Batteries & Supercaps

Perspective
doi.org/10.1002/batt.202300180

Chemistry Europe
European Chemical Societies Publishing

www.batteries-supercaps.org

How to Develop Useful Models for Solid-State Batteries – A Plea for Simplicity and Interdisciplinary Cooperation

Anja Bielefeld*[a, b]

With research on solid-state batteries being on the rise, also simulations and modeling studies become more and more popular. It is therefore time to reflect upon the interplay of experiments and simulations and the upcoming dilemma of drawing general conclusions from increasingly complex model approaches that naturally go along with advancements and insights in the research field. Albeit this perspective focuses on (microstructure) models for composite cathodes, it is also an invitation to contemplate the epistemological considerations and the proposed tentative agenda on how to build useful models for other sub-fields of the solid-state research community.

Introduction

For (all-)solid-state batteries [(A)SSBs] many issues remain unsolved and many research questions are to be answered: From materials design to manufacturing and from "What conditions […] modify lithium plating and stripping behavior?" to "How should composites be designed to maintain their structure and internal connectivity during cycling?".[1] Not all of these questions are (easily) answered by experiments and mathematical as well as geometrical models and/or simulations may offer a different perspective.

Admittedly, introducing models and/or simulations to these problems, a whole bunch of new questions arises:

- (How) Are these research questions accessible by models and simulations?
- Which requirements should these models fulfill? How detailed do they have to be?
- What interfaces with experiments are there?
- How to assure reliability and computational feasibility?

This perspective targets to give answers to these questions in regard to the ASSB research and to assess the publication landscape in this context. It expresses my opinion that can be quite controversial and is not the jack-of-all-trades. It is not intended to deny the importance and progress that rather complex and highly specific approaches offer.

First, we dive into the epistemological view of experiments, mathematical models and simulations, their similarities and differences as well as their interactions. The perspective's heart is the tentative agenda on how to build useful models that is modified from Berro[2] and proposed to the battery modeling community. Finally, the Newman Model as state-of-the-art and the simulation landscape for solid-state batteries with a focus on the cathode composite, are discussed.

The lion's share of this perspective is reprinted from my cumulative dissertation.[3]

Models, Simulations and Experiments

All models are wrong, but some are useful.[4]

To understand the interaction of experiments and simulations, we dive into the epistemological understanding of simulations, their role in knowledge gain.

Similarities and Differences

But first: What are simulations? And how are they distinct from models?

Models are mathematical constructs accompanied by verbal interpretations, that are created to describe phenomena[5] and the underlying structures. When these phenomena get too complex to be modeled and solved analytically there are two ways of investigating the phenomenon anyway: simplification or computer simulation.[6] In the computer simulation, e.g. the finite element method (FEM), complex systems of equations are approximated by numerical methods. In the FEM, also the model geometry is discretized into small elements by the construction of a mesh.[7] Without going too much into detail, computer simulations are approximations of mathematical models, implemented in a software. Or in other words, the ingredients for models are established theory, physical insight and mathematical tricks and by translating these in a computer algorithm, one can simulate the target system behavior.[8]

[a] *Dr. A. Bielefeld*
Center for Materials Research (ZfM)
Justus Liebig University Giessen
Heinrich-Buff Ring 17
35392 Giessen (Germany)
E-mail: anja.bielefeld@phys.chemie.uni-giessen.de

[b] *Dr. A. Bielefeld*
Institute for Physical Chemistry
Justus Liebig University Giessen
Heinrich-Buff Ring 17
35392 Giessen (Germany)

But, as Box[4] puts it, also models, and that includes theories and scientific laws, are approximations of reality. They cannot tell us the whole truth. They might tell us the truth about parts of reality, but one should always bear in mind the underlying assumptions and variables chosen for the model and the limitations that go along with it.[4]

So, what applies for models also holds for computer simulations: To "All models are wrong, but some are useful.",[4] one could add: "All simulations are wrong, but some are useful."

It is essential to understand the underlying assumptions, the use cases and, correspondingly, the limits of validity. In the case of FEM simulations, this means being aware of the limitations of the underlying mathematical model, the geometry model as well as the simulation implementation. At which point does the approach become invalid and what results from it? Because of these inherent similarities for simulations and models, these will not be treated separately, assuming, they fall into the parent category of models in general.

Useful Models

If only some models are useful, what makes a model useful?

As Truran[6] describes, the verification, testing and real world application is, what builds confidence and trust into a model.

The verification assures that the model is internally consistent, from the suitability of the assumptions to the correct implementation of the mathematical equations into program code.

The validation then checks whether the model is capable of providing the information it is intended for. Does it fulfill its purpose and answer the underlying research questions? Is it able to reproduce experimentally measured data under similar model conditions? Or as M. Brenner is cited: "If a model does not tell you something new, it needs to go."[9]

So, how does one assure to build a model that is indeed useful?

For solid-state batteries combinