance between attainable capacity and capacity retention was achieved.

Accordingly, for the first research direction, in **Publication I**, cryo-FIB and cryo-TEM were used to investigate these phenomena. Through EDS and EELS analyses, the presence of TM- and oxygen-involved species at the interface and at varying distances from the interface was confirmed, corroborating the formation of interphases, reported by studies using XPS and ToF-SIMS, as oxygenated phosphorus and sulfur species. EELS further revealed (partial) reduction of TMs at the interface and pronounced reduction in the SSE, far away from the interface. These results demonstrate that TMs can dissolve under solid-state conditions and subsequently form interphases through interdiffusion with S and P species at the interface. Moreover, TMs were found to undergo long-range diffusion into the SSE, where they exist in strongly reduced states and may form TM sulfides and/or oxides, thereby exerting a poisoning effect on the ion conductor. The cryogenic conditions significantly suppressed the volatilization and redeposition of LPSCI, enabling the reliable detection of sulfur enrichment at cracks within the secondary particles of the CAM and providing direct evidence for the high mobility of sulfur species in SSE environments.

Contemporaneous and subsequent studies have increasingly recognized and investigated these phenomena.^[63, 66-67] Beyond SSEs, TM diffusion into oxide electrolytes, such as LLZO (lithium lanthanum zirconium oxide: $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$) has also been reported.^[182] Nevertheless, further studies combining advanced characterization techniques and computational approaches are required to elucidate the driving force behind these processes and their long-term consequences. To suppress TM dissolution

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and its participation in interphase formation, protective coating has been widely considered an effective strategy. However, conventional coating materials and approaches have not been able to completely inhibit TM dissolution, rendering the exploration of advanced strategies and materials an ongoing focus in cathode interfacial research for SSBs.^[63] In **Publications II** and **III**, as supplementary studies, an advanced coating strategy was employed, in which HfO_2 and $\text{HfO}_2/\text{Li}_2\text{HfO}_3$ NPs were uniformly deposited onto the CAM surface. Compared with conventional coating methods (such as sol–gel chemistry) and commonly used materials (e.g., LiNbO_3), key advantages of this strategy lie in the conformality of the coating enabled by the use of well-dispersed NPs, and significantly suppressed gas evolution of O_2 and SO_2 . The resulting oxide NP coating, with thicknesses on the order of ~ 10 nm, led to a pronounced enhancement in electrochemical performance. Specifically, a specific discharge capacity of 203 mAh/g at 0.1C and a capacity retention of 94% after 200 cycles at a high areal loading of 16.4 mg/cm² were achieved.

A direct correlation between electrochemical performance decay and the evolution of the as-formed interface/interphase can be established through rigorous interfacial kinetic analysis. Considering the potential interference arising from the anode/CE, the implementation of a 3E cell configuration is essential for reliable evaluation in SSBs. More critically, the evolution of CE overpotential and interfacial resistance can significantly affect cell performance and may lead to an overestimation of the WE contribution when assessed in conventional 2E setups.

Therefore, in **Publication IV**, a 3E setup for SSBs was developed using LTO composite as the LTO-RE. The optimized LTO-RE design ensured excellent stability, exhibiting a potential drift of only ~ 8 mV over 600 h. In the 3E cell configuration with LTO as the WE and In/InLi as the CE, the electrochemical performance observed in the 2E cell configuration was reproduced, while the potential profiles of individual electrodes were continuously monitored during operation. Notably, 3E EIS-DRT analysis unambiguously revealed overlapping interfacial kinetic processes between the LTO WE and the In/InLi CE across multiple time-constant regimes. In fact, typical anode and cathode materials often exhibit partially overlapping time constants, particularly within the charge-transfer regime. Furthermore, quantitative analysis demonstrated that the R_{ct} of the In/InLi CE was significantly larger than that of the LTO WE.

As a follow-up study, **Publication V** focused on the evolution of CE overpotential and SOC-dependent interfacial kinetic response, particularly under various testing scenarios. One important finding emerged from long-term cycling under delithiation-first operating condition with In/InLi as the CE. Specifically, In/InLi exhibited a progressively pronounced “tail” as the overpotential near the end of delithiation upon cycling. This behavior indicates that during repeated (de)lithiation, lithium transport near the interfacial region becomes increasingly hindered, especially as delithiation approaches completion and the interfacial region becomes severely lithium-deficient, despite the excess lithium inventory provided for the In/InLi CE in the cell design.

Furthermore, qualitative/quantitative analysis of the R_{ct} revealed pronounced SOC-dependent characteristics and a significant increase in R_{ct} for the aged In/InLi CE at the end of its delithiation state. However, the observed cycling stability of the cell was not

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fully consistent with such an increase in overpotential and R_{ct} . This discrepancy suggests that the behavior of In/InLi near the end of delithiation represents a specific condition characterized by severely hindered charge-transfer kinetics at the In/InLi|SSE interface and is strongly convoluted with the sluggish diffusion process. Therefore, this regime does not constitute a robust indicator for quantitatively evaluating capacity fading.

Another critical CE-related scenario was examined through C-rate and long-term cycling tests using NCM85 as the WE. Cells employing In/InLi as the CE exhibited significant cell-to-cell variability at high current densities, and the overpotential at the CE showed clear asymmetry between lithiation and delithiation. In contrast, cells using LTO as the CE demonstrated good consistency at high C-rates and a symmetric overpotential response. These observations indicate that different CEs possess markedly distinct kinetic characteristics. For In/InLi, even under lithiation-first operating condition, the interfacial kinetics remains highly sensitive to current density during delithiation. Such behavior appears to be related to the fabrication method and quality of the In/InLi electrode, rather than being solely associated with the delithiation-first protocol.

Consequently, based on long-term cycling tests, approximately 75% of the total interfacial resistance ($R_{int} + R_{ct}$) can be attributed to the NCM85 WE. However, the contribution from the WE increased only marginally during cycling (by ~10%), whereas the contribution from the In/InLi CE increased strongly (by ~180%). This finding demonstrates that the In/InLi CE can substantially influence the overall performance and may lead to an overestimation of WE aging when the cyclability is evaluated solely in a 2E cell configuration.

It is evident that, in the research of SSBs, the CE can exert a non-negligible influence on both the electrochemical performance of the WE and the associated interfacial kinetic analysis. In addition, reproducibility represents another critical consideration in testing. In fact, performance variations in solid-state systems can arise from multiple factors. For instance, Kissel *et al.* reported that microstructural differences induced by variations in cathode composite mixing can significantly affect electrochemical performance.^[183] Furthermore, a recent large-scale interlaboratory benchmarking study revealed substantial discrepancies in performance even when identical materials are tested across different laboratories.^[176] The kinetic and performance variations associated with the use of In/InLi as the CE have been discussed in detail in sections 2.2 and 2.3.

Therefore, in advancing SSBs, the evaluation of performance and degradation should not be confined solely to the WE, but should adopt a more systematic and objective approach that accounts for the contributions of all cell components.

For the third research direction, presented in **Publication VI**, the primary objective was to enhance the mechanical stability of the cathode. Numerous experimental observations indicate that mechanically induced degradation becomes the dominant contributor to performance decay during the later stages of cycling in SSBs. While CAM coating can effectively suppress (electro)chemical degradation, practical and robust solutions addressing mechanical failure of the cathode remain limited, particularly for PC Ni-rich cathodes.

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At present, strategies considered effective for improving the microstructural integrity of PC cathodes include the incorporation of polymers, either as polymer coatings or as binders. The latter is also essential for the fabrication of sheet-type cathodes and for enabling scalable manufacturing. In the cathode, mechanical degradation primarily manifests as phase transition-induced intergranular cracking of the CAM, as well as contact loss (interfacial delamination) between CAM and SSE caused by the breathing behavior of the active material. Critically, the UP of the cathode is a decisive parameter determining mechanical degradation, and it also represents a key factor in balancing the trade-off between attainable capacity and capacity retention.

Accordingly, the core concept described in **Publication VI** is to transform the UP of the cathode from a fixed, initially predefined value into a flexible and self-adaptive parameter. This was realized through regulation of the n/p ratio via the anode/CE presented in this work. To validate the effectiveness of this strategy in enhancing the mechanical stability of the cathode and its associated performance, a LiNbO_3 coating was applied to the CAM to suppress interfacial electrochemical degradation. The anode/CE employed to verify this concept was required to fulfill three criteria: (1) a lithiation process characterized by a pronounced potential variation and sufficiently extractable capacity near the end of lithiation; (2) excellent electro-chemo-mechanical stability against the SSE; and (3) robust cycling stability. LTO, as a model anode active material at the laboratory scale, satisfies these requirements and was therefore selected to validate the proposed strategy.

By leveraging the lithiation tail of LTO beyond the two-phase equilibrium region, an LB cell architecture was constructed in combination with the cathode. This design introduces two major advantages. First, at the end of charging, the cathode operates under a condition where the IUP remains lower than the DUP. This effectively mitigates phase transition-induced mechanical stress within the CAM by lowering the effective UP, albeit at the expense of some capacity. Second, as cycling proceeds, the polarization accumulated at the cathode side gradually drives the UP toward the DUP, thereby compensating for capacity loss and enabling improved long-term stability. Moreover, the gradual increase of the UP provides a sufficient temporal and spatial buffering for internal structural relaxation of the cathode, thereby enhancing microstructural stability. *In situ* pressure measurements, EIS-DRT analysis, and cross-sectional imaging collectively demonstrated the mechanical stabilization effect of the LB cell. Ultimately, this strategy led to significant performance improvements, including an initial specific discharge capacity of 199 mAh/g at 0.1C and excellent long-term stability at 1C, achieving 80% capacity retention after about 1300 cycles.

Collectively, the results presented in this doctoral research encompass both the elucidation of degradation mechanisms and the development of reliable characterization methodologies. By systematically optimizing components from the cathode to the anode, the electrochemical performance of slurry-cast SSBs was significantly enhanced by effectively mitigating electro-chemo-mechanical degradation at the cell level.

To further advance the commercialization of SSBs, significant challenges remain along the technological pathway combining Ni-rich cathodes with SSEs. These challenges involve not only the development of novel materials and advanced characterization techniques for probing electrode interiors, but also engineering-level optimization and

innovation to address the practical constraints encountered under realistic operating conditions.

In particular, reducing the reliance on high external pressure during operation remains a critical objective. In this regard, functional binder design and optimization of binder-assisted, sheet-type electrode fabrication processes are essential. Meanwhile, another critical aspect is a better understanding of the mechanical coupling between cathode and anode. Furthermore, in the microstructural design of cathodes, key parameters such as porosity require more comprehensive evaluation within the context of the overall electrode architecture, rather than being correlated solely with individual factors, such as ionic and/or electronic partial conductivity. In addition, efforts to develop conventional *ex situ* techniques, such as XPS and ToF-SIMS, into *in situ/operando* characterization tools offer promising opportunities to further elucidate interface-related degradation pathways and mechanisms, as well as SOC- and local microstructural-dependent variations within the electrode. Notably, recent studies have emphasized the necessity of investigating sensitive interfacial regions under cryogenic conditions and have introduced cryogenic XPS for the compositional and oxidation-state analysis of interfacial species in liquid-electrolyte systems.^[184-185] Extending this cryogenic approach to solid-state systems represents a highly promising direction for achieving more reliable and artifact-free interfacial characterization.

Finally, in the pursuit of high-performance SSBs, high-energy-density anodes remain a central research focus. However, under practical constraints, such as long-term cycling stability, manufacturability, and interfacial robustness, lithium metal is not the only viable pathway toward (next-generation) energy dense anodes. In recent years, alloy-type anodes have emerged as a rapidly developing class of electrode materials, attracting increasing attention beyond conventional silicon-based systems. Many newly developed alloy anodes exhibit pronounced, composition-dependent potential variations within specific lithiation ranges, a characteristic that makes them inherently suitable for the adaptive potential-regulation strategy at the cathode proposed in **Publication VI**. Representative systems include, but are not limited to, Li–In–Bi–Sn, Li–Al, and Li–Ga alloys, all of which have demonstrated promising performance in recent SSB studies.^[186-188]

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6. Appendix

6.1. Supporting Information

6.1.1. Supporting Information of Publication I

Electronic Supplementary Material (ESI) for ChemComm.
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Electronic Supplementary Information

Transition-Metal Interdiffusion and Solid Electrolyte Poisoning in All-Solid-State Batteries Revealed by Cryo-TEM

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Materials and Cell Preparation

The pristine cathode active material, $\text{LiNi}_{0.85}\text{Co}_{0.1}\text{Mn}_{0.05}\text{O}_2$ (BASF SE), was first annealed at 750 °C for 3 h under O_2 flow to remove the residual Li (carbonate species) present on the surface (with 5 °C/min heating and cooling rates). Both $\text{Li}_6\text{PS}_5\text{Cl}$ solid electrolyte (NEI Corp.) showing a room-temperature ionic conductivity of around 2 mS/cm and Oppanol binder (polyisobutylene, BASF SE) were used as received. The carbon additive, Super C65 (TIMCAL Ltd.), and carbon-coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (NEI Corp.) were dried at 300 °C in a dynamic vacuum overnight prior to use. The preparation procedure of the slurry-cast cathode and cell assembly are described in detail elsewhere.^{1,2}

Electrochemical Testing

After a 1 h OCV rest period, electrochemical testing was done at different rates of 0.1C, 0.2C, 0.5C, 1.0C and 2.0C for two cycles each (with 1C = 190 mA/g). The subsequent 150 cycles were performed at a 1.0C rate. The voltage range was set to 1.35-2.75 V vs $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_7\text{Ti}_5\text{O}_{12}$ (i.e., around 2.9-4.3V vs Li^+/Li). Galvanostatic cycling was done with the help of a MACCOR battery cycler at 45 °C and 81 MPa external pressure. Two identical cells were cycled to ensure data consistency and reliability.

Cryo-STEM and EELS Measurements

In the current study, the Thermo Scientific IGST workflow solution was used to enable a DualBeam to TEM workflow by protecting both bulk sample and prepared lamella in Ar atmosphere with a CleanConnect™ transfer module. Using the CleanConnect™ module, cathode foils from the SSB cells were successfully transferred from the glovebox to a Helios 5 Hydra DualBeam without signs of surface oxidation. Due to the beam and temperature sensitivity of the solid electrolyte and the cathode electrolyte interphase in the cycled electrodes, the entire TEM lamella preparation process, including bulk milling, lift out, attach to the TEM grid and final thinning, was carried out at cryogenic temperature (−178 °C) with a Thermo Scientific cryo-stage and cryo-EasyLift nano-manipulator. To achieve minimal ion damage to the final lamella, all ion-milling processes were carried out with Ar plasma-focused ion beam from a Helios 5 Hydra multi-ion species plasma FIB. To minimize surface amorphization on the prepared lamella, the final thinned region was polished with 5 kV and then subsequently 2 kV Ar beam. The prepared lamella was then transferred back to the glovebox under Ar-gas protection using the CleanConnect™ transfer module. Inside the glovebox, the lamella was loaded to a MelBuild double tilt LN2 Atmos Defend Holder, which allows lamella transfer from the glovebox to a TEM under Ar-gas protection.

An illustration of the workflow process is shown in Fig. S2. After loading the bulk sample (cathode) into the microscope with the inert gas-transfer module, a 2 µm thick Pt layer was deposited by FIB to protect the top surface of the sample, as well as to reduce curtaining artefacts during subsequent milling. After the protective layer deposition, the bulk sample was cooled down to cryogenic temperature (−178 °C) to avoid beam damage or heat-induced artefact formation upon milling. Once the bulk sample reached the target temperature, two large

trenches were milled with Ar-plasma FIB to form a relatively thick ($40\ \mu\text{m} \times 20\ \mu\text{m} \times 10\ \mu\text{m}$) chunk ready for *in situ* lift out (Fig. S2a). To avoid sample warm-up during the lift-out process, a cryogenic lift-out needle is used. The lift-out needle was cooled to $-178\ ^\circ\text{C}$, together with the stage, to decrease the temperature difference between needle and chunk. Also, the cryogenic needle can keep the temperature of the chunk after lifting it out from the bulk sample (Fig. S2b). Next, the chunk was transferred to a Cu TEM grid. The Cu grid is located on the bulk cryogenic stage and therefore holds a temperature of $-178\ ^\circ\text{C}$ (Fig. S2c). After welding the chunk to the Cu TEM grid with the redeposition method, the cryogenic lift-out needle is cut free from the chunk (Fig. S2d). The chunk is then thinned systematically by gradually reducing the FIB current, from its original thickness ($\sim 10\ \mu\text{m}$) all the way to electron transparency ($100\text{--}200\ \text{nm}$). To keep sample integrity during thinning, the final region of interest was achieved by opening smaller windows on the bulk lamella (Fig. S2e). In summary, the whole TEM sample preparation, including bulk milling, chunk lift out, chunk transfer and chunk thinning, was done at cryogenic temperature to avoid beam damage or heat-induced artefacts.

S/TEM images, EDS and EELS data were acquired with a Thermo Scientific Talos F200X CFEG S/TEM at 200 kV. The temperature was actively controlled at $-155\ ^\circ\text{C}$ using the MelBuild Atmos Defend Holder with the LN2 as a cooling agent to protect the samples from beam damage during data acquisition. TEM images were captured in Velox software using a Ceta-16 M CMOS camera. STEM images with different image contrasts were acquired in Velox software simultaneously using HAADF, DF and BF detectors. Drift-corrected frame integration (DCF1) was utilized to counter any sample drift and to improve the signal-to-noise ratio by integrating multiple frames in both TEM and STEM modes. EDS maps and spectra were collected in STEM mode with a probe current of 100 pA using a Bruker Dual-X EDS system. EELS data were collected using a Gatan GIF Continuum 1066 system with a 5 mm entrance aperture and an energy dispersion of 0.3 eV/Ch. The energy resolution was around 0.8 eV.

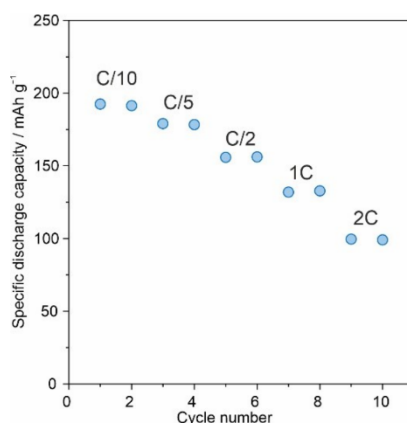


Fig. S1 Rate capability of the slurry-cast cathode in pellet-stack SSB cells at $45\ ^\circ\text{C}$.

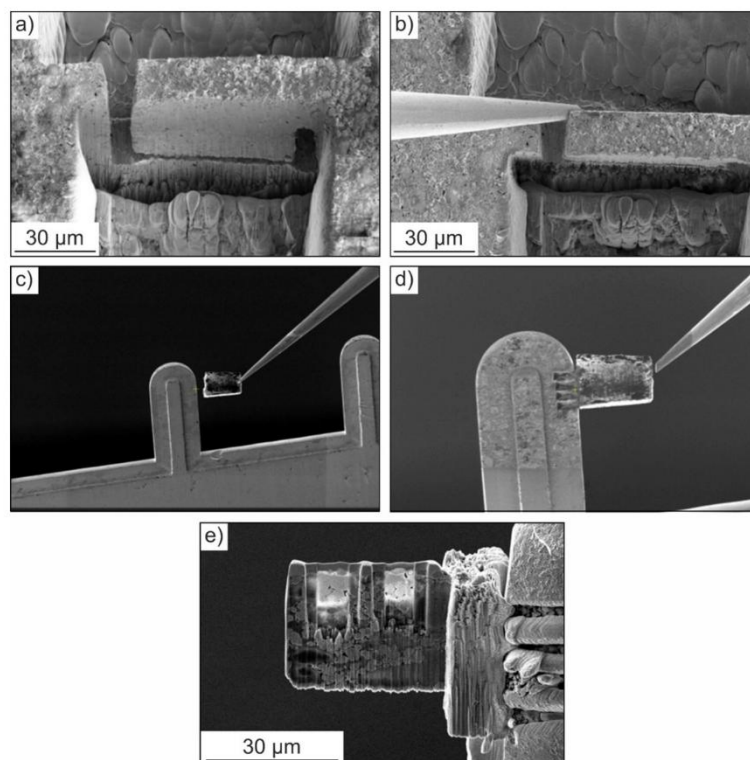


Fig. S2 Specimen preparation for TEM/EELS investigations. (a) Chunk creation and (b) lift out at cryogenic temperature using a cryogenic lift-out needle. (c) Chunk transfer to TEM grid under cryogenic temperature and (d) attachment by redeposition welding. (e) The lamella is thinned at two regions of interest (bright areas) to ensure electron transparency.

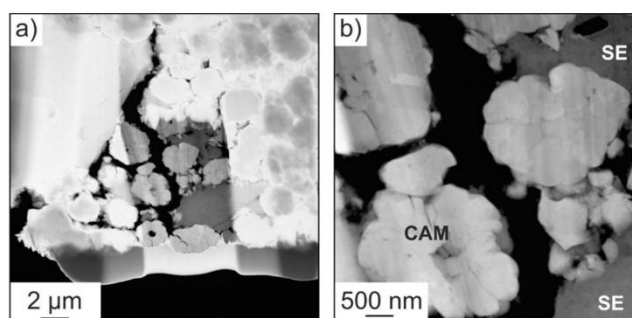


Fig. S3 (a, b) Cross-sectional cryo-STEM (HAADF) images at different magnifications of the cycled cathode. CAM and SE regions are indicated in (b).

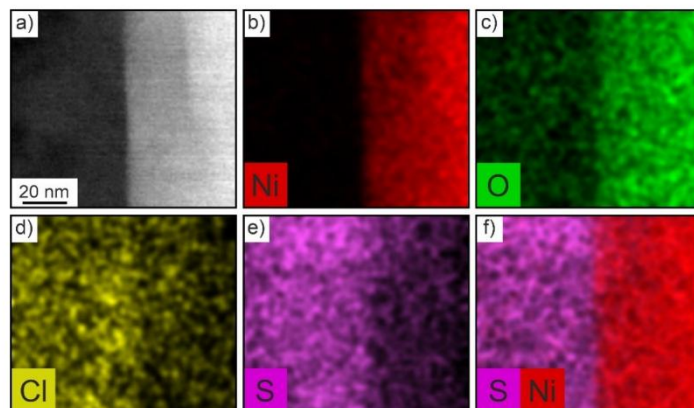


Fig. S4 (a) Cryo-STEM (HAADF) image of the pristine CAM/SE interface and (b-e) corresponding EDS maps for Ni, O, Cl and S. (f) S and Ni overlap map indicating a well-defined and “clean” interface.

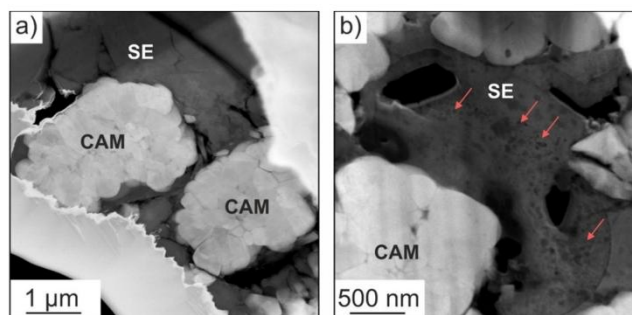


Fig. S5 Cross-sectional cryo-STEM (HAADF) images of (a) pristine and (b) cycled cathode. The formation of darker contrast spots in the SE region is indicated by arrows in (b).

EELS Ionization Edge Treatment and L_3/L_2 Ratio Analysis

Edge Treatment

Background subtraction was done with Digital-Micrograph GMS 3 software using the power-law fit method. A linear least square fit was applied to the log-log transform over an energy region preceding the ionization threshold of the experimental spectrum. The power-law profile was fitted in the pre-edge region and extrapolated to the post-edge region. The core-loss intensities were extracted by subtraction of the background intensity from the acquired signal. Low-pass numerical filtering was used to smooth the spectra.

L_3/L_2 Analysis

The white line ratio of the transition metals was calculated based on the integrated area of L_3 and L_2 . The continuum background was fitted by a straight line within the threshold regions. A

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step function with height ratio of 2:1 for L_3 and L_2 was applied to account for the multiplicity of the 2p states. The area ratio between L_3 and L_2 , which was integrated between white line and fitted background, was used to analyze the valence state.

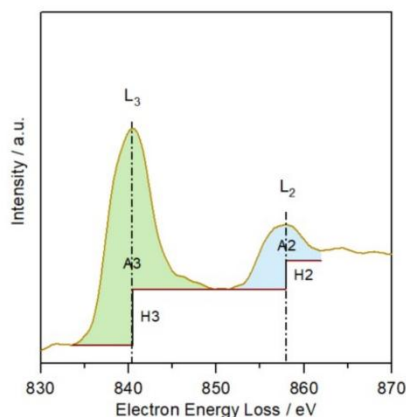


Fig. S6 Example for the calculation of the integrated area ratio between L_3 and L_2 in the high-loss region of transition metals. A linear step function with height $H_3:H_2 = 2:1$ is fitted to the continuum background within the threshold region. The L_3/L_2 ratio analysis is based on the integrated area ratio of $A_3(L_3)$ to $A_2(L_2)$.

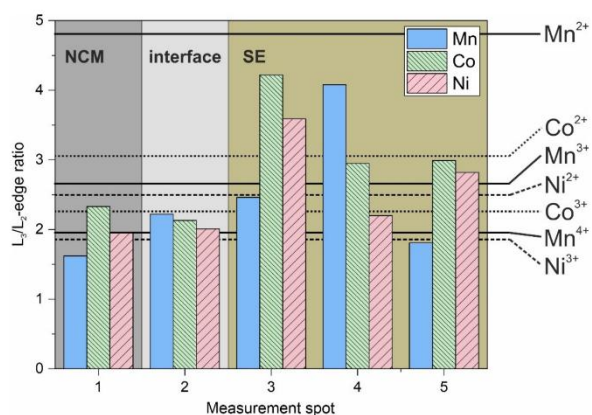


Fig. S7 L_3/L_2 -edge ratios for Ni, Co and Mn from EELS analysis of different areas (P1 to P5, see Figs. 3 and 4 in the main text). Specific values are provided in Tab. S1 and different L_3/L_2 -ratios associated with different oxidation states (from literature) are denoted by solid and dashed lines.³⁻⁸

Tab. S1 Summary of EELS results for O, Ni, Co and Mn. ΔE represents the difference in energy loss between O K-edge and pre-edge. Note that for P3 and P4, no O K pre-edge feature was observed.

Spot	ΔE / eV	Ni L ₃ /L ₂	Co L ₃ /L ₂	Mn L ₃ /L ₂
P1	12.0	1.95	2.33	1.62
P2	10.8	2.01	2.13	2.22
P3	-	3.59	4.22	2.46
P4	-	2.20	2.95	4.08
P5	8.7	2.82	2.99	1.81

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6.1.2. Supporting Information of Publication II

Supporting Information

A Single- to Few-Layer Nanoparticle Cathode Coating for Thiophosphate-Based All-Solid-State Batteries

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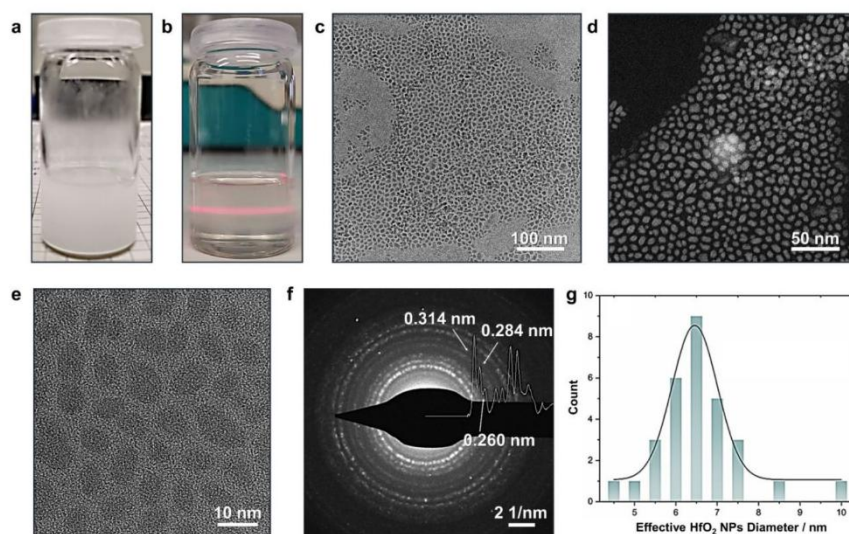


Figure S1. Photographs showing the HfO_2 nanoparticles dispersed in chloroform (a) prior to and (b) after surface functionalization. (c) Bright-field TEM, (d) HAADF STEM, and (e) HRTEM images of the re-dispersed HfO_2 nanoparticles. (f) SAED pattern showing diffraction rings (labeled) corresponding to the (-111) , $(1-11)$, and (002) planes of monoclinic HfO_2 . (g) Particle-size distribution.

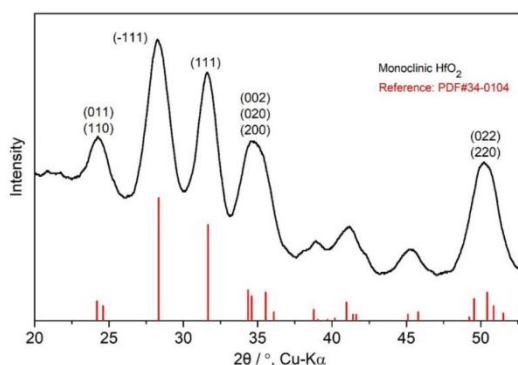


Figure S2. Powder XRD pattern collected from the as-prepared HfO_2 nanoparticles. The presence of broad reflections confirms their nanocrystalline nature. The stick pattern represents monoclinic HfO_2 (JCPDS card no. 34-0104).

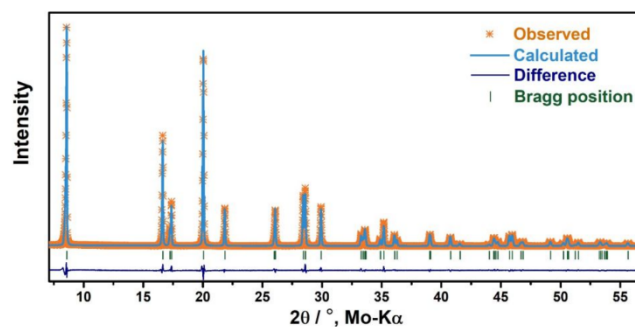


Figure S3. Powder XRD pattern collected from the bare NCM85 CAM particles and corresponding Rietveld refinement plot. Observed, calculated, and difference profiles are shown in orange, cyan, and blue, respectively. Green markers indicate the expected Bragg reflections for NCM85. Refinement results are provided in **Table S2**.

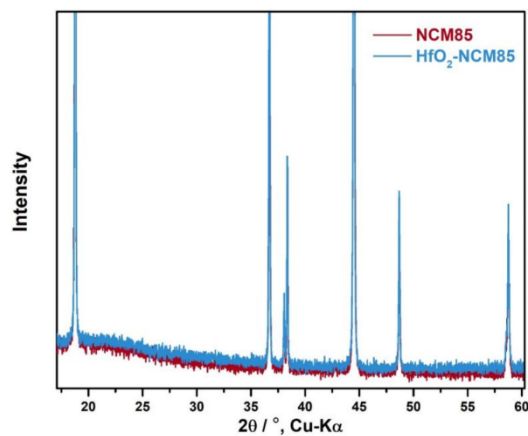


Figure S4. XRD patterns collected from the bare NCM85 (red) and HfO₂-NCM85 CAM particles (blue).

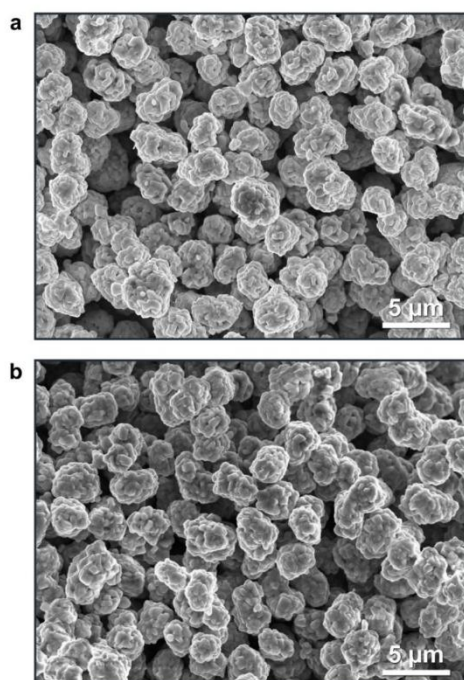


Figure S5. Low-magnification SEM images of (a) the bare NCM85 and (b) HfO₂-NCM85 CAM particles.

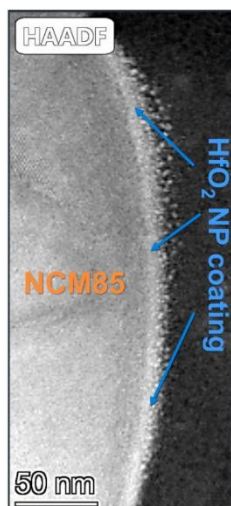


Figure S6. HAADF STEM image of a FIB-prepared HfO₂-NCM85 CAM particle cross-section.

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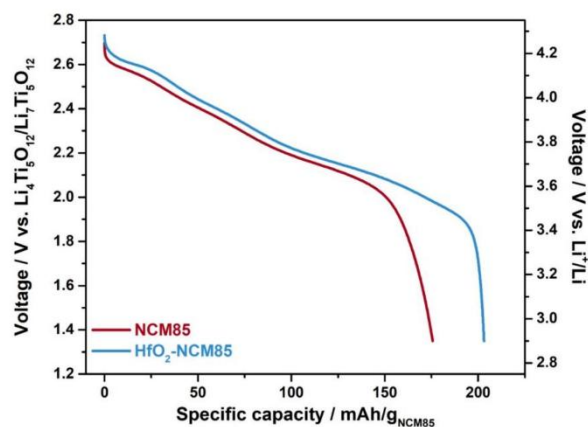


Figure S7. Comparison of first-cycle discharge curves at 0.1C rate and 45 °C for the bare NCM85 (red) and HfO₂-NCM85 CAM (blue) in SSB cells.

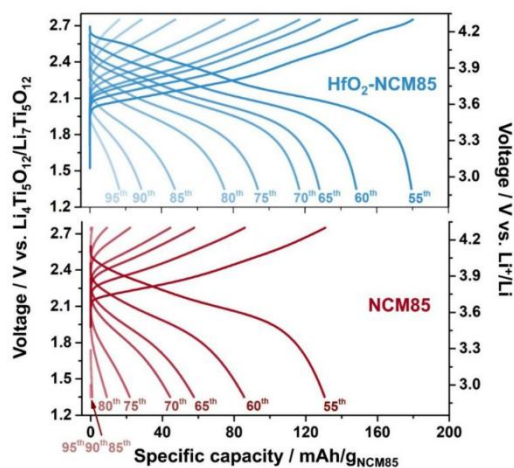


Figure S8. Voltage profiles of selected cycles in the second rate capability test at 45 °C for the bare NCM85 (red) and HfO₂-NCM85 CAM (blue) in SSB cells.

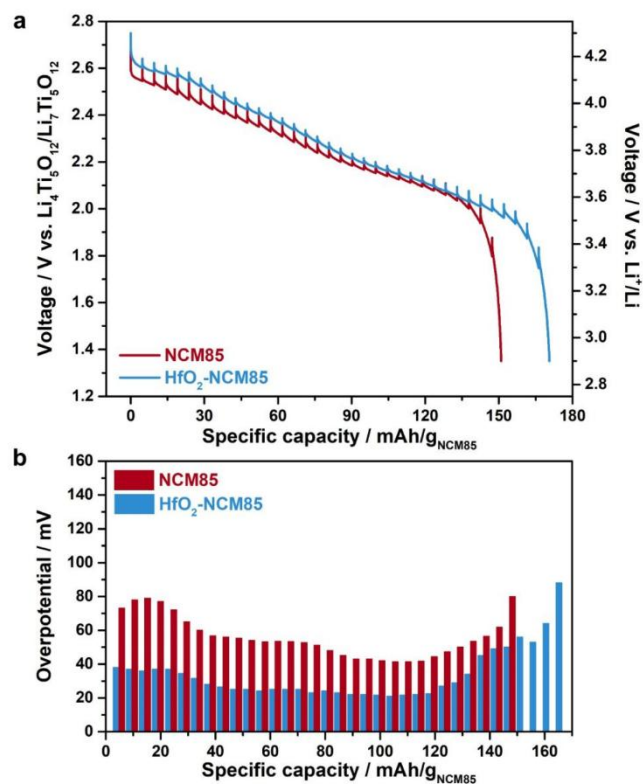


Figure S9. (a) Discharge curves from GITT measurements conducted on SSB cells using the bare NCM85 (red) and HfO₂-NCM85 CAM (blue) after cycling at 0.05C rate and 45 °C and (b) corresponding overpotential between discharge and relax intervals.

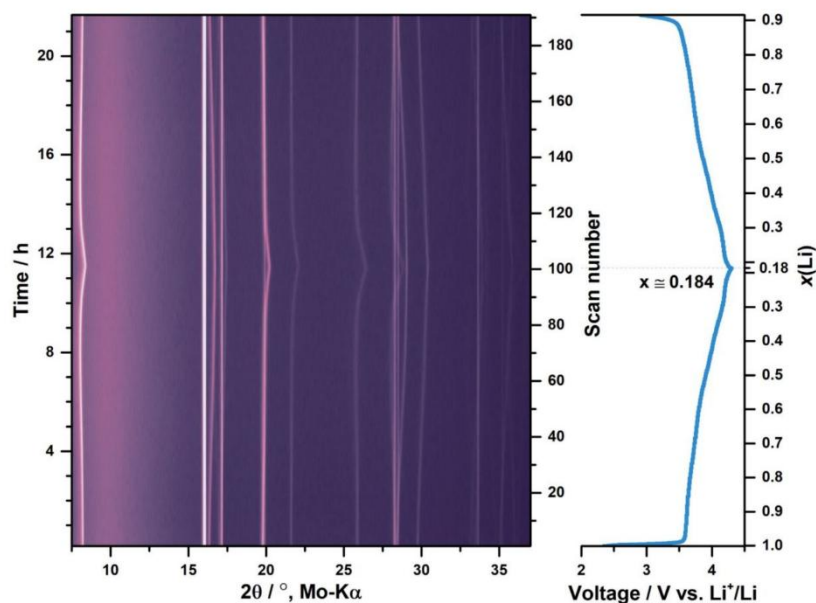


Figure S10. Operando XRD data collected from a liquid-electrolyte-based Li|NCM85 cell at 0.05C rate in the initial cycle. Contour plot showing the evolution of Bragg reflections and corresponding voltage profile as a function of $x(\text{Li})$. The NCM85 CAM remains single phase throughout with no evidence of any first-order transitions.

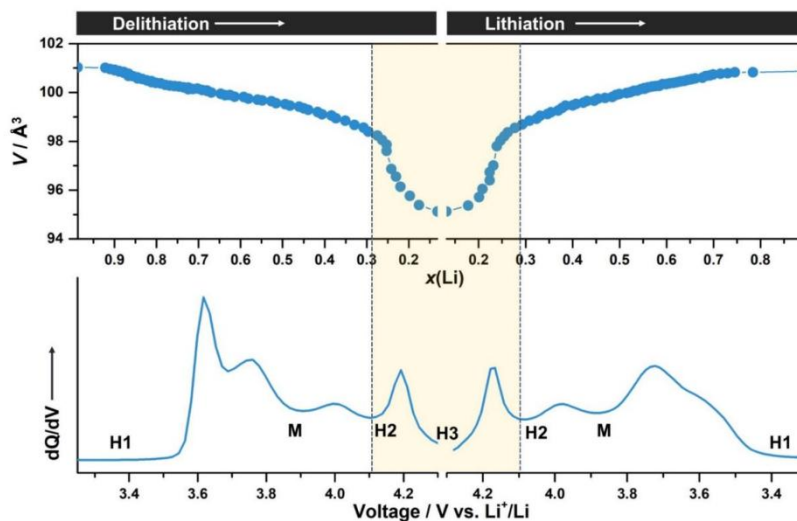


Figure S11. First-cycle differential capacity profile of a liquid-electrolyte-based Li|NCM85 cell and corresponding evolution of cell volume for the NCM85 CAM from operando XRD.

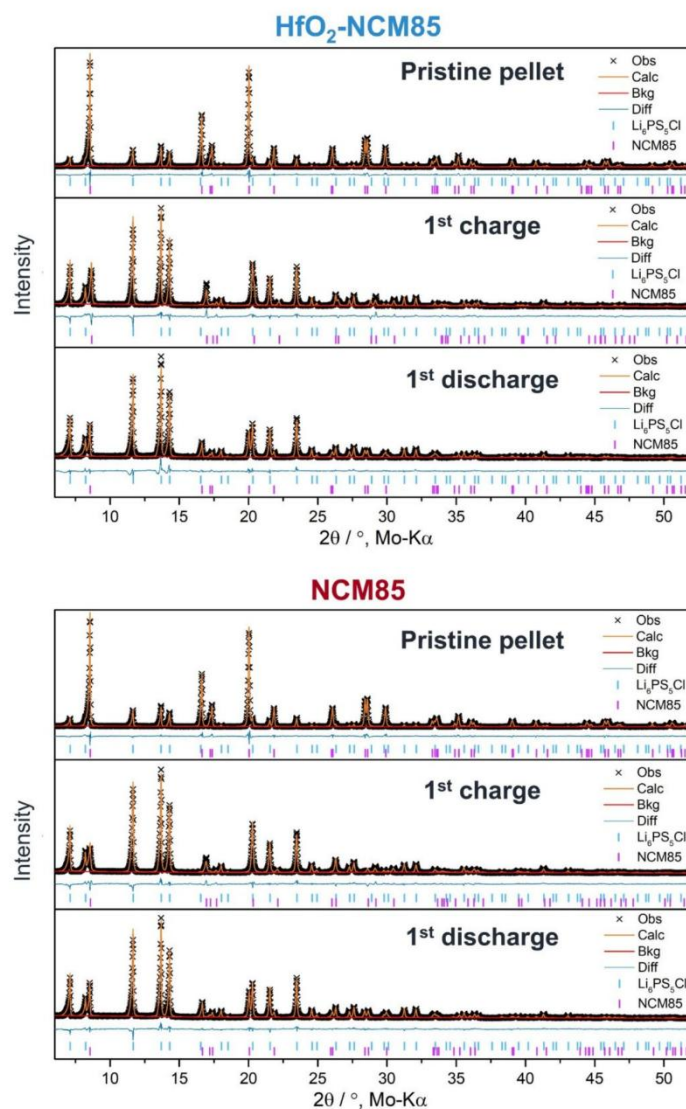


Figure S12. Rietveld refinement profiles of NCM85 and $\text{Li}_6\text{PS}_5\text{Cl}$ against XRD patterns collected from the $\text{HfO}_2\text{-NCM85}$ (top) and bare NCM85 (bottom) cathode composites in the pristine state, and after the first charge and discharge. Observed, calculated, background, and difference profiles are shown in black, orange, red, and blue, respectively. Markers indicate the expected positions of Bragg reflections for NCM85 (violet) and $\text{Li}_6\text{PS}_5\text{Cl}$ (sky blue). Refinement results are provided in **Table S4**.

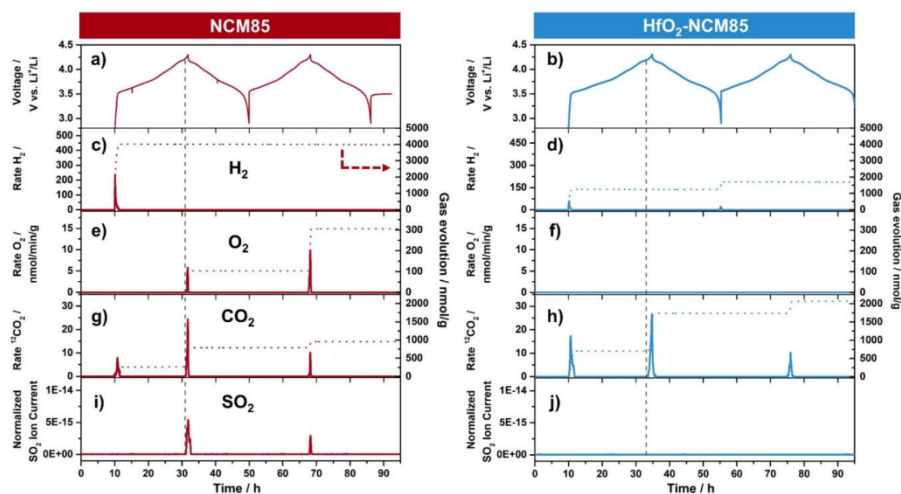


Figure S13. *In situ* gas analysis of SSB cells using the bare NCM85 (red) and HfO₂-NCM85 CAM (blue). (a, b) Voltage profiles for the first two cycles at 0.05C rate and 45 °C and corresponding time-resolved evolution rates (left y-axis) and cumulative amounts (right y-axis) for H₂ (c, d), O₂ (e, f), and CO₂ (g, h), as well as normalized ion currents for SO₂ (i, j).

The evolution of H₂ ($m/z = 2$) in SSBs is usually only observed at the beginning of the first charge cycle and attributed to the reduction of trace water at the anode.^{1–3} The CO₂ mass signal ($m/z = 44$) stems from electrochemical oxidation of residual surface carbonates on the cathode particles, with a first-cycle onset potential of $E > 4.2$ V vs. Li⁺/Li. Furthermore, CO₂ evolution is seen during the beginning of charging.^{1–3} It is reported to be correlated with side reactions at the anode, given that the H₂ and CO₂ mass signals coincide. The cumulative amount of evolved CO₂ was ~1.0 and ~2.0 $\mu\text{mol/g}_{\text{NCM85}}$ for the bare NCM85 and HfO₂-NCM85, respectively. The difference is probably due to the different SOC achieved, since both CO₂ evolution and O₂ evolution in SSB cells increase exponentially upon exceeding a certain threshold.⁴

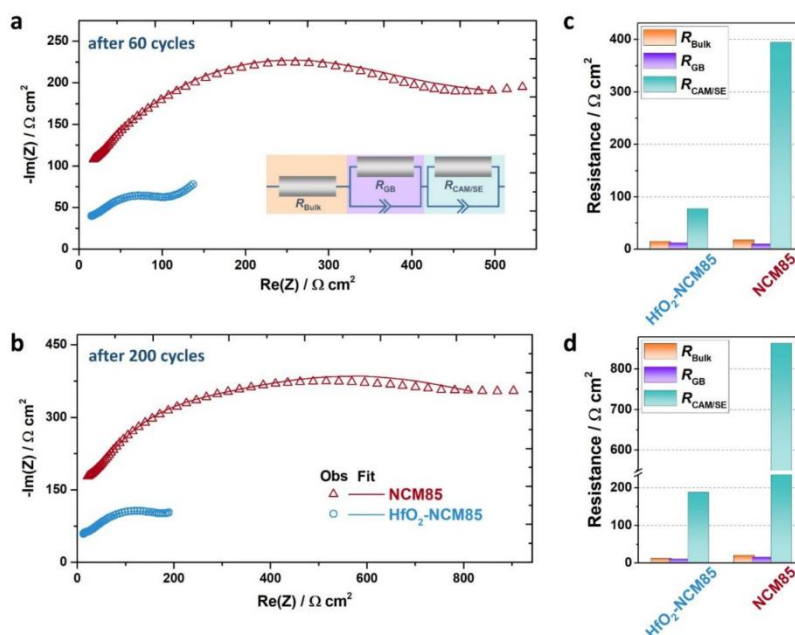


Figure S14. Nyquist plots of the electrochemical impedance of discharged SSB cells using the bare NCM85 (red) and HfO₂-NCM85 CAM (blue) after (a) 60 and (b) 200 cycles at 0.2C rate and 45 °C. The inset in (a) is the equivalent circuit used to fit the data and determine the resistance contributions from the bulk SE (R_{Bulk}), SE grain boundary (R_{GB}), and CAMISE interface (R_{CAMISE}). (c, d) Summary of the fitting results (see also Table S5).

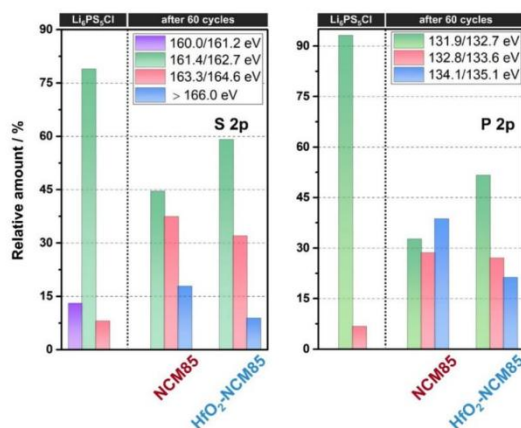


Figure S15. Comparison of relative amounts of the different S 2p/P 2p species detected by XPS in cathodes using the bare NCM85 and HfO₂-NCM85 CAM after 60 cycles at 0.2C rate and 45 °C (pristine Li₆PS₅Cl is shown as a reference).

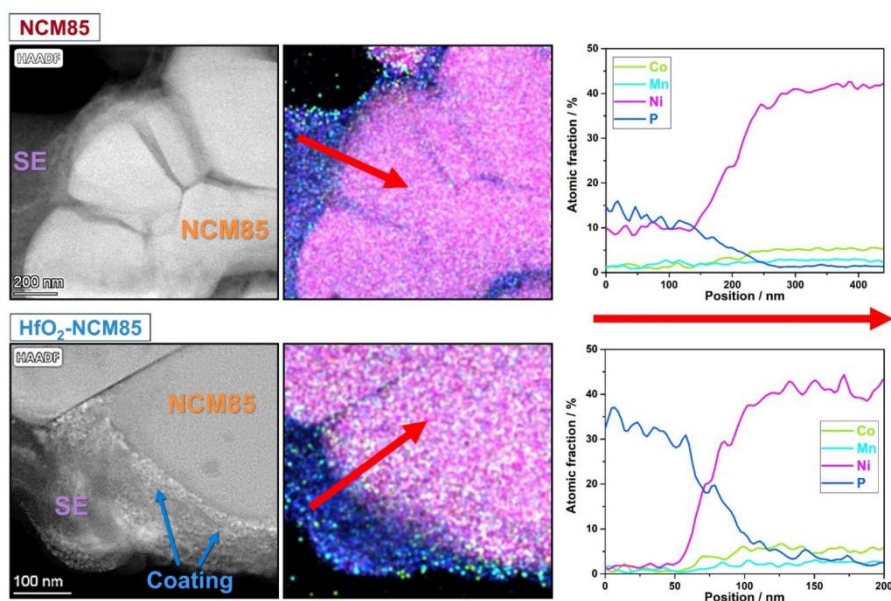


Figure S16. HAADF STEM images with EDS line scans of cathodes using the bare NCM85 (top) and HfO₂-NCM85 (bottom) after 60 cycles at 0.2C rate and 45 °C. The data for the bare NCM85 indicate diffusion of nickel from the CAM into the SE. This is in agreement with the XPS results (formation of oxygenated sulfur and phosphorus species at the CAM|SE interface, see main manuscript). Notably, for the HfO₂-NCM85 cathode, the nickel signal detected in the SE region is much weaker because the NP coating effectively suppresses unfavorable side reactions, thereby preventing interdiffusion.

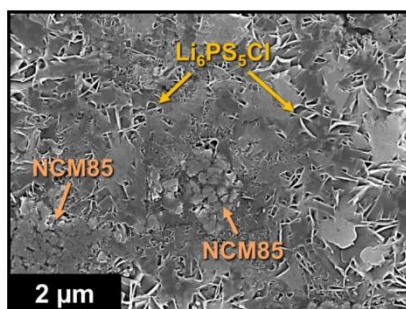


Figure S17. Top-view SEM image of the cathode with bare NCM85 in the pristine state.

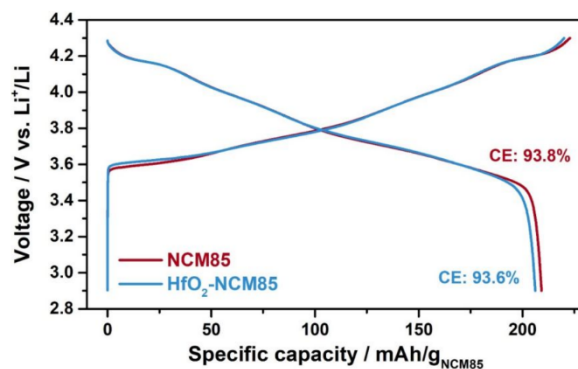


Figure S18. Initial voltage profiles of liquid-electrolyte-based Li|NCM85 (red) and Li|HfO₂-NCM85 (blue) coin cells at 0.2C rate and 45 °C.

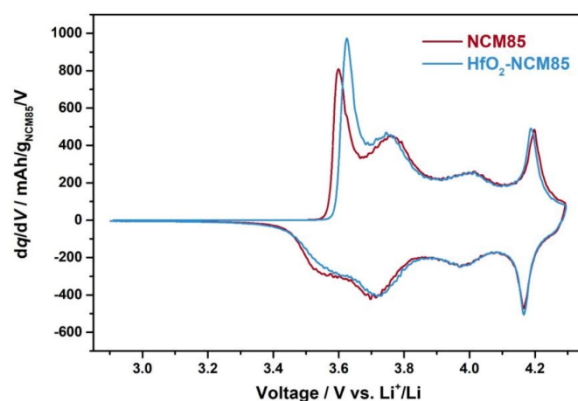


Figure S19. First-cycle differential capacity curves (Figure S18) for liquid-electrolyte-based Li|NCM85 (red) and Li|HfO₂-NCM85 (blue) coin cells at 0.2C rate and 45 °C.

Table S1. Results from ICP-OES for the HfO₂-NCM85 CAM.

Li / wt %	Ni / wt %	Co / wt %	Mn / wt %	Hf / wt %	HfO ₂ / wt %
7.10	49.5	5.78	2.71	0.72	0.83

Table S2. Refined structural parameters for the bare NCM85 and HfO₂-NCM85 CAM particles.

Sample	R_{wp} / %	a / Å	c / Å	V / Å ³	z of O	Ni on Li SOF
Bare NCM85	5.82	2.86898(4)	14.18049(24)	101.083(3)	0.24225(14)	0.039(3)
HfO ₂ -NCM85	5.19	2.87032(4)	14.18161(17)	101.185(2)	0.24215(12)	0.034(2)

6. Appendix

Table S3. Comparison of nanoparticle coatings in the battery field.

Coating material	Active material	Particle size / nm	Coating thickness / nm	Agglomerated	Calcination temperature / °C	Appl. field	Ref.
AlPO ₄	LiCoO ₂	3	15	Yes	700	LIB	5
Li ₃ PO ₄	LiMn ₂ O ₄	-	7	Yes	450	LIB	6
TiO ₂	LiMn ₂ O ₄	3 - 5	5 - 10	Yes	300	LIB	7
Ag	LiMn ₂ O ₄	3 - 5	-	No	700	LIB	8
LiFePO ₄	LiNi _{0.82} Co _{0.12} Mn _{0.06} O ₂	80	1000	Yes	-	LIB	9
ZnO	LiCoO ₂	18 - 45	-	Yes	400	LIB	10
MgO	0.5Li ₂ MnO ₃ · 0.5LiNi _{0.5} Mn _{0.3} Co _{0.2} O ₂	<50	20 - 30	Yes	500	LIB	11
TiO ₂	0.5Li ₂ MnO ₃ · 0.5LiNi _{0.5} Mn _{0.3} Co _{0.2} O ₂	25	20 - 30	Yes	500	LIB	11
CoF ₂	Li _{1.2} Ni _{0.2} Mn _{0.6} O ₂	10 - 11.5	7	Yes	400	LIB	12
TiO ₂	Li[Li _{0.2} Mn _{0.54} Co _{0.13} Ni _{0.13}]O ₂	-	~30	Yes	350	LIB	13
Al ₂ O ₃	LiNi _{1/3} Co _{1/3} Mn _{1/3} O ₂	~50	-	Yes	700	LIB	14
Y ₂ O ₃	LiNi _{0.5} Co _{0.2} Mn _{0.3} O ₂	-	20	Yes	500	LIB	15
SnO ₂	LiNi _{1/3} Co _{1/3} Mn _{1/3} O ₂	~10	-	Yes	500	LIB	16
Al ₂ O ₃	LiNi _{0.6} Co _{0.2} Mn _{0.2} O ₂	13	200 - 500	Yes	-	LIB	17
Al ₂ O ₃	LiNi _{0.6} Co _{0.2} Mn _{0.2} O ₂	15	20 - 25	Yes	400 - 600	LIB	18
MgO	LiCoO ₂	50	-	Yes	600	LIB	19
Al ₂ O ₃	LiNi _{0.6} Co _{0.2} Mn _{0.2} O ₂	15	20 - 25	Yes	500	LIB	20
Al ₂ O ₃	LiNi _{0.6} Co _{0.2} Mn _{0.2} O ₂	2 - 4	>30	Yes	-	LIB	21
Al ₂ O ₃	LiNi _{0.7} Co _{0.15} Mn _{0.15} O ₂	12	~30	Yes	600	SSB	22
Li ₄ Ti ₅ O ₁₂	LiNi _{0.7} Co _{0.15} Mn _{0.15} O ₂	40	~100	Yes	200	SSB	23
Li ₂ TiO ₃	LiNi _{0.8} Co _{0.15} Al _{0.05} O ₂	~20	10 - 20	Yes	600	LIB	24
ZrO ₂	LiNi _{0.85} Co _{0.10} Mn _{0.05} O ₂	4 - 5	10	No	400	SSB LIB	25
HfO ₂	LiNi _{0.85} Co _{0.10} Mn _{0.05} O ₂	6 - 7	~11	No	400	SSB LIB	This work

Table S4. Summary of the fitting results from the data in Figure S12.

Bare NCM85	a / Å	c / Å	V / Å ³	R _{wp} / %
Pristine	2.8677(3)	14.1865(4)	101.044(7)	8.74
1 st Charge	2.8118(7)	14.3409(2)	98.233(4)	10.26
1 st Discharge	2.8611(4)	14.2255(1)	100.827(7)	9.11
HfO ₂ -NCM85	a / Å	c / Å	V / Å ³	R _{wp} / %
Pristine	2.8679(5)	14.1868(4)	101.033(3)	10.07
1 st Charge	2.8096(2)	14.1298(7)	96.566(4)	8.37
1 st Discharge	2.8631(7)	14.2131(5)	100.915(2)	9.37

Table S5. Results from fitting of EIS data collected from SSB cells using the bare NCM85 and HfO₂-NCM85 CAM after the initial charge, and after 60 and 200 cycles (for 0.785 cm² electrode area).

Bare NCM85	1st Charge	60 cycles	200 cycles
$R_{\text{Bulk}} / \Omega \text{ cm}^2$	13.3	18.1	21.2
$R_{\text{GB}} / \Omega \text{ cm}^2$	9.4	10.2	15.7
$\text{CPE}_{\text{GB}} / \text{F s}^{\alpha-1}$	$6.7 \cdot 10^{-5}$	$1.3 \cdot 10^{-5}$	$5.3 \cdot 10^{-5}$
α_{GB}	0.79	0.82	0.65
C_{GB} / F	$1.0 \cdot 10^{-5}$	$1.9 \cdot 10^{-6}$	$1.3 \cdot 10^{-6}$
$R_{\text{CAMISE}} / \Omega \text{ cm}^2$	76.9	394.9	863.5
$\text{CPE}_{\text{CAMISE}} / \text{F s}^{\alpha-1}$	$1.3 \cdot 10^{-4}$	$2.7 \cdot 10^{-4}$	$1.7 \cdot 10^{-4}$
α_{CAMISE}	0.60	0.58	0.61
$C_{\text{CAMISE}} / \text{F}$	$7.1 \cdot 10^{-6}$	$6.4 \cdot 10^{-5}$	$5.8 \cdot 10^{-5}$
HfO₂-NCM85	1st Charge	60 cycles	200 cycles
$R_{\text{Bulk}} / \Omega \text{ cm}^2$	13.3	14.9	12.6
$R_{\text{GB}} / \Omega \text{ cm}^2$	7.1	12.6	11.0
$\text{CPE}_{\text{GB}} / \text{F s}^{\alpha-1}$	$8.8 \cdot 10^{-5}$	$4.8 \cdot 10^{-4}$	$1.2 \cdot 10^{-4}$
α_{GB}	0.62	0.50	0.56
C_{GB} / F	$1.1 \cdot 10^{-6}$	$3.7 \cdot 10^{-6}$	$7.9 \cdot 10^{-7}$
$R_{\text{CAMISE}} / \Omega \text{ cm}^2$	25.9	77.7	188.4
$\text{CPE}_{\text{CAMISE}} / \text{F s}^{\alpha-1}$	$4.9 \cdot 10^{-4}$	$2.4 \cdot 10^{-3}$	$1.2 \cdot 10^{-3}$
α_{CAMISE}	0.61	0.56	0.51
$C_{\text{CAMISE}} / \text{F}$	$3.5 \cdot 10^{-5}$	$7.8 \cdot 10^{-4}$	$3.6 \cdot 10^{-4}$

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6.1.3. Supporting Information of Publication III

Supporting Information

Conformal $\text{Li}_2\text{HfO}_3/\text{HfO}_2$ Nanoparticle Coatings on Layered Ni-Rich Oxide Cathodes for Stabilizing Interfaces in All-Solid-State Batteries

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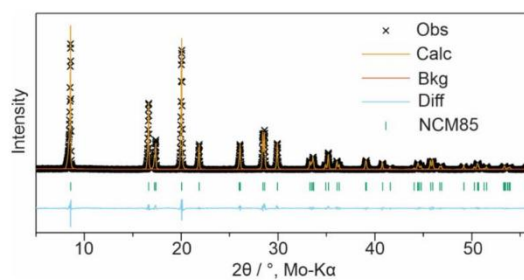


Figure S1. Powder XRD pattern and corresponding Rietveld refinement profile for the Bare-NCM85.

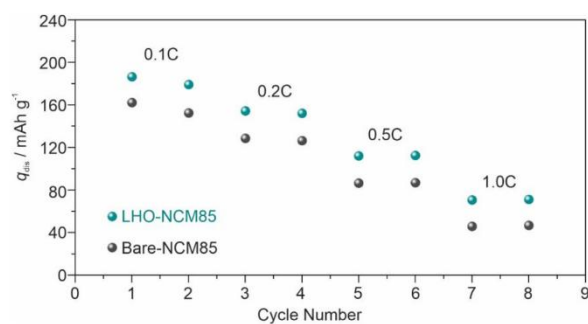


Figure S2. Rate capability of the Bare- and LHO-NCM85-based SSB cells at 0.1C (1st-2nd cycle), 0.2C (3rd-4th cycle), 0.5C (5th-6th cycle), and 1.0C (7th-8th cycle).

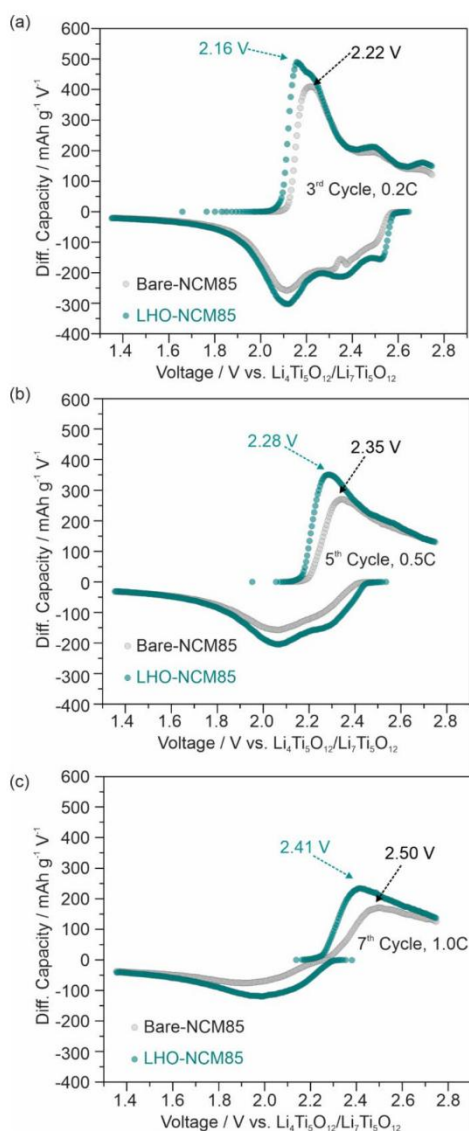


Figure S3. Differential capacity plots for (a) the 3rd cycle at 0.2C, (b) the 5th cycle at 0.5C, and (c) the 7th cycle at 1.0C of the Bare- and LHO-NCM85-based SSB cells.

The enhanced rate performance of LHO-NCM85 is evident from the shift in anodic peak position for the H1-M phase transition, indicating the effectiveness of the protective coating in mitigating SE decomposition and reducing polarization.

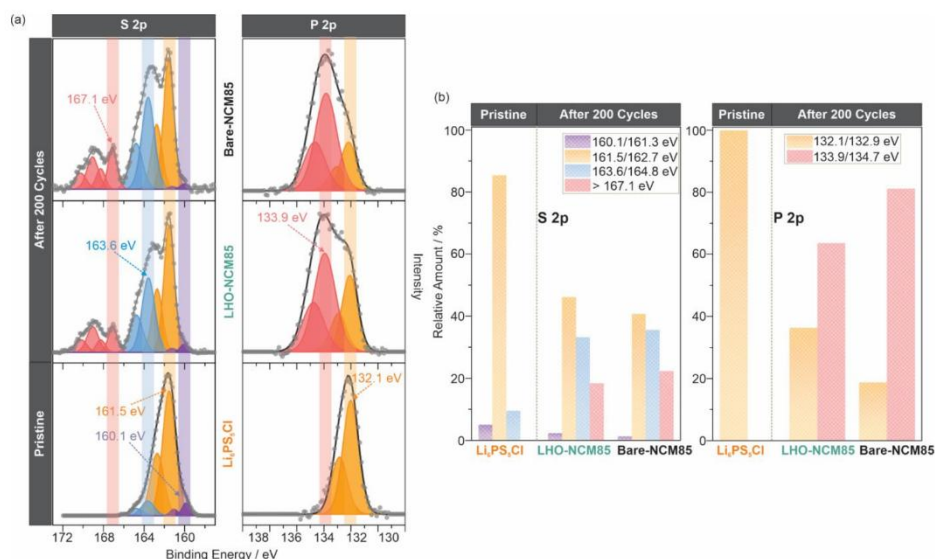


Figure S4. (a) XPS data collected from the S 2p and P 2p core-level regions of the LPSCI SE and the Bare- and LHO-NCM85-based cathodes after 200 cycles. (b) Corresponding relative amounts of sulfur and phosphorus species.

Table S1. Structural parameters determined by refinement of structural models against the XRD patterns of the Bare- and LHO-NCM85.

Sample	R_w / %	a / Å	c / Å	V / Å ³	z of O	Ni on Li SOF
Bare-NCM85	14.84	2.86692(12)	14.17062(44)	100.867(7)	0.24199(20)	0.032(3)
LHO-NCM85	11.35	2.86737(12)	14.17272(45)	100.914(7)	0.24201(21)	0.035(3)

Table S2. Summary of the relative percentage of Hf species with different chemical environments in LHO-NCM85 (from XPS of the Hf 4f core-level region).

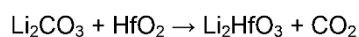
	Hf 4f _{7/2} / %	Hf 4f _{5/2} / %	Total / %
Hf-O (HfO ₂)	28.82	21.58	50.4
Li-Hf-O (Li ₂ HfO ₃)	28.36	21.24	49.6

Table S3. Results from ICP-OES for LHO-NCM85.

Li / wt. %	Ni / wt. %	Co / wt. %	Mn / wt. %	Hf / wt. %
7.17 ± 0.27	50.6 ± 0.7	5.76 ± 0.18	2.64 ± 0.04	0.844 ± 0.105

Discussion on the chemical reaction(s) leading to Li₂HfO₃ formation.

Considering the substantially reduced carbonate vibrational bands (ATR-IR) after coating, two chemical reaction mechanisms seem likely:



or



Based on the Li₂CO₃ content from acid titration experiments¹ (~0.15 wt. %) and the Hf content from ICP-OES, the molar ratio of Li₂HfO₃:Li₂CO₃ was determined to be ~1.15, indicating involvement of an additional lithium source in the Li₂HfO₃ formation during heating (possibly surface Li₂O and/or lithium from the NCM85 lattice). However, the degree of Li⁺/Ni²⁺ intermixing before/after coating determined by Rietveld refinement suggests that lattice lithium consumption can be neglected.

Table S4. Fitting results of EIS data collected from the Bare- and LHO-NCM85-based SSB cells after 200 cycles at the end of discharge.

Parameter	Bare-NCM85	LHO-NCM85
$R_{\text{Bulk}} / \Omega \text{ cm}^2$	20.8	13.5
$R_{\text{GB}} / \Omega \text{ cm}^2$	23.9	16.8
$\text{CPE}_{\text{GB}} / \text{F s}^{\alpha-1}$	$1.7 \cdot 10^{-5}$	$2.2 \cdot 10^{-5}$
α_{GB}	0.36	0.47
$R_{\text{CAMISE}} / \Omega \text{ cm}^2$	871.4	47.5
$\text{CPE}_{\text{CAMISE}} / \text{F s}^{\alpha-1}$	$2.4 \cdot 10^{-4}$	$5.8 \cdot 10^{-4}$
α_{CAMISE}	0.54	0.58

1. Payandeh, S.; Njel, C.; Mazilkin, A.; Teo, J. H.; Ma, Y.; Zhang, R. Z.; Kondrakov, A.; Bianchini, M.; Brezesinski, T., The Effect of Single versus Polycrystalline Cathode Particles on All-Solid-State Battery Performance. *Adv. Mater. Interfaces* **2023**, *10*, 2201806.

6.1.4. Supporting Information of Publication IV

Supporting Information

Timescale Identification of Electrochemical Processes in All-Solid-State Batteries Using an Advanced Three-Electrode Cell Setup

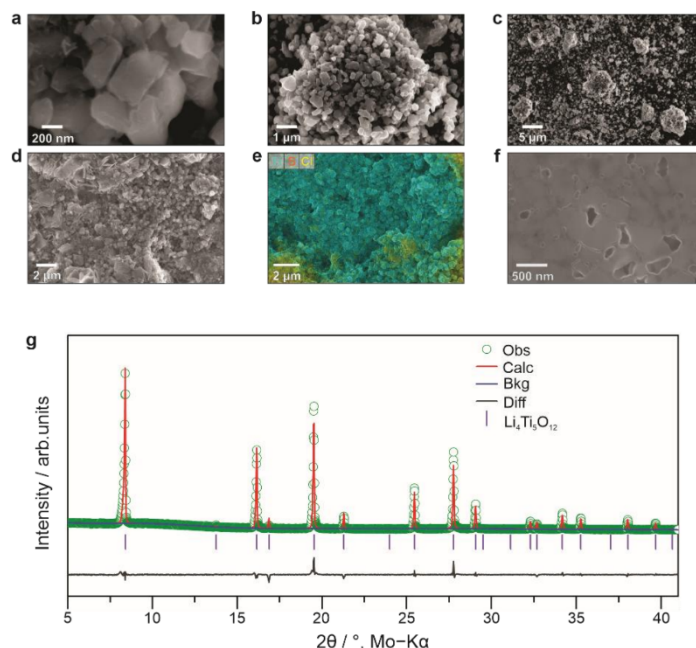


Figure S1. Physical characterization of carbon-coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO). (a–c) SEM images at different magnifications. (d) Cross-sectional view of the densified LTO composite layer and (e) EDS mapping of Ti, S, and Cl. (f) Cross-sectional view of the ion-polished, densified LTO composite layer. (g) XRD pattern and corresponding Rietveld refinement plot.

Supplementary Note 1: The reflections from XRD and the corresponding Rietveld refinement profile confirm the expected structure of the spinel-type LTO ($Fd\bar{3}m$ space group). The refined unit-cell parameter and volume are consistent with values reported in the literature (see Table S1).[1] After pressing at 3.5 t for 3 min, the pristine LTO composite layer was fractured to create a coarse cross-sectional edge. Initially, the microstructure of both the LTO powder and the pelletized composite was examined by SEM and EDS, the latter indicating the presence of Ti, S, and Cl (see Figures S1a–e). The spherical LTO (secondary) particles with an average size of 4 μm formed by agglomeration of the cubic primary particles. Ion polishing was further utilized to create a smooth cross-section, revealing the internal microstructure of the secondary particles within the composite layer, as shown in Figure S1f.

Table S1. Summary of the Rietveld refinement results of structural parameters for LTO.

Sample	R_{wp} / %	a / Å	V / Å ³
$\text{Li}_4\text{Ti}_5\text{O}_{12}$	9.98	8.35108(18)	582.41(4)

SI-2

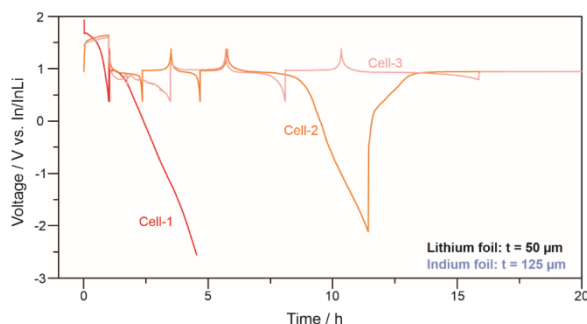


Figure S2. Failure during prelithiation of LTO in 2E cells. Three independent cells exhibited varying failures during prelithiation when using thicker indium foil ($125 \mu\text{m}$), alongside lithium foil of the same thickness ($50 \mu\text{m}$).

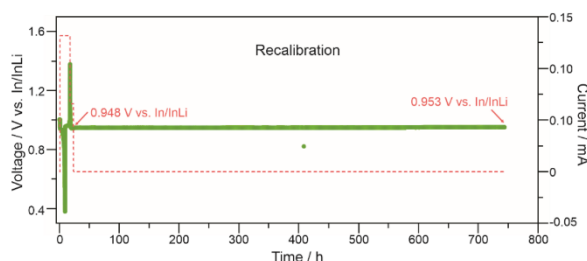


Figure S3. Recalibration of potential drift. In Figure 2a, the OCV of LTO vs. In/InLi showed significant drift after ~ 1000 h of monitoring. To recalibrate the potential of LTO, a simple protocol was applied, involving a complete cycle at 0.1C , followed by lithiation to $50 \text{ mAh g}_{\text{LTO}}^{-1}$ at 0.05C . This kind of recovery successfully returned the potential of the prelithiated LTO to $0.948 \text{ V vs. In/InLi}$ ($\sim 1.57 \text{ V vs. Li}^+/\text{Li}$). Only a minor drift by 5 mV was observed after additional 750 h of OCV monitoring.

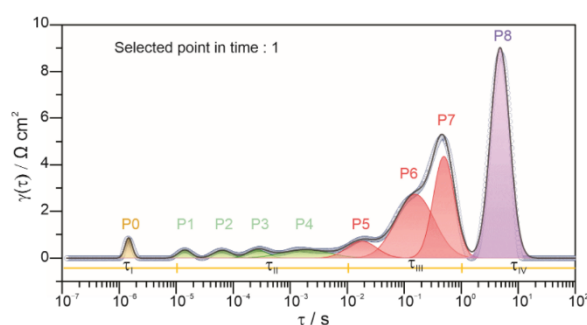


Figure S4. DRT plot of the impedance data presented in Figure 2b with individual peak fitting. The original impedance data were gathered after a certain OCV

monitoring period (cell configuration: In/InLi|SE|LTO). The peaks in the η , η_I , η_{II} , and η_V regimes are highlighted in yellow, green, red, and purple, respectively.

Supplementary Note 2: Fundamentals of DRT, critical parameter selection, and peak fitting: By transforming the EIS data from frequency to time domain, model-independent distribution of relaxation times (DRT) analysis of the complex impedance data was used to qualitatively/quantitatively study the involved kinetic processes.[2, 3] The impedance, $Z(f)$, of the SSB system can be generally broken down into an ohmic contribution, Z_{ohm} , from the bulk of SE, a possible inductive contribution, Z_L , the polarization impedance, $Z_{pol(f)}$, originating from the involved interface-related electrochemical processes, and a capacitive diffusion contribution, Z_{diff} , from the active materials. In DRT analysis, the electrochemical processes are represented by an infinite series of RQ elements (a parallel connection between resistor, R , and CPE, Q), each characterized by its corresponding relaxation time constant, $\tau = (RQ)^{(1/\alpha)}$ (α is the exponential factor of CPE with a number between 0 and 1).

Prior to DRT analysis, the possible inductive part in the high-frequency range from the impedance data is discarded. The capacitive tail in the low-frequency range is insignificant for most of the gathered EIS spectra in this study. Therefore, the relationship between the complex impedance, $Z(f)$, in the frequency domain and the distribution function of relaxation in the time domain can be expressed as:

$$Z(f) = R_0 + R_p \int_0^{\infty} \frac{g(\tau)}{1 + i2\pi f\tau} d\tau \quad (1)$$

with normalized integration:

$$\int_0^{\infty} g(\tau) d\tau = 1 \quad (2)$$

where R_0 represents the ohmic resistance, R_p the total polarization resistance of the system, and $g(\tau)$ is the distribution function of relaxation time. By converting the integral equation into logarithmic form, equation (1) can be rewritten as:

$$Z(f) = R_0 + R_p \int_0^{\infty} \frac{\gamma(\ln\tau)}{1 + i2\pi f\tau} d\ln\tau \quad (3)$$

where $\gamma(\ln\tau) = \tau g(\tau)$.

To solve the distribution function, $\gamma(\ln\tau)$, numerically, the regularized regression approach was applied with radial basis functions (RBF) based discretization.[3] Gaussian function was chosen for RBF discretization with a general expression as:

$$\phi_{\mu}(\mathbf{x}, \mathbf{c}) = \exp(-\mu \|\mathbf{x} - \mathbf{c}\|^2) \quad (4)$$

where $\mathbf{c}$ represents the center of the peak, and μ is the shape factor acting as a crucial regularization parameter, alongside the well-known Tikhonov regularization parameter, λ . The discretized distribution function can be expressed as:

$$\gamma(\ln\tau) = \sum_{m=1}^M x_m \phi_{\mu}(|\ln\tau - \ln\tau_m|) \quad (5)$$

where x_m is the unknown parameter to be fitted, and τ_m represents the centered time constant. By introducing equation (5) into (3), the optimization problem will be solved by applying the Tikhonov regularization between the calculated impedance based on DRT and the experimental data. The optimization function can be expressed in a general form as:

$$S(\mathbf{x})_{\min} = \|\mathbf{Ax} - \mathbf{b}\|^2 + \lambda \|\mathbf{x}\|^2 \quad (6)$$

where $\lambda \|\mathbf{x}\|^2$ is the penalty item, which is the first $\left\|\frac{d\gamma(\ln\tau)}{d\ln\tau}\right\|^2$ or second derivative $\left\|\frac{d^2\gamma(\ln\tau)}{d(\ln\tau)^2}\right\|^2$ of $\gamma(\ln\tau)$ with the regularization parameter, λ . In this work, the second derivative of $\gamma(\ln\tau)$ was used as penalty item for computing the DRT analysis. The selection of appropriate values for the regularization parameters, λ and μ , is crucial for accurately resolving and interpreting the peaks and their underlying physical meaning in DRT analysis.

For the shape factor, μ , a larger value tends to increase oscillations near each collocation point, while a value that is too small flattens the DRT pattern, making the peaks less distinguishable and reducing their characteristic features. In this work, a μ value of 0.5 was found to be optimal and was consistently applied to all computed DRT patterns. For the Tikhonov regularization parameter, the effect is the opposite. A larger value excessively smooths the patterns, while a smaller value introduces oscillations and potential pseudo peaks. Therefore, a moderate λ value, small enough to achieve adequate peak resolution, yet large enough to suppress overfitting-induced oscillations, should be selected. To determine a suitable λ value in this study, a Lambda plot was utilized by calculating the sum of squared residuals (SSR) between the DRT reconstructed spectrum and the experimental spectrum across a wide range of values. The computed DRT was then used to regenerate an impedance spectrum, which was compared to the original experimental data, as shown in Figures S5a–d.

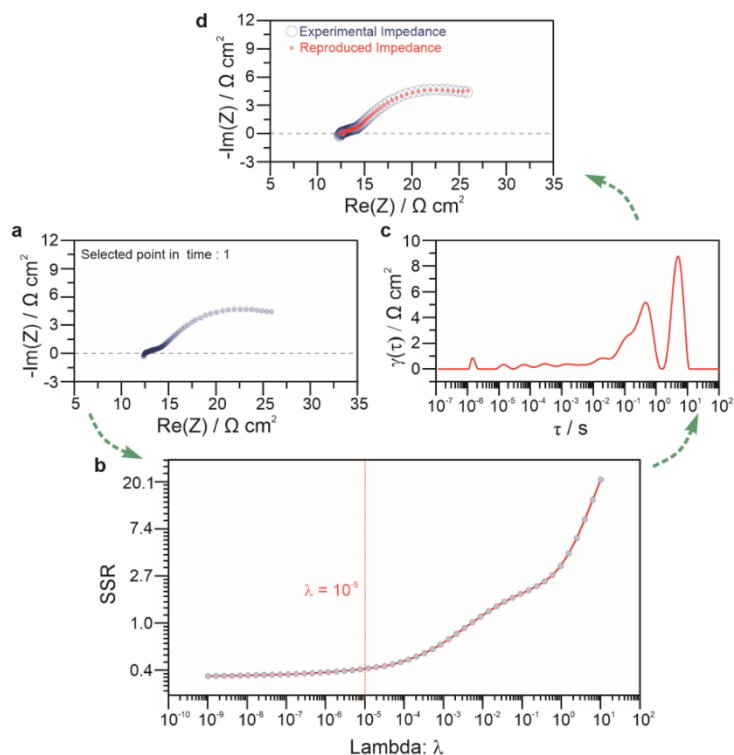


Figure S5. Determination of appropriate regularization parameter, λ , and validation of computed DRT. (a) Exemplary impedance spectrum from Figure 2b after a certain OCV monitoring period (cell configuration: In/InLi|SE|LTO). (b) Lambda plot. (c) Computed DRT pattern using the determined $\lambda = 10^{-5}$. (d) Validation of computed DRT by reproduction of the impedance and comparison with the experimental impedance.

The impedance data of the selected point in time 1, as shown in Figure 2b, were used as an example to demonstrate the process of determining the λ value for this study (Figure S5a). The lambda plot shown in Figure S5b demonstrates a decreasing trend in SSR as smaller λ values are applied, eventually reaching a plateau where further reductions yield no significant improvement anymore. Therefore, a λ value around 10^{-5} was determined to be optimal, as it provides sufficient peak separation resolution without overfitting. The corresponding DRT pattern is displayed in Figure S5c. The computed DRT was further reproduced to an impedance spectrum, which was then compared to the experimental data. As demonstrated in Figure S5d, the results show a good match with the experimental data, indicating that the DRT analysis is both effective and reliable for further qualitative and quantitative analyses.

To quantitatively analyze the evolution of polarization resistances for individual electrochemical processes, the peaks observed in the DRT pattern, identified manually,

were fitted. Note that the peak areas correspond to the respective polarization resistances.[3, 4]

As shown in Figure S4, the DRT pattern from Figure S5c was fitted using multiple Gaussian peak functions to accurately represent the individual peaks expressed as:

$$\gamma(\ln\tau) = \sum_{p=0,1,2...}^P a_p \cdot \exp\left(-\frac{(\ln\tau - \ln\tau_p)^2}{2 \cdot c_p^2}\right) \quad (7)$$

where a_p is the peak height, τ_p is the peak center (characteristic time constant), and c_p represents the standard deviation, which determines how broad the peak is. The peak width is described by the full width at half maximum (FWHM), which can be derived as $2\sqrt{2\ln 2} \cdot c_p$. The area, A_p , can be calculated as:

$$A_p = a_p \cdot c_p \cdot \sqrt{2\pi} \quad (8)$$

Within the characteristic pre-defined regimes, the individual peaks were shaded using the same color. The sum of the calculated area, A_p , within the same regime was used to quantitatively analyze the evolution of the corresponding polarization resistances, as shown in this study. The DRT analysis, including peak fitting, was performed using RelaxIS software, 3.0.22.29 version (rhd instruments).

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Table S2. Summary of peak fitting results from DRT patterns during OCV monitoring in Figure 2 (In/InLi|SE|LTO 2E cell).

	P0		P1		P2		P3		P4		P5		P6		P7		P8	
	Center τ / s	Area / $\Omega \cdot \text{cm}^2$	Center τ / s	Area / $\Omega \cdot \text{cm}^2$	Center τ / s	Area / $\Omega \cdot \text{cm}^2$	Center τ / s	Area / $\Omega \cdot \text{cm}^2$	Center τ / s	Area / $\Omega \cdot \text{cm}^2$	Center τ / s	Area / $\Omega \cdot \text{cm}^2$	Center τ / s	Area / $\Omega \cdot \text{cm}^2$	Center τ / s	Area / $\Omega \cdot \text{cm}^2$	Center τ / s	Area / $\Omega \cdot \text{cm}^2$
1	$1.4 \cdot 10^{-5}$	0.3	$1.4 \cdot 10^{-5}$	0.2	$6.4 \cdot 10^{-5}$	0.3	$2.7 \cdot 10^{-4}$	0.4	$1.8 \cdot 10^{-5}$	0.9	$1.8 \cdot 10^{-2}$	1.1	$1.5 \cdot 10^{-1}$	5.3	$4.9 \cdot 10^{-1}$	4.7	$4.8 \cdot 10^0$	8.7
2	$1.4 \cdot 10^{-5}$	0.4	$1.8 \cdot 10^{-5}$	0.3	$9.7 \cdot 10^{-5}$	0.3	$5.7 \cdot 10^{-4}$	0.8	$3.9 \cdot 10^{-5}$	0.5	$2.1 \cdot 10^{-2}$	1.1	$1.7 \cdot 10^{-1}$	5.6	$5.0 \cdot 10^{-1}$	5.1	$4.7 \cdot 10^0$	9.8
3	$1.4 \cdot 10^{-5}$	0.4	$1.8 \cdot 10^{-5}$	0.3	$1.1 \cdot 10^{-4}$	0.5	$6.1 \cdot 10^{-4}$	0.5	$3.4 \cdot 10^{-5}$	0.5	$2.0 \cdot 10^{-2}$	1.1	$1.6 \cdot 10^{-1}$	5.6	$5.1 \cdot 10^{-1}$	5.7	$4.7 \cdot 10^0$	10.8
4	$1.4 \cdot 10^{-5}$	0.4	$1.8 \cdot 10^{-5}$	0.3	$8.5 \cdot 10^{-5}$	0.4	$5.3 \cdot 10^{-4}$	0.5	$3.5 \cdot 10^{-5}$	0.5	$2.2 \cdot 10^{-2}$	1.2	$1.8 \cdot 10^{-1}$	6.2	$5.5 \cdot 10^{-1}$	5.2	$4.4 \cdot 10^0$	11.4
5	$1.4 \cdot 10^{-5}$	0.4	$1.8 \cdot 10^{-5}$	0.3	$8.1 \cdot 10^{-5}$	0.3	$2.2 \cdot 10^{-4}$	0.2	$1.4 \cdot 10^{-5}$	0.7	$1.8 \cdot 10^{-2}$	1.2	$1.7 \cdot 10^{-1}$	6.0	$5.4 \cdot 10^{-1}$	5.8	$4.4 \cdot 10^0$	12.5
6	$1.4 \cdot 10^{-5}$	0.5	$1.8 \cdot 10^{-5}$	0.4	$1.2 \cdot 10^{-4}$	0.5	$7.3 \cdot 10^{-4}$	0.4	$4.0 \cdot 10^{-5}$	0.5	$2.2 \cdot 10^{-2}$	1.1	$1.7 \cdot 10^{-1}$	6.0	$5.3 \cdot 10^{-1}$	6.4	$4.4 \cdot 10^0$	14.8
7	$1.4 \cdot 10^{-5}$	0.6	$1.9 \cdot 10^{-5}$	0.4	$1.0 \cdot 10^{-4}$	0.4	$4.2 \cdot 10^{-4}$	0.4	$2.3 \cdot 10^{-5}$	0.5	$1.5 \cdot 10^{-2}$	1.1	$1.3 \cdot 10^{-1}$	5.5	$5.1 \cdot 10^{-1}$	7.7	$4.6 \cdot 10^0$	18.2

Table S3. Summary of resistances classified by characteristic time constants during OCV monitoring in Figure 2 (In/InLi|SE|LTO 2E cell).

Selected Time	R_{Bulk}	$R_{\text{GB+Contact}}$	R_{int}	R_{ct}
		$\tau_{\text{c}}: <10^{-5} \text{ s}$	$\tau_{\text{il}}: 10^{-5} \text{--} 10^{-2} \text{ s}$	$\tau_{\text{el}}: <10^{-2} \text{--} 10^0 \text{ s}$
1	$12.4 \Omega \cdot \text{cm}^2$	$0.3 \Omega \cdot \text{cm}^2$	$1.8 \Omega \cdot \text{cm}^2$	$11.1 \Omega \cdot \text{cm}^2$
2	$12.7 \Omega \cdot \text{cm}^2$	$0.4 \Omega \cdot \text{cm}^2$	$1.9 \Omega \cdot \text{cm}^2$	$11.9 \Omega \cdot \text{cm}^2$
3	$12.7 \Omega \cdot \text{cm}^2$	$0.4 \Omega \cdot \text{cm}^2$	$1.8 \Omega \cdot \text{cm}^2$	$12.4 \Omega \cdot \text{cm}^2$
4	$12.4 \Omega \cdot \text{cm}^2$	$0.4 \Omega \cdot \text{cm}^2$	$1.7 \Omega \cdot \text{cm}^2$	$12.6 \Omega \cdot \text{cm}^2$
5	$13.1 \Omega \cdot \text{cm}^2$	$0.4 \Omega \cdot \text{cm}^2$	$1.6 \Omega \cdot \text{cm}^2$	$13.1 \Omega \cdot \text{cm}^2$
6	$12.9 \Omega \cdot \text{cm}^2$	$0.5 \Omega \cdot \text{cm}^2$	$1.7 \Omega \cdot \text{cm}^2$	$13.5 \Omega \cdot \text{cm}^2$
7	$12.9 \Omega \cdot \text{cm}^2$	$0.6 \Omega \cdot \text{cm}^2$	$1.6 \Omega \cdot \text{cm}^2$	$14.3 \Omega \cdot \text{cm}^2$

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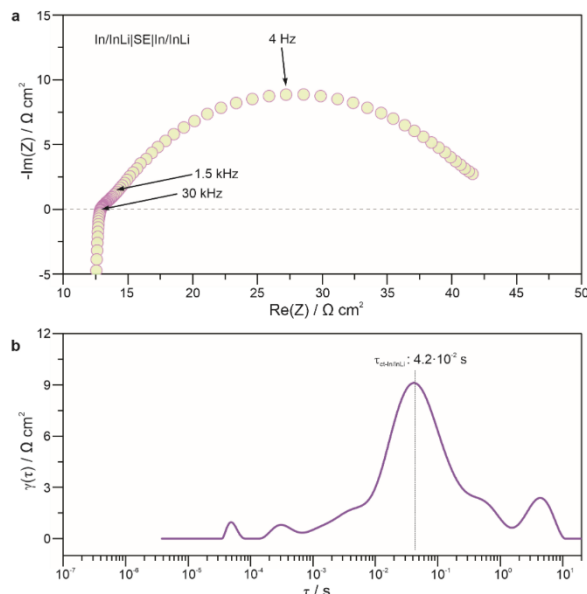


Figure S6. Impedance measurement and corresponding DRT pattern of an In/InLi|SE|In/InLi symmetrical cell. (a) Nyquist plot with selected frequencies indicated and (b) corresponding DRT plot.

After assembly, the In/InLi|SE|In/InLi cell underwent nine partial charge/discharge cycles using a current of $65.6 \mu\text{A}$ with a capacity limit of 0.375 mAh , following the pre-lithiation protocol used in the In/InLi|SE|LTO cell. This approach was intended to mimic the conditions of the 2E setup and facilitate the formation of representative interfaces between the indium-lithium alloy electrode and the SE on both sides of the cell. An impedance measurement was taken at the end of each step. The impedance data from the fourth cycle were selected for detailed analysis and are displayed. Of note, frequencies higher than 30 kHz were excluded from the corresponding DRT analysis. The major peak having a time constant of $4.2 \cdot 10^{-2} \text{ s}$ is located in the region between 10^{-2} and 10^0 s (charge-transfer process).

Table S4. Specific capacity and OCV for selected SOC's during *in situ* EIS measurement.

Lithiation of LTO & delithiation of In/InLi									
SOC	1	2	3	4	5	6	7	8	9
$q / \text{mAh g}_{\text{LTO}}^{-1}$	20	40	50	60	79	99	119	139	169
OCV / V vs. In/InLi	0.952	0.951	0.950	0.950	0.949	0.948	0.947	0.946	0.942
Delithiation of LTO & lithiation of In/InLi									
SOC	10	11	12	13	14	15	16	17	18
$q / \text{mAh g}_{\text{LTO}}^{-1}$	20	40	50	60	79	99	119	139	141
OCV / V vs. In/InLi	0.951	0.953	0.953	0.954	0.956	0.958	0.964	1.102	1.304

Supplementary Note 3: Calculation of Li_xIn composition during *in situ* EIS measurement in Figure 3: The as-prepared indium-lithium electrode in the In/InLi|SE|LTO 2E cell was constructed by stacking discs of indium foil and lithium foil on top of the SE separator layer. Based on the parameters given in Table S4, the initial composition was calculated.

Table S5. Physical properties of metal foils.

Metal	Density (ρ)	Molar mass (M)	Diameter (d)	Thickness (t)
Indium	7.31 g cm^{-3}	$114.82 \text{ g mol}^{-1}$	9 mm	100 μm
Lithium	0.534 g cm^{-3}	6.94 g mol^{-1}	6 mm	50 μm

Based on the following equations:

$$m = \rho \cdot \pi \left(\frac{d}{2} \right)^2 \cdot t \quad (9)$$

$$n = \frac{m}{M} \quad (10)$$

the lithium and indium contents in the indium-lithium electrode were determined to be $n_{\text{Li}} = 1.09 \cdot 10^{-4} \text{ mol}$ and $n_{\text{In}} = 4.05 \cdot 10^{-4} \text{ mol}$. Therefore, x in Li_xIn can be calculated as:

$$x = \frac{n_{\text{Li}}}{n_{\text{In}}} \quad (11)$$

The initial (integral) composition of the indium-lithium alloy corresponds to $\text{Li}_{0.27}\text{In}$ (lithiated state). Given the composition of the LTO composite (LTO:SE:C65 = 30:65:5 by weight), the loading of the LTO composite (25 mg), and the molar mass of LTO

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(459.11 g mol⁻¹), the amount of Li required for full transition from Li₄Ti₅O₁₂ to Li₇Ti₅O₁₂ can be calculated as:

$$n_{\text{inserted Li}} = \frac{3 \cdot (0.025 \text{ g} \cdot 0.3)}{459.11 \frac{\text{g}}{\text{mol}}} = 4.95 \cdot 10^{-5} \text{ mol}$$

After full lithiation of LTO, the composition of the indium-lithium electrode (x in Li _{x} In) corresponds to:

$$x = \frac{n_{\text{Li}} - n_{\text{intercalated Li}}}{n_{\text{In}}} = 0.15$$

Therefore, the composition of the indium-lithium alloy reversibly changes between Li_{0.27}In (lithiated state) and Li_{0.15}In (delithiated state) during cycling.

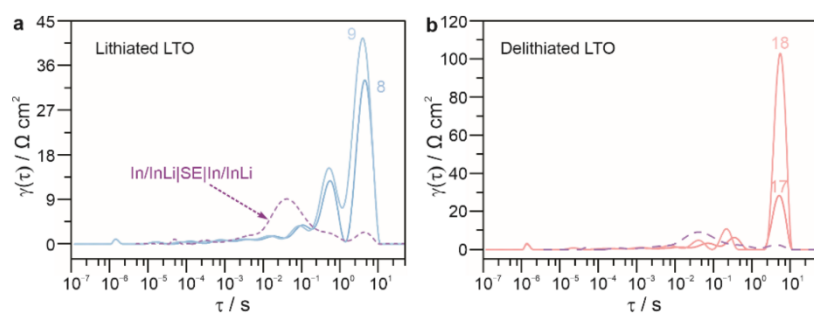


Figure S7. DRT patterns for the In/InLi|SE|LTO 2E cell. (a) Near full lithiation and (b) near full delithiation of LTO.

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Table S6. Summary of peak fitting results from DRT patterns (*in situ* EIS measurement during discharge process). In/InLi|SE|LTO 2E cell; LTO was lithiated until 0.38 V vs. In/InLi (referring to SOC 9).

	P0		P1		P2		P3		P4		P5		P6		P7		P8		P9	
	Center τ /s	Area / $\Omega\cdot\text{cm}^2$	Center τ /s	Area / $\Omega\cdot\text{cm}^2$	Center τ /s	Area / $\Omega\cdot\text{cm}^2$	Center τ /s	Area / $\Omega\cdot\text{cm}^2$	Center τ /s	Area / $\Omega\cdot\text{cm}^2$	Center τ /s	Area / $\Omega\cdot\text{cm}^2$	Center τ /s	Area / $\Omega\cdot\text{cm}^2$	Center τ /s	Area / $\Omega\cdot\text{cm}^2$	Center τ /s	Area / $\Omega\cdot\text{cm}^2$	Center τ /s	Area / $\Omega\cdot\text{cm}^2$
1	$1.4\cdot 10^{-3}$	0.4	$1.6\cdot 10^{-3}$	0.3	$1.3\cdot 10^{-4}$	0.5	$8.7\cdot 10^{-4}$	0.5	$6.1\cdot 10^{-3}$	0.7	$7.4\cdot 10^{-2}$	4.0	$5.1\cdot 10^{-1}$	1.2	$4.5\cdot 10^0$	3.9				
2	$1.4\cdot 10^{-3}$	0.4	$1.4\cdot 10^{-3}$	0.3	$9.1\cdot 10^{-5}$	0.5	$6.2\cdot 10^{-4}$	0.7	$3.9\cdot 10^{-3}$	0.9	$2.1\cdot 10^{-2}$	1.3	$1.1\cdot 10^{-1}$	3.2	$5.9\cdot 10^{-1}$	1.8	$4.5\cdot 10^0$	4.4		
3	$1.4\cdot 10^{-3}$	0.4	$1.5\cdot 10^{-3}$	0.3	$7.8\cdot 10^{-5}$	0.4	$4.1\cdot 10^{-4}$	0.7	$2.2\cdot 10^{-3}$	0.8	$1.1\cdot 10^{-2}$	0.9	$1.0\cdot 10^{-1}$	4.9	$6.1\cdot 10^{-1}$	1.7	$4.5\cdot 10^0$	5.5		
4	$1.4\cdot 10^{-3}$	0.4	$5.4\cdot 10^{-3}$	0.4	$3.0\cdot 10^{-4}$	0.6	$1.1\cdot 10^{-3}$	0.7	$7.1\cdot 10^{-3}$	1.4	$2.7\cdot 10^{-2}$	0.8	$1.2\cdot 10^{-1}$	4.4	$5.9\cdot 10^{-1}$	2.5	$4.5\cdot 10^0$	6.9		
5	$1.4\cdot 10^{-3}$	0.4	$1.8\cdot 10^{-3}$	0.3	$9.7\cdot 10^{-5}$	0.4	$5.5\cdot 10^{-4}$	0.9	$3.4\cdot 10^{-3}$	1.1	$1.6\cdot 10^{-2}$	1.4	$1.0\cdot 10^{-1}$	4.5	$5.2\cdot 10^{-1}$	5.2	$4.2\cdot 10^0$	10.2		
6	$1.4\cdot 10^{-3}$	0.4	$1.3\cdot 10^{-3}$	0.3	$6.2\cdot 10^{-5}$	0.3	$2.3\cdot 10^{-4}$	0.5	$1.1\cdot 10^{-3}$	1.0	$7.0\cdot 10^{-3}$	1.5	$1.9\cdot 10^{-1}$	0.5	$1.2\cdot 10^{-1}$	5.8	$5.4\cdot 10^{-1}$	6.6	$4.3\cdot 10^0$	15.0
7	$1.4\cdot 10^{-3}$	0.4	$1.2\cdot 10^{-3}$	0.2	$6.2\cdot 10^{-5}$	0.5	$3.2\cdot 10^{-4}$	0.5	$2.3\cdot 10^{-3}$	1.8	$1.3\cdot 10^{-2}$	0.9	$1.5\cdot 10^{-1}$	8.0	$5.5\cdot 10^{-1}$	7.4	$4.2\cdot 10^0$	18.4		
8	$1.4\cdot 10^{-3}$	0.4	$1.6\cdot 10^{-3}$	0.4	$1.2\cdot 10^{-4}$	0.6	$7.3\cdot 10^{-4}$	0.8	$4.3\cdot 10^{-3}$	1.8	$1.8\cdot 10^{-2}$	1.4	$1.2\cdot 10^{-1}$	6.5	$5.4\cdot 10^{-1}$	12.9	$4.3\cdot 10^0$	36.5		
9	$1.4\cdot 10^{-3}$	0.4	$1.5\cdot 10^{-3}$	0.3	$6.9\cdot 10^{-5}$	0.4	$3.0\cdot 10^{-4}$	0.6	$1.3\cdot 10^{-3}$	1.2	$3.3\cdot 10^{-3}$	0.7	$1.4\cdot 10^{-1}$	2.6	$8.4\cdot 10^{-2}$	4.1	$5.2\cdot 10^{-1}$	20.4	$3.8\cdot 10^0$	52.8

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Table S7. Summary of resistances classified by characteristic time constants during discharge, as shown in Figure 3.

SOC	R_{Bulk}	$R_{\text{GB-Contact}}$	R_{int}	R_{ct}
		τ_1 : $<10^{-5}$ s	τ_{H} : $10^{-5}\text{--}10^{-2}$ s	τ_{H} : $<10^{-2}\text{--}10^0$ s
1	$12.9\ \Omega\cdot\text{cm}^2$	$0.4\ \Omega\cdot\text{cm}^2$	$1.9\ \Omega\cdot\text{cm}^2$	$5.1\ \Omega\cdot\text{cm}^2$
2	$12.8\ \Omega\cdot\text{cm}^2$	$0.4\ \Omega\cdot\text{cm}^2$	$2.4\ \Omega\cdot\text{cm}^2$	$6.3\ \Omega\cdot\text{cm}^2$
3	$12.7\ \Omega\cdot\text{cm}^2$	$0.4\ \Omega\cdot\text{cm}^2$	$2.2\ \Omega\cdot\text{cm}^2$	$7.6\ \Omega\cdot\text{cm}^2$
4	$12.7\ \Omega\cdot\text{cm}^2$	$0.4\ \Omega\cdot\text{cm}^2$	$3.1\ \Omega\cdot\text{cm}^2$	$7.7\ \Omega\cdot\text{cm}^2$
5	$12.7\ \Omega\cdot\text{cm}^2$	$0.4\ \Omega\cdot\text{cm}^2$	$2.8\ \Omega\cdot\text{cm}^2$	$11.1\ \Omega\cdot\text{cm}^2$
6	$12.7\ \Omega\cdot\text{cm}^2$	$0.4\ \Omega\cdot\text{cm}^2$	$3.6\ \Omega\cdot\text{cm}^2$	$12.9\ \Omega\cdot\text{cm}^2$
7	$12.7\ \Omega\cdot\text{cm}^2$	$0.4\ \Omega\cdot\text{cm}^2$	$3.1\ \Omega\cdot\text{cm}^2$	$16.3\ \Omega\cdot\text{cm}^2$
8	$12.7\ \Omega\cdot\text{cm}^2$	$0.4\ \Omega\cdot\text{cm}^2$	$3.7\ \Omega\cdot\text{cm}^2$	$20.7\ \Omega\cdot\text{cm}^2$
9	$12.6\ \Omega\cdot\text{cm}^2$	$0.4\ \Omega\cdot\text{cm}^2$	$3.2\ \Omega\cdot\text{cm}^2$	$27.2\ \Omega\cdot\text{cm}^2$

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Table S8. Summary of peak fitting results from DRT patterns (*in situ* EIS measurement during charge process). In/InLi|SE|LTO 2E cell; LTO was delithiated until 1.38 V vs. In/InLi (referring to SOC 18).

	P0		P1		P2		P3		P4		P5		P6		P7		P8		P9	
	Center τ / s	Area / $\Omega \cdot \text{cm}^2$	Center τ / s	Area / $\Omega \cdot \text{cm}^2$	Center τ / s	Area / $\Omega \cdot \text{cm}^2$	Center τ / s	Area / $\Omega \cdot \text{cm}^2$	Center τ / s	Area / $\Omega \cdot \text{cm}^2$	Center τ / s	Area / $\Omega \cdot \text{cm}^2$	Center τ / s	Area / $\Omega \cdot \text{cm}^2$	Center τ / s	Area / $\Omega \cdot \text{cm}^2$	Center τ / s	Area / $\Omega \cdot \text{cm}^2$	Center τ / s	Area / $\Omega \cdot \text{cm}^2$
10	$1.4 \cdot 10^{-6}$	0.5	$1.6 \cdot 10^{-5}$	0.4	$7.8 \cdot 10^{-5}$	0.3	$2.6 \cdot 10^{-4}$	0.6	$1.9 \cdot 10^{-3}$	1.4	$2.1 \cdot 10^{-2}$	1.9	$8.8 \cdot 10^{-2}$	2.4	$1.5 \cdot 10^{-1}$	0.8	$5.9 \cdot 10^{-1}$	14.6	$4.0 \cdot 10^0$	18.1
11	$1.4 \cdot 10^{-6}$	0.5	$1.6 \cdot 10^{-5}$	0.4	$1.1 \cdot 10^{-4}$	0.6	$6.3 \cdot 10^{-4}$	0.8	$3.5 \cdot 10^{-3}$	0.7	$2.3 \cdot 10^{-2}$	1.9	$1.2 \cdot 10^{-1}$	3.8	$5.8 \cdot 10^{-1}$	10.2	$4.1 \cdot 10^0$	12.7		
12	$1.4 \cdot 10^{-6}$	0.5	$1.6 \cdot 10^{-5}$	0.4	$1.2 \cdot 10^{-4}$	0.5	$1.3 \cdot 10^{-3}$	1.5	$1.9 \cdot 10^{-2}$	1.6	$1.1 \cdot 10^{-1}$	4.2	$5.5 \cdot 10^{-1}$	8.6	$4.1 \cdot 10^0$	11.7				
13	$1.4 \cdot 10^{-6}$	0.5	$1.6 \cdot 10^{-5}$	0.3	$8.4 \cdot 10^{-5}$	0.5	$3.9 \cdot 10^{-4}$	0.6	$2.3 \cdot 10^{-3}$	0.9	$2.1 \cdot 10^{-2}$	1.8	$1.2 \cdot 10^{-1}$	4.0	$5.4 \cdot 10^{-1}$	7.7	$4.2 \cdot 10^0$	10.6		
14	$1.4 \cdot 10^{-6}$	0.6	$1.6 \cdot 10^{-5}$	0.4	$7.6 \cdot 10^{-5}$	0.4	$2.9 \cdot 10^{-4}$	0.5	$1.5 \cdot 10^{-3}$	0.7	$1.2 \cdot 10^{-2}$	1.2	$1.2 \cdot 10^{-1}$	5.8	$5.4 \cdot 10^{-1}$	5.1	$4.3 \cdot 10^0$	9.6		
15	$1.4 \cdot 10^{-6}$	0.6	$1.9 \cdot 10^{-5}$	0.4	$8.5 \cdot 10^{-5}$	0.1	$2.9 \cdot 10^{-4}$	0.8	$3.5 \cdot 10^{-3}$	0.8	$1.8 \cdot 10^{-2}$	1.0	$1.3 \cdot 10^{-1}$	5.7	$5.5 \cdot 10^{-1}$	3.9	$4.3 \cdot 10^0$	8.8		
16	$1.4 \cdot 10^{-6}$	0.7	$1.9 \cdot 10^{-5}$	0.4	$8.3 \cdot 10^{-5}$	0.3	$2.8 \cdot 10^{-4}$	0.4	$1.5 \cdot 10^{-3}$	0.5	$7.5 \cdot 10^{-3}$	0.6	$5.8 \cdot 10^{-2}$	3.1	$1.8 \cdot 10^{-1}$	3.3	$5.2 \cdot 10^{-1}$	3.2	$4.3 \cdot 10^0$	9.0
17	$1.4 \cdot 10^{-6}$	0.9	$2.3 \cdot 10^{-5}$	0.5	$1.6 \cdot 10^{-4}$	0.5	$1.5 \cdot 10^{-3}$	1.2	$1.3 \cdot 10^{-2}$	1.6	$7.2 \cdot 10^{-2}$	4.2	$3.4 \cdot 10^{-1}$	5.8	$5.1 \cdot 10^0$	28.1				
18	$1.4 \cdot 10^{-6}$	1.1	$2.2 \cdot 10^{-5}$	0.5	$1.8 \cdot 10^{-4}$	0.8	$1.3 \cdot 10^{-3}$	1.2	$7.2 \cdot 10^{-3}$	2.2	$3.9 \cdot 10^{-2}$	4.5	$2.1 \cdot 10^{-1}$	8.3	$5.4 \cdot 10^0$	87.0				

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Table S9. Summary of resistance classified by characteristic time constants during charge, as shown in Figure 3.

SOC	R_{Bulk}	$R_{\text{GB+Contact}}$	R_{Int}	R_{ct}
		τ_1 : $<10^{-5}$ s	τ_{11} : 10^{-5} – 10^{-2} s	τ_{111} : $<10^{-2}$ – 10^0 s
10	$13.3 \Omega \cdot \text{cm}^2$	$0.5 \Omega \cdot \text{cm}^2$	$2.8 \Omega \cdot \text{cm}^2$	$19.8 \Omega \cdot \text{cm}^2$
11	$13.3 \Omega \cdot \text{cm}^2$	$0.5 \Omega \cdot \text{cm}^2$	$2.5 \Omega \cdot \text{cm}^2$	$15.9 \Omega \cdot \text{cm}^2$
12	$13.4 \Omega \cdot \text{cm}^2$	$0.5 \Omega \cdot \text{cm}^2$	$2.4 \Omega \cdot \text{cm}^2$	$14.4 \Omega \cdot \text{cm}^2$
13	$13.5 \Omega \cdot \text{cm}^2$	$0.5 \Omega \cdot \text{cm}^2$	$2.3 \Omega \cdot \text{cm}^2$	$13.5 \Omega \cdot \text{cm}^2$
14	$13.6 \Omega \cdot \text{cm}^2$	$0.6 \Omega \cdot \text{cm}^2$	$1.9 \Omega \cdot \text{cm}^2$	$12.1 \Omega \cdot \text{cm}^2$
15	$13.7 \Omega \cdot \text{cm}^2$	$0.6 \Omega \cdot \text{cm}^2$	$2.2 \Omega \cdot \text{cm}^2$	$10.6 \Omega \cdot \text{cm}^2$
16	$13.7 \Omega \cdot \text{cm}^2$	$0.7 \Omega \cdot \text{cm}^2$	$2.2 \Omega \cdot \text{cm}^2$	$9.7 \Omega \cdot \text{cm}^2$
17	$13.5 \Omega \cdot \text{cm}^2$	$0.9 \Omega \cdot \text{cm}^2$	$2.2 \Omega \cdot \text{cm}^2$	$11.6 \Omega \cdot \text{cm}^2$
18	$13.4 \Omega \cdot \text{cm}^2$	$1.1 \Omega \cdot \text{cm}^2$	$4.8 \Omega \cdot \text{cm}^2$	$12.7 \Omega \cdot \text{cm}^2$

SI-15

Supplementary Note 4: Evaluation of quality of the 3E impedance data: The Kramers-Kronig (K-K) test was applied to validate the 2E and 3E impedance data. In principle, they are required to fulfill the conditions of causality, linearity, and stability for further use in EIS analysis.[5] In the K-K test using the Lin-KK tool (<https://www.iam.kit.edu/et/english/Lin-KK.php>),[6, 7] the WE, CE, and 2E impedance data exhibit less than $\pm 0.3\%$ residuals for both the real and imaginary parts, as shown in Figures S8a–c. In general, the relative residuals should be less than $\pm 1.0\%$ to fulfill the K-K relation. Therefore, the relative residuals strongly support the high quality of impedance data collected using the 3E setup described herein (i.e., the corresponding DRT analyses are reliable). By analyzing the involved electrochemical processes from DRT, suitable ranges for ECM fitting (for revealing the interface-related processes) could be 100 kHz–100 mHz for the WE:LTO and 1.5 kHz–100 mHz for the CE:In/InLi.

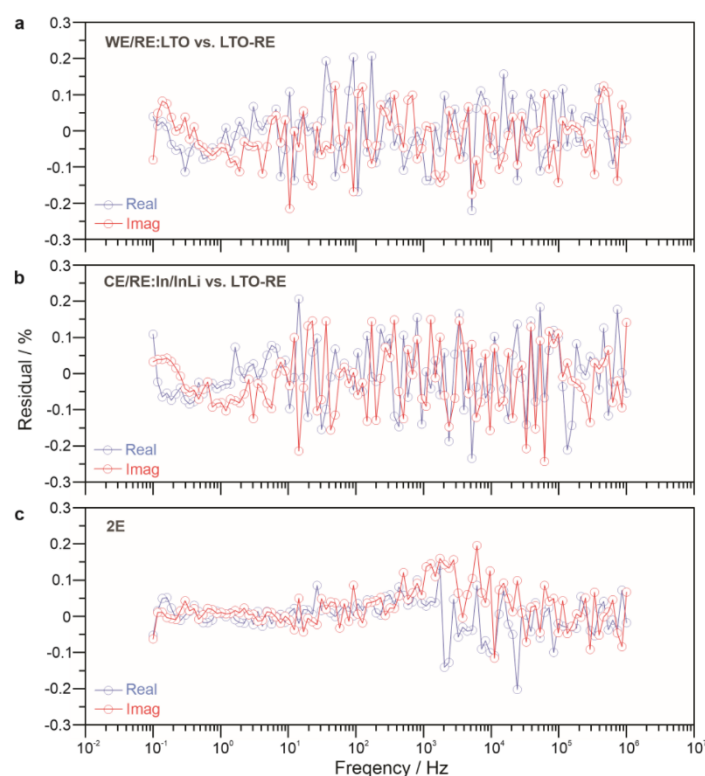


Figure S8. Validation of 3E and 2E impedance data by Kramers-Kronig test. (a–c) K-K test results for the WE/RE (3E), CE/RE (3E), and WE/CE (2E). The impedance spectra collected from the In/InLi|SE|LTO-RE|SE|LTO 3E cell are depicted in Figure 5a.

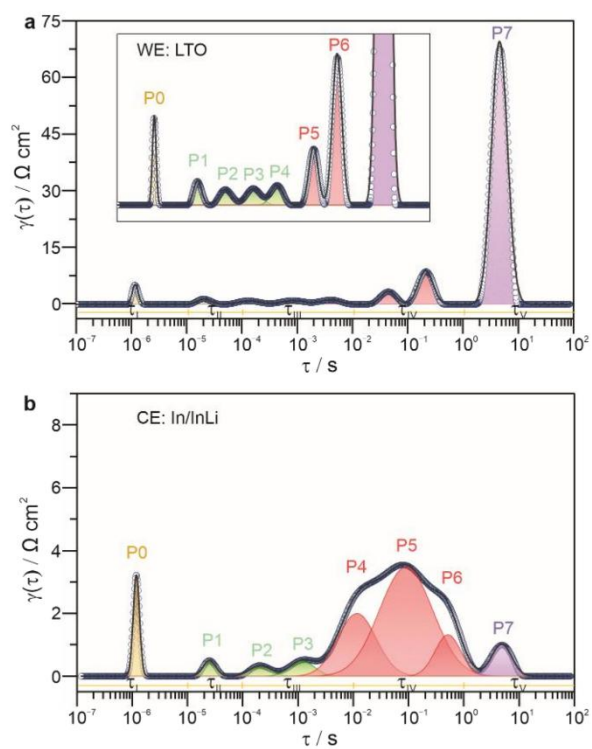


Figure S9. Individual peak fitting for (a) WE:LTO and (b) CE:In/InLi.

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Table S10. Summary of peak fitting results from DRT patterns. In/InLi|SE|LTO-RE|SE|LTO 3E cell; the cell was fully charged, i.e. the WE:LTO was fully delithiated (~ 1.38 V vs. In/InLi), and the CE:In/InLi was lithiated.

	P0		P1		P2		P3		P4		P5		P6		P7	
	Centered τ / s	Area / $\Omega \cdot \text{cm}^2$	Centered τ / s	Area / $\Omega \cdot \text{cm}^2$	Centered τ / s	Area / $\Omega \cdot \text{cm}^2$	Centered τ / s	Area / $\Omega \cdot \text{cm}^2$	Centered τ / s	Area / $\Omega \cdot \text{cm}^2$	Centered τ / s	Area / $\Omega \cdot \text{cm}^2$	Centered τ / s	Area / $\Omega \cdot \text{cm}^2$	Centered τ / s	Area / $\Omega \cdot \text{cm}^2$
LTO	$1.2 \cdot 10^{-6}$	1.6	$2.0 \cdot 10^{-5}$	1.0	$1.3 \cdot 10^{-4}$	0.9	$8.3 \cdot 10^{-4}$	1.2	$3.9 \cdot 10^{-3}$	1.2	$4.4 \cdot 10^{-2}$	2.6	$2.1 \cdot 10^{-1}$	6.8	$4.6 \cdot 10^0$	58.0
In/InLi	$1.2 \cdot 10^{-6}$	1.1	$2.5 \cdot 10^{-5}$	0.3	$2.0 \cdot 10^{-4}$	0.4	$1.2 \cdot 10^{-3}$	0.6	$1.2 \cdot 10^{-2}$	4.0	$8.9 \cdot 10^{-2}$	9.7	$5.1 \cdot 10^{-1}$	1.8	$4.8 \cdot 10^0$	1.1

Table S11. Summary of resistances classified by characteristic time constants, as shown in Figure 6.

	$R_{\text{SE+Contact}}$	R_{int}	R_{ct}
	τ_i : $<10^{-5}$ s	τ_{II} : 10^{-5} – 10^{-2} s	τ_{III} : $<10^{-2}$ – 10^0 s
LTO	$1.6 \Omega \cdot \text{cm}^2$	$4.2 \Omega \cdot \text{cm}^2$	$9.4 \Omega \cdot \text{cm}^2$
In/InLi	$1.1 \Omega \cdot \text{cm}^2$	$1.3 \Omega \cdot \text{cm}^2$	$15.5 \Omega \cdot \text{cm}^2$

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6.1.5. Supporting Information of Publication V

Supporting Information

Interfacial Anode Kinetics and Its Influence on Cycling Performance of Sulfide Solid-State Batteries

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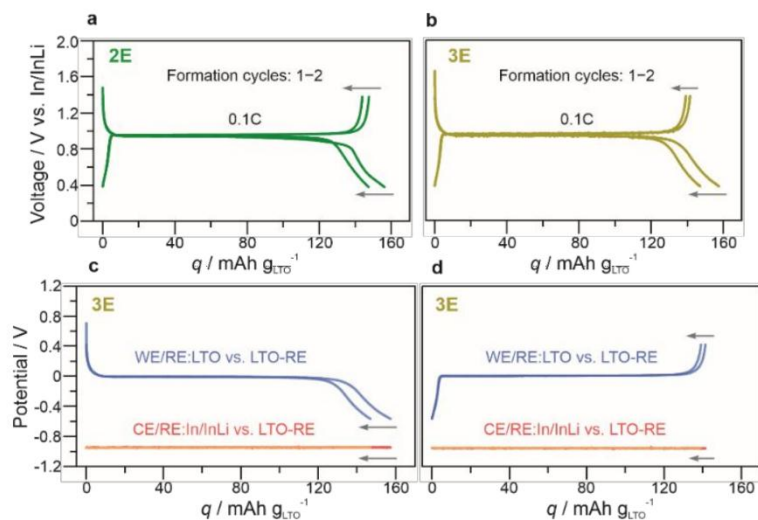


Figure S1. Potential/voltage profiles of the 2E and 3E SSB cells with LTO and In/InLi as WE and CE, respectively. Formation cycles of (a) 2E and (b–d) 3E cells with deconvoluted potentials of the WE/RE (blue) and CE/RE (red).

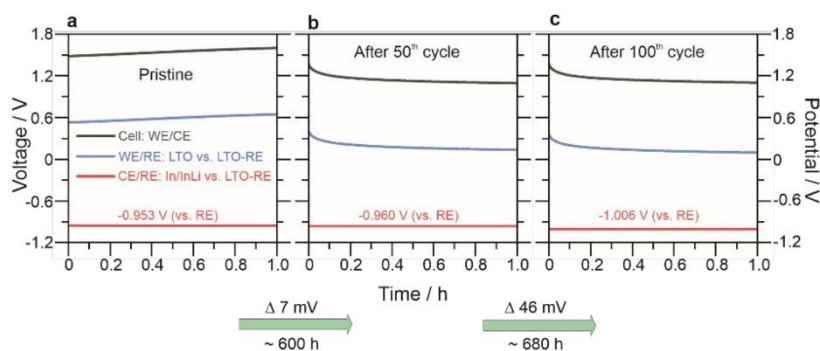


Figure S2. Potential drift of the LTO-RE during long-term cycling. Monitoring of potential of both the LTO WE and the In/InLi CE and of cell voltage during OCV resting (a) in the pristine state, (b) after 50 cycles, and (c) after 100 cycles. The potential of the LTO-RE was indirectly derived from that of the CE and the equilibrium potential of In/InLi (0.622 V vs. Li⁺/Li).

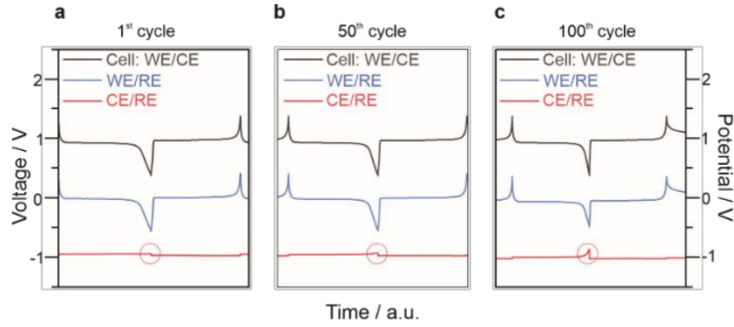


Figure S3. Voltage profiles of the 3E SSB cells with LTO and In/InLi as WE and CE, respectively, for selected cycles, with deconvoluted potentials of the WE/RE (blue) and CE/RE (red). The dotted red circles at the end of discharge (delithiated state of In/InLi) denote the sharp increase in CE potential upon cycling.

Supplementary note 1 (quantitative overpotential analysis of the 3E SSB cells with LTO and In/InLi as WE and CE, respectively).

Overpotential-I for the In/InLi and LTO electrodes was defined as the potential difference ($V_{\text{Diff-50}}$) between the delithiated and lithiated states (for 50 mAh g_{LTO}^{-1}) in the corresponding plateau regions, as shown in **Figure S4a**.

Overpotential-II for the In/InLi electrode was defined as the potential difference between the equilibrium and end of (de)lithiation states (V_{End}). During cycling, some potential drift of the RE is inevitable. To minimize overestimation of overpotential growth upon cycling, an accumulated algorithm was applied (see **Figure S4b**). The equilibrium potential of the In/InLi electrode was determined by averaging the potential of the CE/RE during the initial 1 h OCV period ($\bar{V}_{\text{Eq}}$). The latter was used as the initial reference potential for the In/InLi electrode at both the delithiated and lithiated states (V_{EoD}^0 and V_{EoL}^0). This means that $V_{\text{EoD}}^0 = V_{\text{EoL}}^0 = \bar{V}_{\text{Eq}}$.

For the *overpotential-II* growth of the In/InLi electrode at the end of (de)lithiation in the following cycles, the relative increase can be extracted as follows: $V_{\text{EoD or EoL}}^n - V_{\text{EoD or EoL}}^{n-1}$, where $V_{\text{EoD or EoL}}^n$ is the CE/RE potential at the end of (de)lithiation in the n th cycle.

Consequently, it can be calculated according to the following equations: $\eta_{\text{EoD}}^m = \sum_{n=1}^m |V_{\text{EoD}}^n - V_{\text{EoD}}^{n-1}|$ and $\eta_{\text{EoL}}^m = \sum_{n=1}^m |V_{\text{EoL}}^n - V_{\text{EoL}}^{n-1}|$, with η_{EoD}^m and η_{EoL}^m representing the overpotential-II at the end of (de)lithiation in the m th cycle.

Overpotential-II for the LTO electrode was defined as the decrease (reduction) in potential window, as shown in **Figure S4b**. Initially, the potential range was set to 0.38–1.38 V vs. In/InLi. The last point of the OCV resting period was taken as initial WE/RE potential, i.e. $V_{\text{EoD}}^0 = V_{\text{Eq}}^{\text{End}}$. The corresponding decrease (reduction) in potential window of the LTO electrode in the n th cycle after (de)lithiation can be calculated as: $\Delta V_{\text{L}}^n = 1 \text{ V} - (V_{\text{EoD}}^{n-1} - V_{\text{EoL}}^n)$ and ΔV_{D}^n

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$= 1 \text{ V} - (V_{\text{EoD}}^n - V_{\text{EoL}}^n)$, with ΔV_{D}^n and ΔV_{L}^n representing the shrinkage and V_{EoD}^n and V_{EoL}^n the potential of the WE/RE at the end of (de)lithiation in the n th cycle.

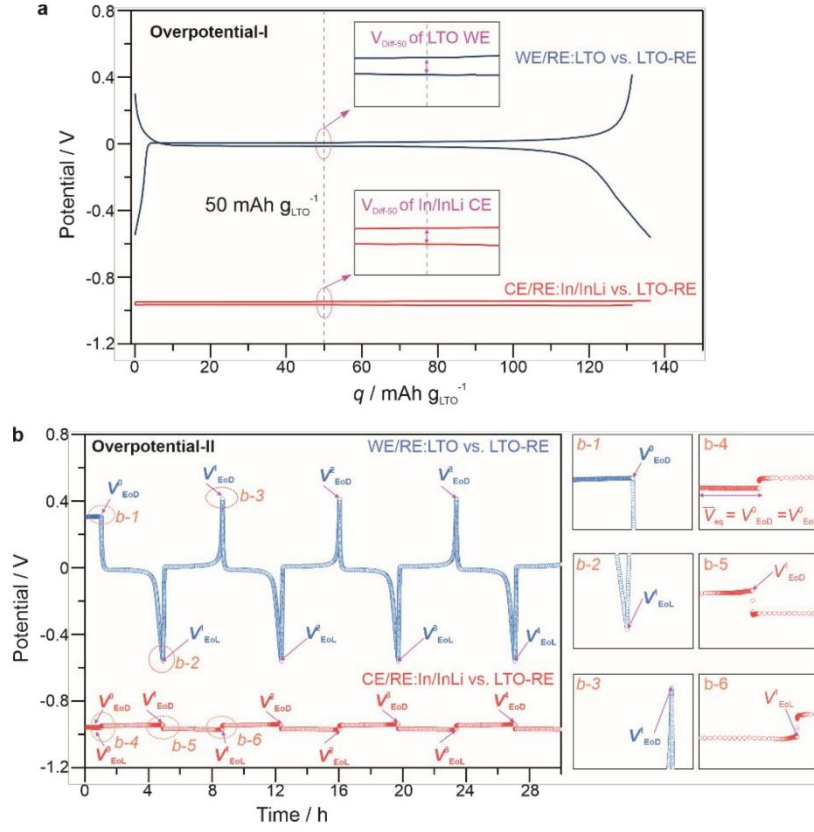


Figure S4. Definition of overpotential in the 3E SSB cells with LTO and In/InLi as WE and CE, respectively. (a) Overpotential-I for the In/InLi and LTO electrodes at $50 \text{ mAh g}_{\text{LTO}}^{-1}$. (b) Overpotential-II for the In/InLi and LTO electrodes at the end of (de)lithiation with zoomed-in views of the regions denoted as b-1 to b-6. By combining the overpotential-II at the lithiated and delithiated states, the overall effect within a single cycle was quantitatively determined (represented as overpotential-III for the In/InLi electrode), as shown in **Figure S5a,b**.

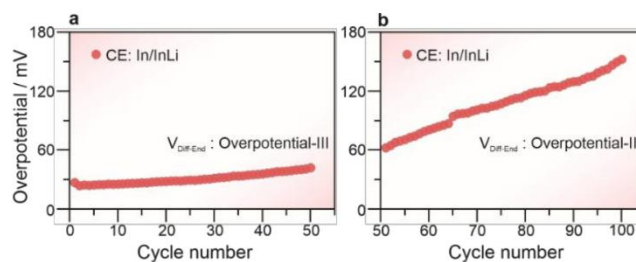


Figure S5. Overpotential for the In/InLi electrode in the 3E SSB cells based on the potential differences at the end of (de)lithiation ($V_{\text{Diff-End}}$). Denoted as overpotential-III, the evolution of overpotential was calculated for cycles (a) 1–50 and (b) 51–100. The discontinuity between the 50th and 51st cycles is due to *in situ* 3E-EIS measurements (see also **Figure 2**).

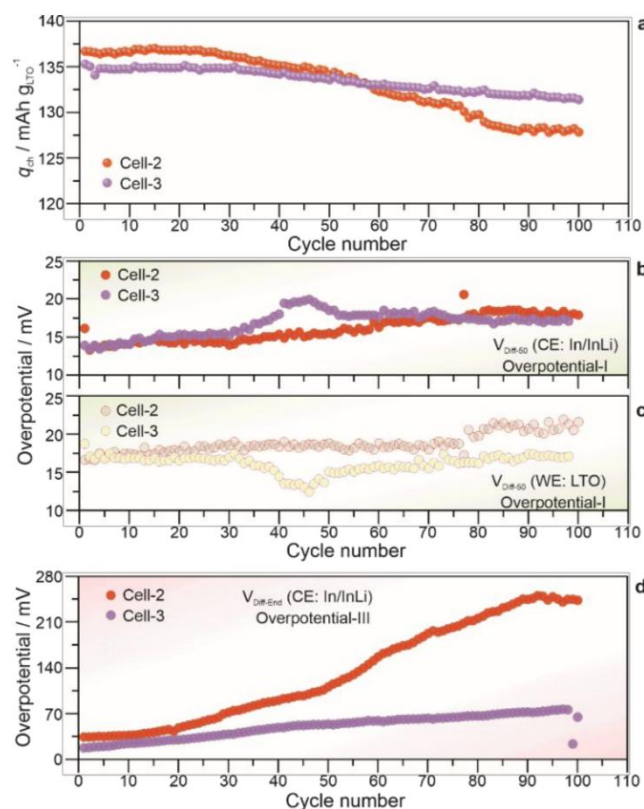


Figure S6. Long-term cycling performance of two additional 3E SSB cells and continuous monitoring of overpotential. (a) Cyclability of cell-2 and cell-3 at 0.2C (see **Figure 1d** for cell-1). (b,c) Overpotential-I ($V_{\text{Diff-50}}$) for the In/InLi and LTO electrodes and (d) overpotential-III for the In/InLi electrode for cycles 1–100.

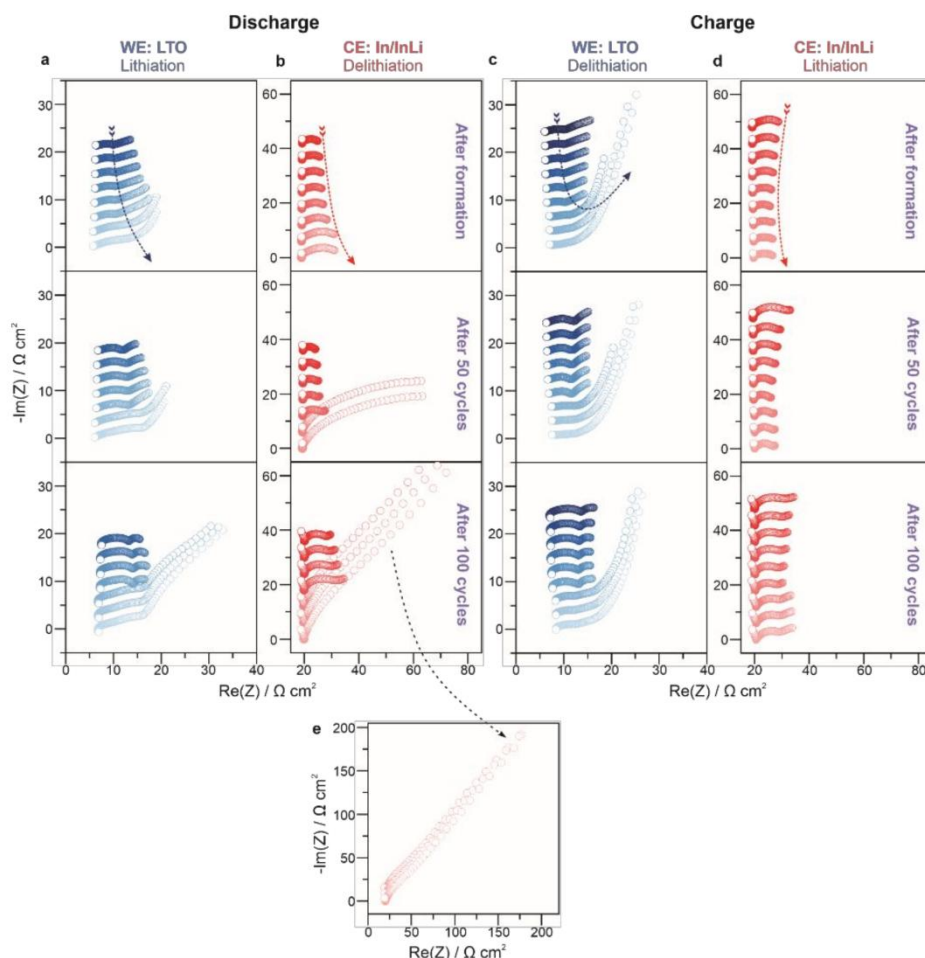


Figure S7. Nyquist plots of the electrochemical impedance for the 3E SSB cells from *in situ* EIS measurements. (a,c) LTO WE and (b,d) In/InLi CE upon (de)lithiation after cell formation as well as after 50 and 100 cycles. (e) Full view of the Nyquist plots for the In/InLi CE upon approaching the end of delithiation after 100 cycles.

Supplementary note 2 (quantitative analysis of interface-related resistances by DRT analysis).

As shown in **Figure S8**, peaks in the DRT patterns reflect the corresponding electrochemical processes with specific physical meanings characterized by their time constants. Four major regimes can be distinguished, namely τ_I ($\tau < 10^{-5}$ s), τ_{II} ($\tau = 10^{-5}$ – 10^{-2} s), τ_{III} ($\tau = 10^{-2}$ – 10^0 s), and τ_{IV} ($\tau > 10^0$ s). Specifically, the peaks within τ_I and τ_{III} account for the as-formed interphase(s) and charge-transfer processes, respectively.^{1, 2} By applying multiple Gaussian functions, peaks within certain regimes can be fitted, and the sum of peak areas was used to quantitatively examine the evolution of interfacial resistance (R_{int} or R_{ct}) without assigning

individual peaks to specific processes. The fitting results for both the τ_{II} and τ_{III} regimes (see also **Figure 4b**) are summarized in **Tables S1–S3**.

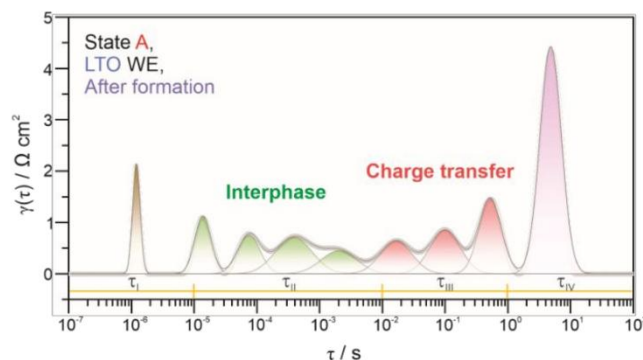


Figure S8. Representative DRT pattern with individual peak fits. In state A, after cell formation, the impedance data was converted into time domain for subsequent DRT analysis. The interface-related kinetics comprises transport through the as-formed interphase(s) and charge-transfer processes.

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Table S1. Summary of peak fitting of the DRT patterns for the LTO WE and In/InLi CE in 3E SSB cells (see **Figure 4b**). State A: Lithiation of LTO to 50 mAh g_{LTO}⁻¹ and delithiation of In/InLi.

After formation	P1		P2		P3		P4		P5		P6		P7		P8	
	Centered τ/s	Area / Ω cm ²	Centered τ/s	Area / Ω cm ²	Centered τ/s	Area / Ω cm ²	Centered τ/s	Area / Ω cm ²	Centered τ/s	Area / Ω cm ²	Centered τ/s	Area / Ω cm ²	Centered τ/s	Area / Ω cm ²	Centered τ/s	Area / Ω cm ²
LTO	1.4 · 10 ⁻³	0.8	7.3 · 10 ⁻³	0.8	3.8 · 10 ⁻³	1.2	2.0 · 10 ⁻³	0.7	1.6 · 10 ⁻³	0.9	9.9 · 10 ⁻³	1.2	5.2 · 10 ⁻³	1.5		
In/InLi	3.5 · 10 ⁻³	1.0	1.6 · 10 ⁻³	1.6	1.1 · 10 ⁻³	2.6	4.5 · 10 ⁻³	1.2								

After 50 cycles	P1		P2		P3		P4		P5		P6		P7		P8	
	Centered τ/s	Area / Ω cm ²	Centered τ/s	Area / Ω cm ²	Centered τ/s	Area / Ω cm ²	Centered τ/s	Area / Ω cm ²	Centered τ/s	Area / Ω cm ²	Centered τ/s	Area / Ω cm ²	Centered τ/s	Area / Ω cm ²	Centered τ/s	Area / Ω cm ²
LTO	1.3 · 10 ⁻³	1.0	6.5 · 10 ⁻³	0.7	3.7 · 10 ⁻³	2.1	1.3 · 10 ⁻³	0.5	4.5 · 10 ⁻³	0.7	2.1 · 10 ⁻²	0.8	1.2 · 10 ⁻³	0.7	6.2 · 10 ⁻³	1.8
In/InLi	2.7 · 10 ⁻³	1.2	1.2 · 10 ⁻³	2.2	5.7 · 10 ⁻³	1.1	3.2 · 10 ⁻³	0.6								

After 100 cycles	P1		P2		P3		P4		P5		P6		P7		P8	
	Centered τ/s	Area / Ω cm ²	Centered τ/s	Area / Ω cm ²	Centered τ/s	Area / Ω cm ²	Centered τ/s	Area / Ω cm ²	Centered τ/s	Area / Ω cm ²	Centered τ/s	Area / Ω cm ²	Centered τ/s	Area / Ω cm ²	Centered τ/s	Area / Ω cm ²
LTO	9.4 · 10 ⁻⁴	0.7	4.4 · 10 ⁻³	1.3	1.6 · 10 ⁻³	0.8	8.4 · 10 ⁻⁴	2.1	4.6 · 10 ⁻³	1.2	1.5 · 10 ⁻²	0.2	1.5 · 10 ⁻³	0.9	5.6 · 10 ⁻³	2.0
In/InLi	4.6 · 10 ⁻³	1.6	2.2 · 10 ⁻³	4.2	8.8 · 10 ⁻⁴	3.0	5.3 · 10 ⁻³	1.9								

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Table S2. Summary of peak fitting of the DRT patterns for the LTO WE and In/InLi CE in 3E SSB cells (see **Figure 4b**). State B: End of delithiation of LTO and end of lithiation of In/InLi.

After formation	P1		P2		P3		P4		P5		P6		P7		P8	
	Centered τ/s	Area / Ω cm ²	Centered τ/s	Area / Ω cm ²	Centered τ/s	Area / Ω cm ²	Centered τ/s	Area / Ω cm ²	Centered τ/s	Area / Ω cm ²	Centered τ/s	Area / Ω cm ²	Centered τ/s	Area / Ω cm ²	Centered τ/s	Area / Ω cm ²
LTO	1.7 · 10 ⁻³	0.9	1.0 · 10 ⁻⁴	0.9	6.1 · 10 ⁻⁴	1.4	3.6 · 10 ⁻³	1.1	2.0 · 10 ⁻³	2.2	1.4 · 10 ⁻³	3.9				
In/InLi	8.2 · 10 ⁻⁴	0.5	4.0 · 10 ⁻³	0.9	1.4 · 10 ⁻³	1.7	7.4 · 10 ⁻³	1.6	3.5 · 10 ⁻³	1.4						

After 50 cycles	P1		P2		P3		P4		P5		P6		P7		P8	
	Centered τ/s	Area / Ω cm ²	Centered τ/s	Area / Ω cm ²	Centered τ/s	Area / Ω cm ²	Centered τ/s	Area / Ω cm ²	Centered τ/s	Area / Ω cm ²	Centered τ/s	Area / Ω cm ²	Centered τ/s	Area / Ω cm ²	Centered τ/s	Area / Ω cm ²
LTO	1.7 · 10 ⁻³	1.3	1.1 · 10 ⁻²	1.0	6.2 · 10 ⁻³	1.3	4.2 · 10 ⁻³	1.3	2.1 · 10 ⁻²	2.0	1.6 · 10 ⁻³	4.0				
In/InLi	6.5 · 10 ⁻⁴	0.8	3.4 · 10 ⁻³	0.9	1.3 · 10 ⁻³	3.5	7.1 · 10 ⁻³	1.0	3.8 · 10 ⁻³	0.8						

After 100 cycles	P1		P2		P3		P4		P5		P6		P7		P8	
	Centered τ/s	Area / Ω cm ²	Centered τ/s	Area / Ω cm ²	Centered τ/s	Area / Ω cm ²	Centered τ/s	Area / Ω cm ²	Centered τ/s	Area / Ω cm ²	Centered τ/s	Area / Ω cm ²	Centered τ/s	Area / Ω cm ²	Centered τ/s	Area / Ω cm ²
LTO	1.1 · 10 ⁻³	1.3	4.8 · 10 ⁻³	0.9	1.4 · 10 ⁻³	0.8	6.6 · 10 ⁻⁴	1.2	3.3 · 10 ⁻³	1.7	1.7 · 10 ⁻³	2.0	1.4 · 10 ⁻³	4.2		
In/InLi	1.1 · 10 ⁻³	0.9	5.7 · 10 ⁻³	1.1	1.9 · 10 ⁻⁴	3.4	7.2 · 10 ⁻³	3.4	7.9 · 10 ⁻³	3.4						

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Table S3. Summary of peak fitting of the DRT patterns for the LTO WE and In/InLi CE in 3E SSB cells (see **Figure 4b**). State C: End of lithiation of LTO and end of delithiation of In/InLi.

After formation	P1		P2		P3		P4		P5		P6		P7		P8	
	Centered τ/s	Area / $\Omega \text{ cm}^2$	Centered τ/s	Area / $\Omega \text{ cm}^2$	Centered τ/s	Area / $\Omega \text{ cm}^2$	Centered τ/s	Area / $\Omega \text{ cm}^2$	Centered τ/s	Area / $\Omega \text{ cm}^2$	Centered τ/s	Area / $\Omega \text{ cm}^2$	Centered τ/s	Area / $\Omega \text{ cm}^2$	Centered τ/s	Area / $\Omega \text{ cm}^2$
LTO	$1.3 \cdot 10^{-3}$	0.7	$6.5 \cdot 10^{-3}$	0.7	$4.2 \cdot 10^{-2}$	1.9	$1.9 \cdot 10^{-3}$	1.0	$8.3 \cdot 10^{-3}$	2.0	$4.3 \cdot 10^{-2}$	1.8	$2.6 \cdot 10^{-1}$	3.0		
In/InLi	$5.7 \cdot 10^{-3}$	1.6	$2.7 \cdot 10^{-2}$	2.3	$1.8 \cdot 10^{-1}$	6.4	$5.3 \cdot 10^{-1}$	1.8								

After 50 cycles	P1		P2		P3		P4		P5		P6		P7		P8	
	Centered τ/s	Area / $\Omega \text{ cm}^2$	Centered τ/s	Area / $\Omega \text{ cm}^2$	Centered τ/s	Area / $\Omega \text{ cm}^2$	Centered τ/s	Area / $\Omega \text{ cm}^2$	Centered τ/s	Area / $\Omega \text{ cm}^2$	Centered τ/s	Area / $\Omega \text{ cm}^2$	Centered τ/s	Area / $\Omega \text{ cm}^2$	Centered τ/s	Area / $\Omega \text{ cm}^2$
LTO	$1.1 \cdot 10^{-2}$	0.8	$5.7 \cdot 10^{-2}$	0.9	$3.7 \cdot 10^{-1}$	2.0	$2.8 \cdot 10^{-2}$	1.9	$1.5 \cdot 10^{-2}$	2.8	$5.5 \cdot 10^{-2}$	1.3	$3.2 \cdot 10^{-1}$	2.3		
In/InLi	$4.5 \cdot 10^{-3}$	1.5	$2.1 \cdot 10^{-2}$	3.0	$9.8 \cdot 10^{-2}$	17.6	$5.8 \cdot 10^{-2}$	20.1								

After 100 cycles	P1		P2		P3		P4		P5		P6		P7		P8	
	Centered τ/s	Area / $\Omega \text{ cm}^2$	Centered τ/s	Area / $\Omega \text{ cm}^2$	Centered τ/s	Area / $\Omega \text{ cm}^2$	Centered τ/s	Area / $\Omega \text{ cm}^2$	Centered τ/s	Area / $\Omega \text{ cm}^2$	Centered τ/s	Area / $\Omega \text{ cm}^2$	Centered τ/s	Area / $\Omega \text{ cm}^2$	Centered τ/s	Area / $\Omega \text{ cm}^2$
LTO	$1.5 \cdot 10^{-3}$	0.7	$8.3 \cdot 10^{-3}$	1.6	$3.1 \cdot 10^{-1}$	0.7	$1.8 \cdot 10^{-3}$	2.8	$1.1 \cdot 10^{-3}$	3.2	$6.2 \cdot 10^{-2}$	1.4	$5.0 \cdot 10^{-1}$	10.4		
In/InLi	$2.5 \cdot 10^{-2}$	1.3	$9.2 \cdot 10^{-2}$	2.9	$4.6 \cdot 10^{-1}$	17.7	$2.4 \cdot 10^{-2}$	30.8								

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Table S4. Summary of accumulated interface-related resistances for the LTO WE and In/InLi CE in 3E SSB cells classified by characteristic time constants (see **Figure 4b**).

LTO	State A		State B		State C	
	R_{int}	R_{ct}	R_{int}	R_{ct}	R_{int}	R_{ct}
	$\tau_{\text{H}}: 10^{-5}\text{--}10^{-2} \text{ s}$	$\tau_{\text{H}}: 10^{-2}\text{--}10^0 \text{ s}$	$\tau_{\text{H}}: 10^{-5}\text{--}10^{-2} \text{ s}$	$\tau_{\text{H}}: 10^{-2}\text{--}10^0 \text{ s}$	$\tau_{\text{H}}: 10^{-5}\text{--}10^{-2} \text{ s}$	$\tau_{\text{H}}: 10^{-2}\text{--}10^0 \text{ s}$
After formation	$3.6 \Omega \text{ cm}^2$	$3.6 \Omega \text{ cm}^2$	$4.4 \Omega \text{ cm}^2$	$6.0 \Omega \text{ cm}^2$	$6.4 \Omega \text{ cm}^2$	$4.9 \Omega \text{ cm}^2$
After 50 cycles	$5.0 \Omega \text{ cm}^2$	$3.3 \Omega \text{ cm}^2$	$4.9 \Omega \text{ cm}^2$	$6.0 \Omega \text{ cm}^2$	$5.6 \Omega \text{ cm}^2$	$6.4 \Omega \text{ cm}^2$
After 100 cycles	$6.1 \Omega \text{ cm}^2$	$3.1 \Omega \text{ cm}^2$	$5.7 \Omega \text{ cm}^2$	$6.3 \Omega \text{ cm}^2$	$5.8 \Omega \text{ cm}^2$	$14.9 \Omega \text{ cm}^2$

In/InLi	State A		State B		State C	
	R_{int}	R_{ct}	R_{int}	R_{ct}	R_{int}	R_{ct}
	$\tau_{\text{H}}: 10^{-5}\text{--}10^{-2} \text{ s}$	$\tau_{\text{H}}: 10^{-2}\text{--}10^0 \text{ s}$	$\tau_{\text{H}}: 10^{-5}\text{--}10^{-2} \text{ s}$	$\tau_{\text{H}}: 10^{-2}\text{--}10^0 \text{ s}$	$\tau_{\text{H}}: 10^{-5}\text{--}10^{-2} \text{ s}$	$\tau_{\text{H}}: 10^{-2}\text{--}10^0 \text{ s}$
After formation	$1.0 \Omega \text{ cm}^2$	$5.5 \Omega \text{ cm}^2$	$1.3 \Omega \text{ cm}^2$	$4.8 \Omega \text{ cm}^2$	$1.6 \Omega \text{ cm}^2$	$10.5 \Omega \text{ cm}^2$
After 50 cycles	$1.3 \Omega \text{ cm}^2$	$4.0 \Omega \text{ cm}^2$	$1.5 \Omega \text{ cm}^2$	$5.7 \Omega \text{ cm}^2$	$1.5 \Omega \text{ cm}^2$	$40.7 \Omega \text{ cm}^2$
After 100 cycles	$1.6 \Omega \text{ cm}^2$	$9.0 \Omega \text{ cm}^2$	$2.0 \Omega \text{ cm}^2$	$10.2 \Omega \text{ cm}^2$	$4.2 \Omega \text{ cm}^2$	$54.5 \Omega \text{ cm}^2$

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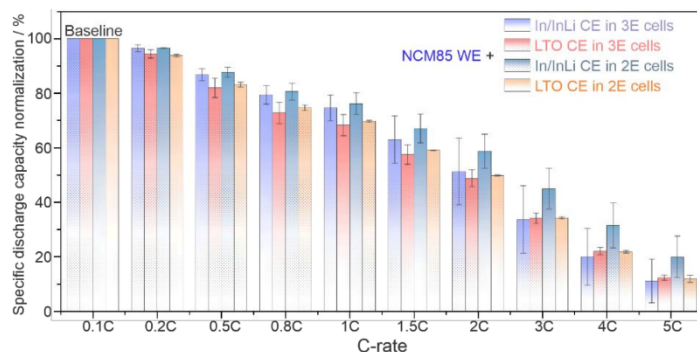


Figure S9. Normalized discharge capacities for different cell configurations: LiNbO_3 -coated NCM85 cathode as WE in combination with either In/InLi or LTO CE in 2E or 3E cells. The mean values and corresponding standard deviations are based on 2–3 independent cells for each configuration.

Table S5. Summary of specific and normalized discharge capacities during rate performance testing, as shown in **Figure 5**.

C-rate		0.1C	0.2C	0.5C	0.8C	1C	1.5C	2C	3C	4C	5C
In/InLi CE	$q_{\text{dis}} / \text{mAh g}_{\text{NCM85}}^{-1}$	201	194	176	160	151	129	109	77	50	30
	Normalized $q_{\text{dis}} / \%$	100.0	96.5	87.6	79.6	75.1	64.2	54.2	38.3	24.9	14.9
	SD / %	-	0.9	1.9	3.0	4.0	7.0	10.1	11.4	10.5	8.3
LTO CE	$q_{\text{dis}} / \text{mAh g}_{\text{NCM85}}^{-1}$	201	188	167	150	141	121	104	76	52	33
	Normalized $q_{\text{dis}} / \%$	100.0	93.5	83.1	74.6	70.1	60.2	51.7	37.8	25.9	16.4
	SD / %	-	1.0	2.2	2.6	2.4	2.2	1.9	1.1	0.8	1.0

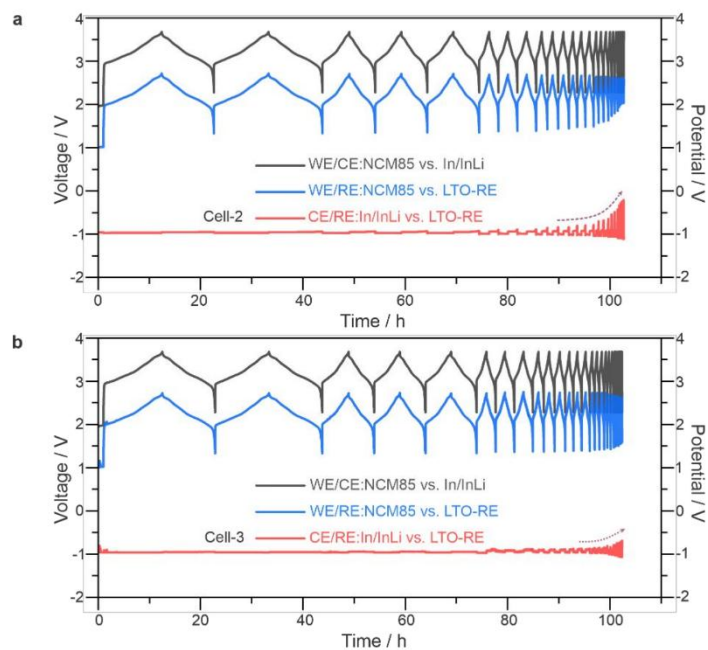


Figure S10. Voltage profiles and deconvoluted potentials of WE/RE and CE/RE for the 3E SSB cells with LiNbO_3 -coated NCM85 cathode and In/InLi anode. Independent cells denoted as (a) cell-2 and (b) cell-3.

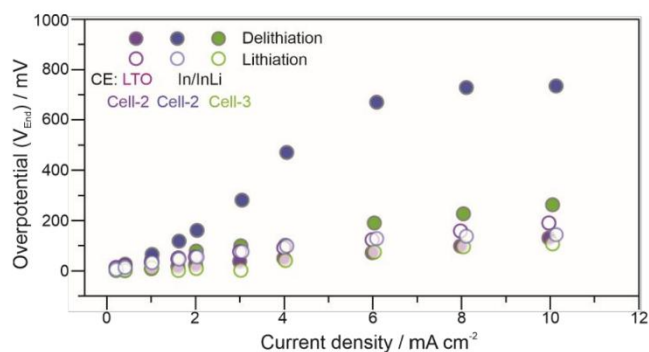


Figure S11. Overpotential for the LTO and In/InLi electrodes at the end of (de)lithiation as a function of current density.

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Table S6. Summary of design parameters used for the In/InLi CE prepared by stacking indium and lithium foils from the literature (for “stable” cycling over more than 500 cycles).

WE	Φ : indium / mm	t : indium / mm	Φ : lithium / mm	t : lithium / mm	Li_xIn	In/InLi delithiation current density / mA cm ⁻²	Temp. / °C	p / MPa	Ref.
$\text{LiNi}_{0.85}\text{Co}_{0.1}\text{Mn}_{0.05}\text{O}_2$ (PC-NCM85)	10	0.1	5	0.1	$\text{Li}_{0.29}\text{In}$	3.36	RT	250	3
$\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ (PC-NCM622)	24.5 mg		0.5 mg		$\text{Li}_{0.34}\text{In}$	3.8	RT	150	4
$\text{LiNi}_{0.85}\text{Co}_{0.12}\text{Mn}_{0.03}\text{O}_2$ (SC-NCM83)	9	0.125	6	0.05	$\text{Li}_{0.22}\text{In}$	2	45	81	5
$\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ (SC-NCM811)	10	0.05	0.287 mg		$\text{Li}_{0.17}\text{In}$	4.8	RT	760	6
$\text{LiNi}_{0.9}\text{Co}_{0.06}\text{Mn}_{0.04}\text{O}_2$ (SC-NCM90)	9	0.03	4	0.01	$\text{Li}_{0.08}\text{In}$	3.6	RT	120	7
TiS_2	10	0.05	8	0.03	$\text{Li}_{0.46}\text{In}$	2.44	30	30	8
Sulfur/C/SE	9	0.2	7	0.1	$\text{Li}_{0.37}\text{In}$	26.1	60	64	9
Cu_2S	9	0.1	0.5–1.0 mg		$\text{Li}_{0.18-0.36}\text{In}$	10	60	25	10

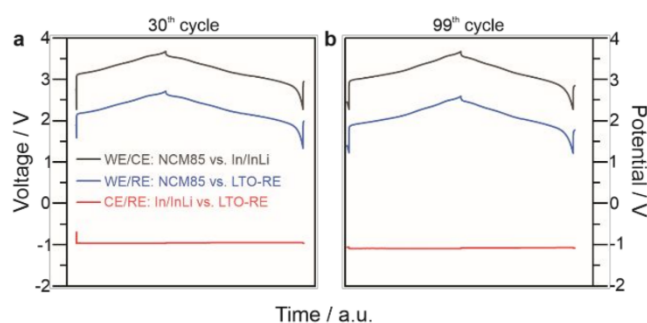


Figure S12. Monitoring of potential of the NCM85 and In/InLi electrodes and of cell voltage for cell-3. The (a) 30th and (b) 99th cycles are shown.

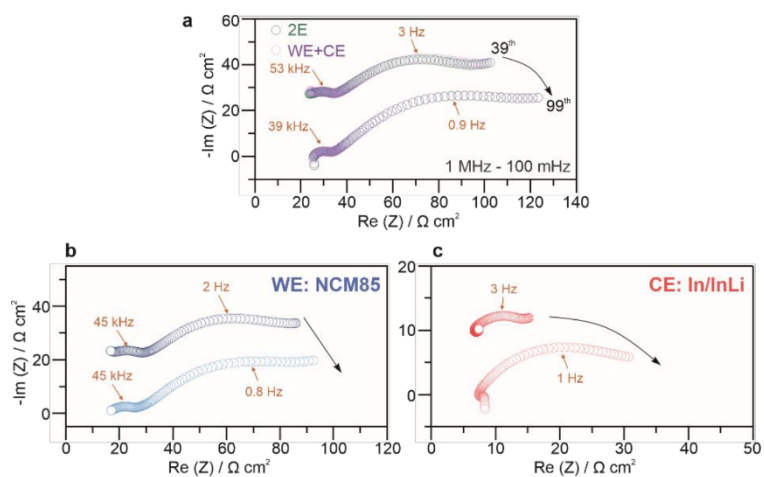


Figure S13. Nyquist plots of the electrochemical impedance at the end of discharge for cell-3. (a) 2E and 3E SSB cell data for cycles 39 and 99 measured between 1 MHz and 100 mHz and (b,c) corresponding deconvoluted impedances for the NCM85 and In/InLi electrodes. Characteristic frequencies are indicated.

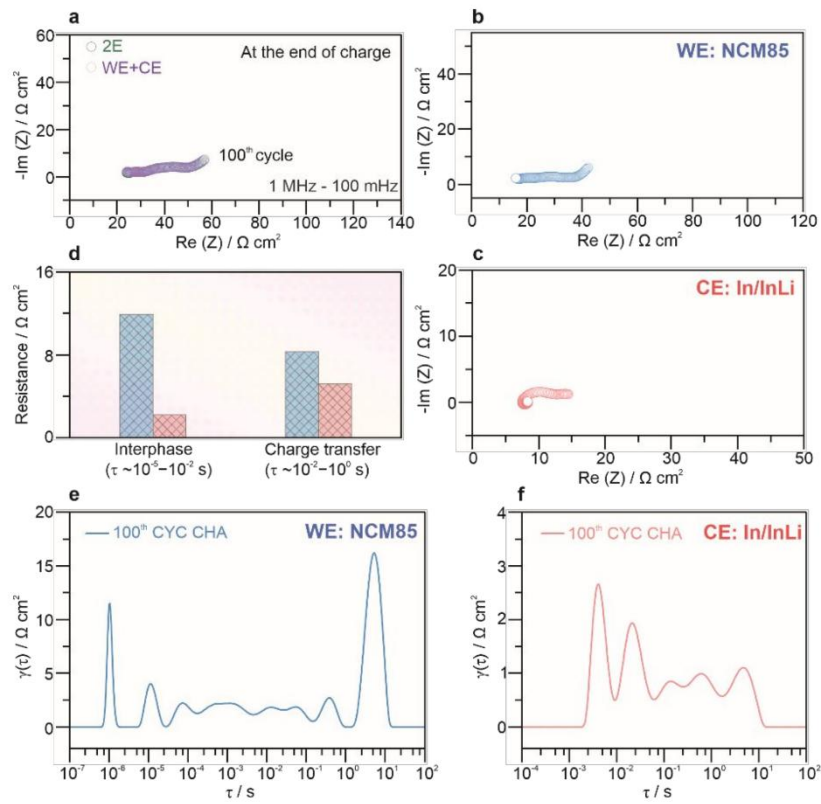


Figure S14. EIS-DRT analysis of cell-3 at the end of charge in the 100th cycle. (a) Nyquist plots of the electrochemical impedance for 2E and 3E SSB cell configurations measured between 1 MHz and 100 mHz. (b,c) Deconvoluted impedances for the NCM85 and In/InLi electrodes and (e,f) corresponding DRT patterns. (d) Interface-related resistances from peak fitting of the DRT patterns.

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Table S7. Summary of peak fitting of the DRT patterns for the NCM85 WE and In/InLi CE in 3E SSB cells (see **Figures 7** and **S13**).

DCH 39 th cycle	P1		P2		P3		P4		P5		P6		P7		P8	
	Centered τ/s	Area / Ω cm^2	Centered τ/s	Area / Ω cm^2	Centered τ/s	Area / Ω cm^2	Centered τ/s	Area / Ω cm^2	Centered τ/s	Area / Ω cm^2	Centered τ/s	Area / Ω cm^2	Centered τ/s	Area / Ω cm^2	Centered τ/s	Area / Ω cm^2
NCM85	$1.1 \cdot 10^{-3}$	4.4	$7.7 \cdot 10^{-4}$	2.5	$4.2 \cdot 10^{-4}$	3.1	$2.1 \cdot 10^{-3}$	4.4	$1.4 \cdot 10^{-3}$	13.6	$6.1 \cdot 10^{-3}$	19.2	$3.2 \cdot 10^{-1}$	14.5		
In/InLi	$9.7 \cdot 10^{-4}$	0.6	$4.2 \cdot 10^{-3}$	1.0	$2.7 \cdot 10^{-2}$	3.4	$8.3 \cdot 10^{-3}$	1.8	$4.3 \cdot 10^{-1}$	1.5						

DCH 99 th cycle	P1		P2		P3		P4		P5		P6		P7		P8	
	Centered τ/s	Area / Ω cm^2	Centered τ/s	Area / Ω cm^2	Centered τ/s	Area / Ω cm^2	Centered τ/s	Area / Ω cm^2	Centered τ/s	Area / Ω cm^2	Centered τ/s	Area / Ω cm^2	Centered τ/s	Area / Ω cm^2	Centered τ/s	Area / Ω cm^2
NCM85	$9.8 \cdot 10^{-4}$	3.3	$5.8 \cdot 10^{-3}$	1.6	$4.2 \cdot 10^{-4}$	4.2	$5.3 \cdot 10^{-3}$	7.3	$1.8 \cdot 10^{-2}$	4.5	$9.9 \cdot 10^{-2}$	31.3	$5.1 \cdot 10^{-1}$	15.6		
In/InLi	$1.6 \cdot 10^{-3}$	0.5	$9.3 \cdot 10^{-3}$	2.7	$2.5 \cdot 10^{-2}$	1.6	$1.1 \cdot 10^{-3}$	12.8	$5.9 \cdot 10^{-1}$	5.3						

CHA 100 th cycle	P1		P2		P3		P4		P5		P6		P7		P8	
	Centered τ/s	Area / Ω cm^2	Centered τ/s	Area / Ω cm^2	Centered τ/s	Area / Ω cm^2	Centered τ/s	Area / Ω cm^2	Centered τ/s	Area / Ω cm^2	Centered τ/s	Area / Ω cm^2	Centered τ/s	Area / Ω cm^2	Centered τ/s	Area / Ω cm^2
NCM85	$1.1 \cdot 10^{-3}$	3.2	$7.1 \cdot 10^{-4}$	2.1	$5.3 \cdot 10^{-4}$	5.2	$1.9 \cdot 10^{-3}$	1.4	$1.3 \cdot 10^{-3}$	3.3	$5.9 \cdot 10^{-2}$	2.2	$3.7 \cdot 10^{-1}$	2.8		
In/InLi	$4.1 \cdot 10^{-2}$	2.2	$2.1 \cdot 10^{-1}$	2.3	$1.2 \cdot 10^{-1}$	1.0	$6.1 \cdot 10^{-1}$	1.9								

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Table S8. Summary of accumulated interface-related resistances for the NCM85 WE and In/InLi CE in 3E SSB cells classified by characteristic time constants (see **Figures 7** and **S13**).

	NCM85		In/InLi	
	R_{int}	R_{ct}	R_{int}	R_{ct}
	$\tau_{H1}: 10^{-5}-10^{-2} \text{ s}$	$\tau_{H1}: 10^{-2}-10^0 \text{ s}$	$\tau_{H1}: 10^{-5}-10^{-2} \text{ s}$	$\tau_{H1}: 10^{-2}-10^0 \text{ s}$
DCH 39 th cycle	$14.4 \Omega \cdot \text{cm}^2$	$47.3 \Omega \cdot \text{cm}^2$	$1.6 \Omega \cdot \text{cm}^2$	$6.6 \Omega \cdot \text{cm}^2$
DCH 99 th cycle	$16.5 \Omega \cdot \text{cm}^2$	$51.5 \Omega \cdot \text{cm}^2$	$3.3 \Omega \cdot \text{cm}^2$	$19.7 \Omega \cdot \text{cm}^2$
CHA 100 th cycle	$11.9 \Omega \cdot \text{cm}^2$	$8.3 \Omega \cdot \text{cm}^2$	$2.2 \Omega \cdot \text{cm}^2$	$5.2 \Omega \cdot \text{cm}^2$

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6.1.6. Supporting Information of Publication VI

Supporting Information

Compromise between energy density and stability: Proper capacity balancing enables high-performance solid-state batteries

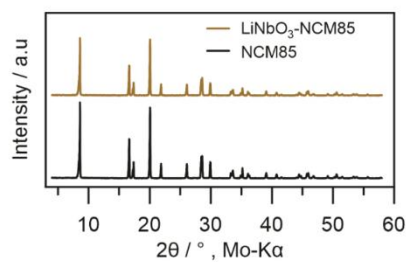


Figure S1. Powder XRD patterns collected from NCM85 before and after coating.

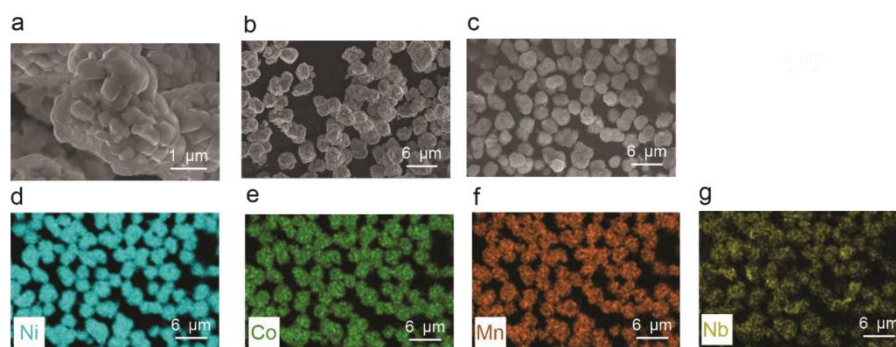


Figure S2. SEM-EDS of the as-prepared $\text{LiNbO}_3\text{-NCM85}$ particles. (a) High- and (b, c) low-magnification SEM images, along with (d–g) corresponding EDS maps for Ni, Co, Mn, and Nb, as indicated.

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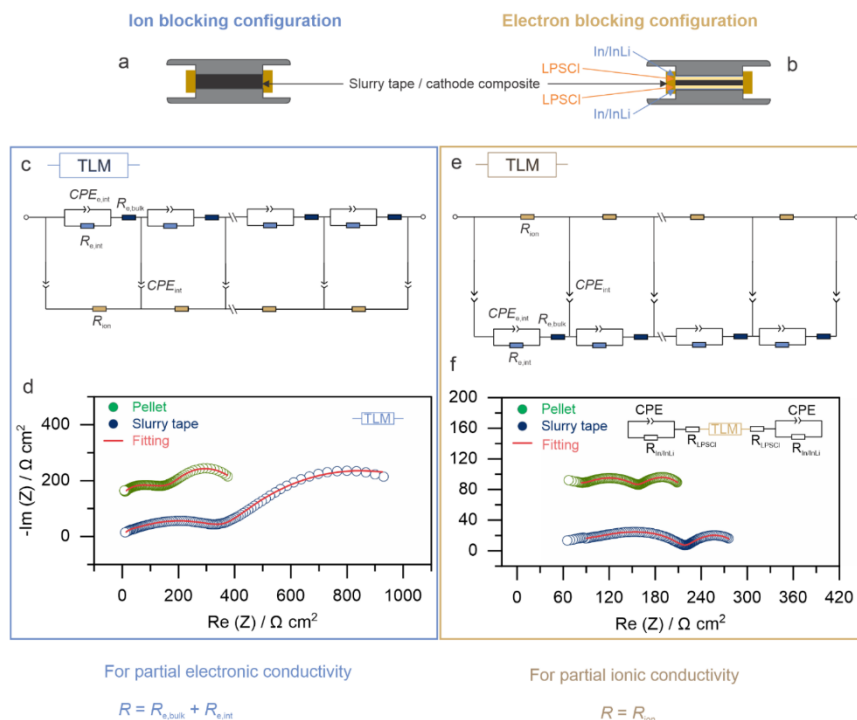


Figure S3. Transmission line model (TLM) fitting for determining effective ionic/electronic partial conductivities of pelletized and slurry-cast cathodes by AC polarization measurements at 81 MPa and 45 °C. (a, b) Schematics of the ion- and electron-blocking cell configurations used. (c–f) Corresponding TLMs and Nyquist plots with curve fits.

In the electronic branch, the resistance comprises the bulk transport ($R_{e,\text{bulk}}$, CAM) and interfacial charge transfer (CAM|CAM, CAM|Super C65, and Super C65|SuperC65). In the ionic branch, the resistance is modeled considering a resistor R_{ion} . For the electron-blocking configuration, the resistance of LPSCI (R_{LPSCI}) and the interfacial charge-transfer resistance ($R_{\text{In/InLi}}$) between In/InLi and LPSCI [see inset in panel (f)] were determined by impedance analysis of In/InLi|LPSCI|In/InLi cells.

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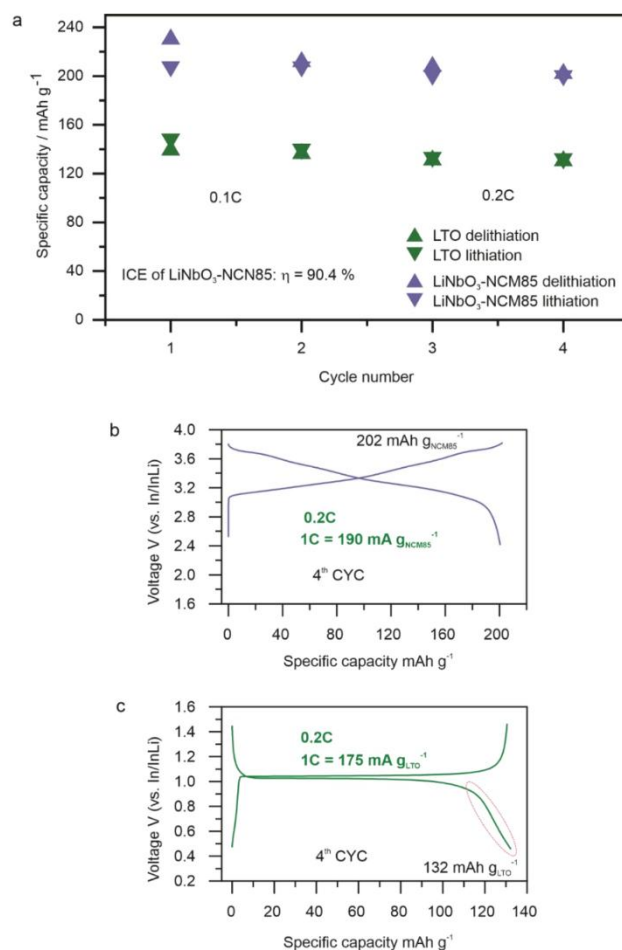


Figure S4. Electrochemical performance of the LiNbO₃-NCM85 cathode and LTO anode with In/InLi as counter electrode. The respective voltage windows were set to 2.28–3.68 V vs. In/InLi (equivalent to approx. 2.9–4.3 V vs. Li⁺/Li) and 0.38–1.38 V vs. In/InLi (equivalent to approx. 1.0–2.0 V vs. Li⁺/Li), respectively. (a) Specific capacities achieved in the initial four cycles at rates of 0.1C and 0.2C. (b, c) Voltage profiles of the fourth cycle at 0.2C for both the LiNbO₃-NCM85 and LTO cells.

The initial Coulomb efficiency (ICE) of the LiNbO₃-NCM85 cathode was 90.4%. The red dotted ellipse in the lithiation profile of LTO indicates the potential drop from the plateau

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to the end of lithiation. For capacity balancing, the specific charge capacity of $q_{\text{ch}} = 202 \text{ mAh g}_{\text{NCM85}}^{-1}$ and specific discharge capacity of $q_{\text{dis}} = 132 \text{ mAh g}_{\text{LTO}}^{-1}$ were used (see Figure 2).

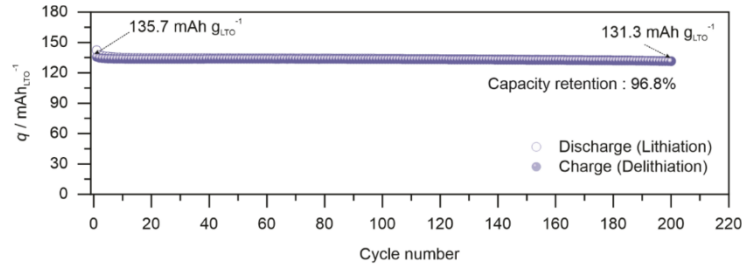


Figure S5. Long-term cycling performance of an In/InLi|LPSCI|LTO cell at 0.2C.

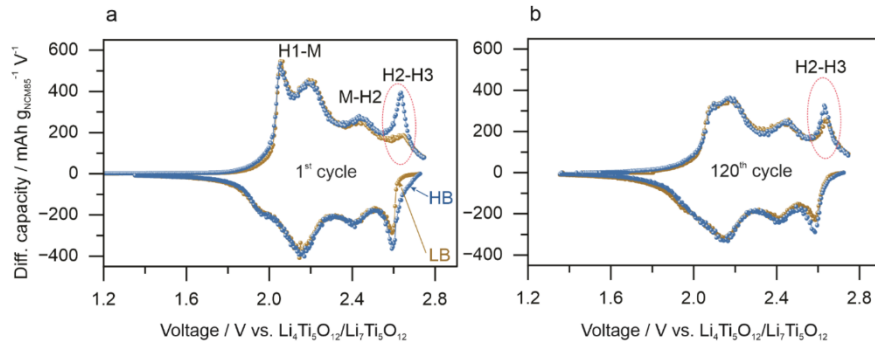


Figure S6. Differential capacity (dq/dV) curves. (a) First and (b) 120th cycle of the LTO|LPSCI|NCM85 HB and LB cells. The H2-H3 phase transition is highlighted.

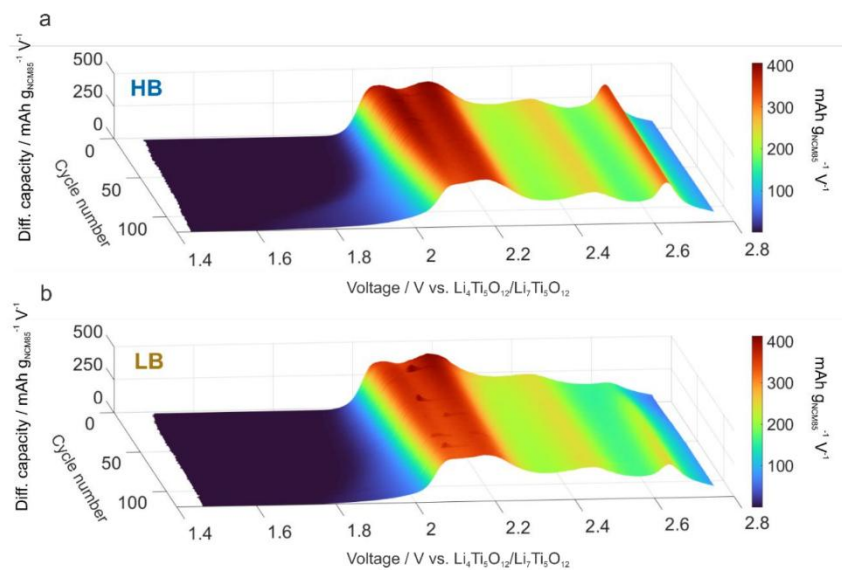


Figure S7. 3D differential capacity (dq/dV) plots as a function of cycle number and cell voltage. LTO|LPSC||NCM85 HB (a) and LB cells (b) during charge.

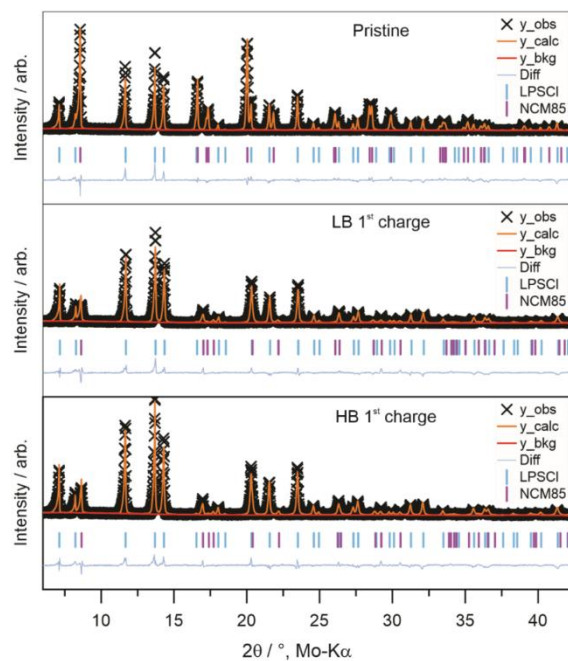


Figure S8. Rietveld refinement profiles of $\text{LiNbO}_3\text{-NCM85}$ and LPSCI against XRD patterns collected from the pristine cathode composite, and after first charge of the LTO|LPSCI|NCM85 HB and LB cells. The refined parameters are provided in Table S2.

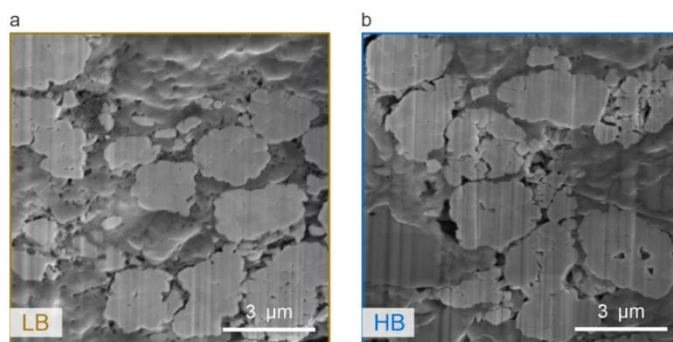


Figure S9. Low-magnification cross-sectional SEM images of the cathode (a) in LTO|LPSCI|NCM85 LB and (b) HB cells after long-term cycling (see Figure 4).

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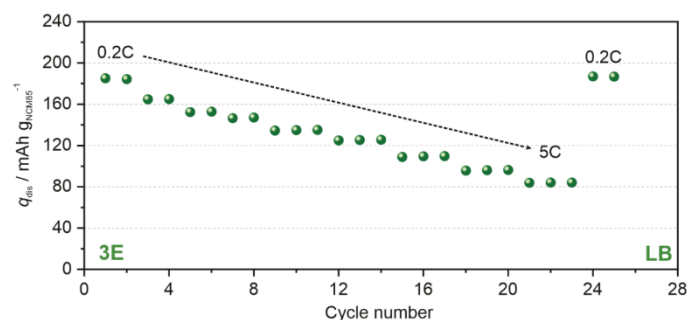


Figure S10. Rate performance (0.2, 0.5, 0.8, 1, 1.5, 2, 3, 4, and 5C) of a 3E LB cell.

Table S1. Effective ionic/electronic partial conductivities of pelletized and slurry-cast cathodes determined by TLM fitting of AC polarization data.

AC polarization	Pellet			Slurry		
	Cell #1	Cell #2	Cell #3	Cell #1	Cell #2	Cell #3
$\sigma_{\text{ion}} / \text{mS cm}^{-1}$	$4.7 \cdot 10^{-1}$	$2.0 \cdot 10^{-1}$	$4.4 \cdot 10^{-1}$	$1.7 \cdot 10^{-1}$	$1.1 \cdot 10^{-1}$	$1.5 \cdot 10^{-1}$
$\sigma_{\text{el}} / \text{mS cm}^{-1}$	$1.0 \cdot 10^{-1}$	$1.7 \cdot 10^{-1}$	$1.1 \cdot 10^{-1}$	$3.3 \cdot 10^{-2}$	$4.1 \cdot 10^{-2}$	$7.0 \cdot 10^{-2}$

Table S2. Summary of Rietveld refinement results. The respective XRD patterns are shown in Figure S8.

Sample	$a / \text{\AA}$	$c / \text{\AA}$	$V / \text{\AA}^3$	$R_{\text{wp}} / \%$
Pristine	2.8679(5)	14.1868(4)	100.940(3)	12.61
HB	2.8096(2)	14.1298(7)	95.771(4)	13.87
LB	2.8631(7)	14.2131(5)	96.575(2)	15.08

Table S3. Specific and normalized discharge capacities achieved in the rate performance testing of the LTO|LPSCI|NCM85 HB and LB cells (see Figure 4).

C-rate		0.1C	0.2C	0.5C	0.8C	1C	1.5C	2C	3C	4C	5C
HB	$q_{\text{dis}} / \text{mAh}$	204	197	181	170	164	152	141	122	108	96
	g_{NCM85}^{-1}										

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	Normalized $q_{\text{dis}} / \%$	100.0	96.6	88.7	83.3	80.4	74.5	69.1	59.8	52.9	47.1
LB	$q_{\text{dis}} / \text{mAh}$ $\text{g}_{\text{NCM85}}^{-1}$	199	186	165	153	147	134	125	110	97	85
	Normalized $q_{\text{dis}} / \%$	100.0	93.5	82.9	76.9	73.9	67.3	62.8	55.3	48.7	42.7

Table S4. Peak fitting results for the DRT patterns collected from the LTO|LPSCI|NCM85 HB and LB cells after 290 cycles at the end of discharge (see Figure 4).

	P1		P2		P3		P4		P5		P6	
	Centered τ / s	Area $/ \Omega \text{ cm}^2$	Centered τ / s	Area $/ \Omega \text{ cm}^2$	Centered τ / s	Area $/ \Omega \text{ cm}^2$	Centered τ / s	Area $/ \Omega \text{ cm}^2$	Centered τ / s	Area $/ \Omega \text{ cm}^2$	Centered τ / s	Area $/ \Omega \text{ cm}^2$
HB	$1.4 \cdot 10^{-6}$	2.8	$1.2 \cdot 10^{-5}$	2.3	$2.1 \cdot 10^{-4}$	6.9	$1.8 \cdot 10^{-3}$	10.1	$1.5 \cdot 10^{-2}$	26.4	$1.1 \cdot 10^{-1}$	20.4
LB	$1.5 \cdot 10^{-6}$	2.1	$1.2 \cdot 10^{-5}$	1.3	$5.2 \cdot 10^{-5}$	2.2	$8.7 \cdot 10^{-4}$	10.6	$1.1 \cdot 10^{-2}$	6.5	$1.2 \cdot 10^{-1}$	8.7

Table S5. Summary of accumulated interface-related resistances for the LTO|LPSCI|NCM85 HB and LB cells (see Figure 4 and Table S4).

	R_{int}	R_{ct}
	10^{-6} – 10^{-2} s	10^{-2} – 10^0 s
HB	$19.3 \Omega \text{ cm}^2$	$46.8 \Omega \text{ cm}^2$
LB	$14.1 \Omega \text{ cm}^2$	$15.2 \Omega \text{ cm}^2$

Table S6. Comparison of specific discharge capacities achieved with the 2E and 3E LB cells (see Figures 4 and S10).

C-rate		0.1C	0.2C	0.5C	0.8C	1C	1.5C	2C	3C	4C	5C
2E	$q_{\text{dis}} / \text{mAh}$	199	186	165	153	147	134	125	110	97	85
	$\text{g}_{\text{NCM85}}^{-1}$										
3E	$q_{\text{dis}} / \text{mAh}$	-	185	165	153	147	135	125	109	96	84
	$\text{g}_{\text{NCM85}}^{-1}$										

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Table S7. Summary of the cut-off potentials of WE, CE, and full cell voltage at the end of charge and discharge during rate capability testing for the 3E LB cell shown in Figure 6a. The predefined voltage window was 1.35–2.75 V vs. $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_7\text{Ti}_5\text{O}_{12}$, with the reference potential of LTO-RE being 1.55 V vs. Li^+/Li .

LB 3E		At the end of charge			At the end of discharge		
C-rate	Cycle no.	WE / V vs. Li^+/Li	CE / V vs. Li^+/Li	WE-CE / V	WE / V vs. Li^+/Li	CE / V vs. Li^+/Li	WE-CE / V
0.2C	1	4.1919	1.4418	2.7501	2.9370	1.5870	1.3500
	2	4.1931	1.4431	2.7500	2.9445	1.5944	1.3501
0.5C	3	4.1694	1.4193	2.7501	2.9554	1.6054	1.3500
	4	4.1738	1.4236	2.7502	2.9621	1.6120	1.3501
0.8C	5	4.1580	1.4078	2.7502	2.9706	1.6207	1.3499
	6	4.1603	1.4103	2.7500	2.9760	1.6259	1.3501
1C	7	4.1521	1.4021	2.7500	2.9830	1.6329	1.3501
	8	4.1537	1.4036	2.7501	2.9856	1.6356	1.3500
1.5C	9	4.1345	1.3845	2.7500	2.9899	1.6399	1.3500
	10	4.1353	1.3853	2.7500	2.9945	1.6445	1.3500
	11	4.1379	1.3876	2.7503	2.9993	1.6492	1.3501
2C	12	4.1295	1.3794	2.7501	3.0002	1.6502	1.3500
	13	4.1296	1.3796	2.7500	3.0050	1.6549	1.3501
	14	4.1293	1.3791	2.7502	3.0081	1.6581	1.3500
3C	15	4.1159	1.3658	2.7501	3.0075	1.6575	1.3500
	16	4.1204	1.3704	2.7500	3.0178	1.6678	1.3500
	17	4.1176	1.3675	2.7501	3.0167	1.6668	1.3499
4C	18	4.1182	1.3682	2.7500	3.0168	1.6668	1.3500
	19	4.1155	1.3655	2.7500	3.0225	1.6725	1.3500
	20	4.1157	1.3656	2.7501	3.0268	1.6768	1.3500
5C	21	4.1173	1.3672	2.7501	3.0297	1.6796	1.3501
	22	4.1151	1.3650	2.7501	3.0322	1.6823	1.3499

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	23	4.1160	1.3660	2.7500	3.0317	1.6817	1.3500
0.2C	24	4.2237	1.4736	2.7501	2.9879	1.6378	1.3501
	25	4.2303	1.4803	2.7500	3.0104	1.6603	1.3501

6.2. Scientific Contributions

6.2.1. List of Publications

Publication/manuscript within this thesis

06. **R. Zhang**, S. Payandeh, Y. Ma, D. Goonetilleke, Y. Tang, A. Kondrakov, J. Janek, T. Brezesinski. Compromise between energy density and stability: Proper capacity balancing enables high-performance solid-state batteries. *Energy Storage Mater.* **2026**, 87, 105045.
05. **R. Zhang**, A. Kondrakov, J. Janek, T. Brezesinski. Interfacial anode kinetics and its influence on cycling performance of sulfide solid-state batteries. *ACS Nano*, **2026**, 20, 1225–1237.
04. **R. Zhang**, A. Kondrakov, J. Janek, T. Brezesinski, Timescale identification of electrochemical processes in all-solid-state batteries using an advanced three-electrode cell setup. *Energy Storage Mater.* **2025**, 75, 104000.
03. **R. Zhang**, Y. Ma, Y. Tang, D. Goonetilleke, T. Diemant, J. Janek, A. Kondrakov, T. Brezesinski. Conformal $\text{Li}_2\text{HfO}_3/\text{HfO}_2$ Nanoparticle coatings on layered Ni-rich oxide cathodes for stabilizing interfaces in all-solid-state batteries. *Chem. Mat.* **2023**, 35, 6835–6844.
02. **R. Zhang**, F. Strauss, L. Jiang, L. Casalena, L. Li, J. Janek, A. Kondrakov, T. Brezesinski. Transition-metal interdiffusion and solid electrolyte poisoning in all-solid-state batteries revealed by cryo-TEM. *Chem. Commun.* **2023**, 59, 4600–4603.
01. Y. Ma*, **R. Zhang***, Y. Tang, Y. Ma, J.H. Teo, T. Diemant, D. Goonetilleke, J. Janek, M. Bianchini, A. Kondrakov, T. Brezesinski. Single-to few-layer nanoparticle cathode coating for thiophosphate-based all-solid-state batteries. *ACS Nano*, **2022**, 16, 18682–18694.

* Shared first authorship

Publications in preparation and contributed works during doctoral research

2026:

34. Y. Ma*, **R. Zhang***, Y. Tang, D. Goonetilleke, T. Diemant, J. Janek, A. Kondrakov, T. Brezesinski. Co-modified single-crystal Ni-rich cathode for high-performance all-solid-state batteries. *In preparation*.
33. **R. Zhang**, D. Goonetilleke, T. Lombardo, J. Du, A. Kondrakov, J. Janek, T. Brezesinski. NMX in LIBs and SSBs. *In preparation*.

32. P. Henkel, **R. Zhang**, R. Sahu, C. Kübel, J. Seenath, M. Schmitt, J. Janek, A. Kondrakov, T. Brezesinski. Improving the electro-chemo-mechanical stability of nickel-rich cathodes through tungsten modification for high-performance solid-state batteries. *In preparation*.
31. M. Schmitt, P. Dippell, P. Henkel, **R. Zhang**, P. Räke, J. Janek, M. Rohnke, A. Kondrakov, T. Brezesinski, F. Strauss. (Chemo-)Mechanical stability governs performance in dry-processed sheet-type solid-state batteries. *Submitted*.
30. H. Song, **R. Zhang**, C. Zheng, K. Münch, K. Shen, F. Liu, X. Hong, H. Wang, J. Meng, Y. Yan, W. Shi, M. He, Y. Ma, Y. Li, Z. Xiao, M.B. Shafqat, J. Wu, T. Song, C. Ma, L. Zheng, P. Gao, M. Safari, P. Henkel, J. Janek, T. Brezesinski, Q. Pang. High-rate, long-life all-solid-state lithium-sulfur batteries enabled by pre-embedded solid-solid redox mediator. *In preparation*.
29. J. Yang, **R. Zhang**, R. Zimmermanns, M. Schaller, S. Indris, J. Choi, S. Fleischmann, T. Brezesinski, F. Strauss. Tailored redox active catholytes enabling high-rate and high-loading all-solid-state lithium-sulfur batteries. *Adv. Mater.* **2026**, e13204.

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28. P. Henkel, **R. Zhang**, R. Sahu, C. Kübel, J. Janek, A. Kondrakov, T. Brezesinski. Beyond conventional coatings: Melt-infiltration of antiperovskites for high-voltage all-solid-state batteries. *ChemElectroChem* **2025**, 12, e202500286.
27. S. An, R. Sahu, **R. Zhang**, F. Ulusoy, C. Kübel, A. Kondrakov, J. Janek, T. Brezesinski. Titanium substitution to advance the prospect of NaMnO₂ cathodes for practical application in sodium-ion batteries. *ACS Appl. Energy Mater.* **2025**, 8, 10508–10518.
26. J. Lin, M. Schaller, **R. Zhang**, V. Baran, H. Liu, Z. Ding, S. Indris, A. Kondrakov, T. Brezesinski, F. Strauss. High-entropy argyrodite glass–ceramic electrolytes for all-solid-state batteries. *Mater. Futures* **2025**, 4, 025105.
25. J. Yang, M. Schaller, G. Cherkashinin, **R. Zhang**, S. Indris, D. A. D. Corte, A. Kondrakov, T. Brezesinski, F. Strauss. Glass-ceramic lithium thiophosphate electrolytes with enhanced conductivity and (chemo)mechanical properties for all-solid-state batteries. *Chem. Mater.* **2025**, 37, 4016–4026.
24. B. N. Nunes, L. Karger, **R. Zhang**, A. Kondrakov, T. Brezesinski. Enhanced cycling performance of the LiNiO₂ cathode in Li-ion batteries enabled by Nb-based surface coating. *ChemSusChem* **2025**, 18, e202402202.

23. S. An, L. Karger, P. Müller, J. Lin, S. Vasala, V. Baran, S.L. Dreyer, **R. Zhang**, F. Ulusoy, A. Kondrakov, J. Janek, T. Brezesinski. Exploring calcium pillaring of O3-type $\text{NaNi}_{0.9}\text{Ti}_{0.1}\text{O}_2$ to advance Na-ion battery technology. *Chem. Eng. J.* **2025**, 509, 160939.
22. M. Kissel, F. Walther, J. Hertle, T. Demuth, **R. Zhang**, P. Bröner, T. Brezesinski, K. Volz, J. Janek. Engineering the artificial cathode-electrolyte interphase coating for solid-state batteries via tailored annealing. *Chem. Mater.* **2025**, 37, 2192–2203.
21. Z. Tan, F. Xu, **R. Zhang**, Y. Huang, X. Liu, S. Yang, Y. Guo, Q. Liu, T. Wu, Y. Huang, T. Brezesinski, Y. Tang, W. Zhao. Surface stabilization for enhancing air/moisture resistance of layered Ni-rich oxide cathodes. *Energy Storage Mater.* **2025**, 76, 104169.
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19. H. Song, K. Münch, X. Liu, K. Shen, **R. Zhang**, T. Weintraut, Y. Yusim, D. Jiang, X. Hong, J. Meng, Y. Liu, M. He, Y. Li, P. Henkel, T. Brezesinski, J. Janek, Q. Pang. All-solid-state Li-S batteries with fast solid-solid sulfur reaction. *Nature* **2025**, 637, 846–853.

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18. B.N. Nunes, M. Ibrahim, **R. Zhang**, W. Zhao, Z. Zhang, A. Kondrakov, T. Brezesinski. Polyoxovanadates as effective coating materials for layered Ni-rich oxide cathodes in liquid- and solid-state batteries. *Batteries Supercaps* **2024**, 8, e202400601.
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15. L. Karger, S. Korneychuk, S. Siculo, H. Li, W. van den Bergh, **R. Zhang**, S. Indris, A. Kondrakov, J. Janek, T. Brezesinski. Decoupling substitution effects from point defects in layered Ni-rich oxide cathode materials for lithium-ion batteries. *Adv. Funct. Mater.* **2024**, 34, 2402444.
14. S. An, L. Karger, S. L. Dreyer, Y. Hu, E. Barbosa, **R. Zhang**, J. Lin, M. Fichtner, A. Kondrakov, J. Janek, T. Brezesinski. Improving cycling performance of the NaNiO_2 cathode in sodium-ion batteries by titanium substitution. *Mater. Futures* **2024**, 3, 035103.
13. L. Karger, B. N. Nunes, Y. Yusim, A. Mazilkin, **R. Zhang**, W. Zhao, A. Henss, A. Kondrakov, J. Janek, T. Brezesinski. Protective nanosheet coatings for thiophosphate-based all-solid-state batteries. *Adv. Mater. Interfaces* **2024**, 11, 2301067.
12. Y. Ma, **R. Zhang**, Y. Ma, T. Diemant, Y. Tang, S. Payandeh, D. Goonetilleke, D. Kitsche, X. Liu, J. Lin, A. Kondrakov, T. Brezesinski. Interface and electrode microstructure engineering for optimizing performance of the LiNiO_2 cathode in all-solid-state batteries. *Chem. Mater.* **2024**, 36, 2588–2598.
11. L. Karger, P. Henkel, S. Murugan, **R. Zhang**, A. Kondrakov, T. Brezesinski. From Li_2NiO_3 to high-performance LiNiO_2 cathodes for application in Li-ion and all-solid-state batteries. *Chem. Commun.* **2024**, 60, 11355–11358.
10. J. Du, J. Lin, **R. Zhang**, S. Wang, S. Indris, H. Ehrenberg, A. Kondrakov, T. Brezesinski, F. Strauss. Electrochemical testing and benchmarking of compositionally complex lithium argyrodite electrolytes for all-solid-state battery application. *Batteries Supercaps* **2024**, 7, e202400112.
09. W. van den Bergh, R. Yao, **R. Zhang**, A. Kondrakov, J. Janek, T. Brezesinski. Effect of salt selection and molar ratio in molten salt synthesis of single-crystalline LiNiO_2 . *J. Mater. Chem. A* **2024**, 12, 8683–8688.
08. L. Karger, S. Korneychuk, W. van den Bergh, S. L. Dreyer, **R. Zhang**, A. Kondrakov, J. Janek, T. Brezesinski. Seesaw effect of substitutional point defects on the electrochemical performance of single-crystal LiNiO_2 cathodes. *Chem. Mater.* **2024**, 36, 1497–1512.

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07. S. An, Y. Ma, S. Payandeh, A. Mazilkin, **R. Zhang**, J. Janek, A. Kondrakov, T. Brezesinski. Comparative analysis of aqueous and nonaqueous polymer binders for the silicon anode in all-solid-state batteries. *Adv. Energy Sustainability Res.* **2023**, 4, 2300092.
06. W. Zhao, K. Wang, X. Fan, F. Ren, X. Xu, Y. Liu, S. Xiong, X. Liu, Z. Zhang, M. Si, **R. Zhang**, W. van den Bergh, P. Yan, C. Battaglia, T. Brezesinski, Y. Yang. Quantifying degradation parameters of single-crystalline Ni-rich cathodes in lithium-ion batteries. *Angew. Chem. Int. Ed.* **2023**, 135, e202305281.
05. S. L. Dreyer, **R. Zhang**, J. Wang, A. Kondrakov, Q. Wang, T. Brezesinski, J. Janek. The effect of configurational entropy on acoustic emission of P2-type layered oxide cathodes for sodium-ion batteries. *JPhys Energy* **2023**, 5, 035002.
04. L. Karger, D. Weber, D. Goonetilleke, A. Mazilkin, H. Li, **R. Zhang**, Y. Ma, S. Indris, A. Kondrakov, J. Janek, T. Brezesinski. Low-temperature ion exchange synthesis of layered LiNiO₂ single crystals with high ordering. *Chem. Mat.* **2023**, 35, 648–657.
03. S. Murugan, **R. Zhang**, J. Janek, A. Kondrakov, T. Brezesinski. Facile solid-state synthesis of a layered Co-free, Ni-rich cathode material for all-solid-state batteries. *Chem. Commun.* **2023**, 59, 10024–10027.
02. S. Payandeh, C. Njel, A. Mazilkin, J.H. Teo, Y. Ma, **R. Zhang**, A. Kondrakov, M. Bianchini, T. Brezesinski. The effect of single versus polycrystalline cathode particles on all-solid-state battery performance. *Adv. Mater. Interfaces.* **2023**, 10, 2201806.

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01. Y. Ma, J.H. Teo, F. Walther, Y. Ma, **R. Zhang**, A. Mazilkin, Y. Tang, D. Goonetilleke, J. Janek, M. Bianchini, T. Brezesinski. Advanced nanoparticle coatings for stabilizing layered Ni-rich oxide cathodes in solid-state batteries. *Adv. Funct. Mater.* **2022**, 32, 2111829.

6.2.3. List of Conference/Workshop Contributions

2025 Material Research Society Spring Meeting & Exhibit (MRS Spring 2025)

Seattle, US, 2025

Oral 1: Unveiling anode kinetics and its impact on all-solid-state battery performance by three-electrode measurements.

Oral 2: Systematic optimization of slurry-cast all-solid-state battery cathodes and their characterization.

International Bunsen Discussion Meeting on Solid-State Batteries VI – From Fundamentals to Application

Frankfurt am Main, DE, 2024

Poster: Systematic optimization of slurry-cast all-solid-state battery cathodes and characterization of critical components.^[189]

Joint workshop: The directions of in-situ AFM-in-SEM microscopy for better batteries

Karlsruhe, DE, 2024

Role as co-organizer.

Nenovision Distributors Days 2024

Oral (online): Battery material research and its characterizations.

2023 Material Research Society Fall Meeting & Exhibit (MRS Fall 2023)

Boston, US, 2023

Oral: Ni-rich layered cathodes in sulfide-based all-solid-state batteries: Improving interface stability by oxide nanoparticle coating.

Deutsche Gesellschaft für Materialkunde Webinar 2023

Oral: Transition-metal interdiffusion and solid electrolyte poisoning in all-solid-state batteries revealed by cryo-TEM.

7. Acknowledgements

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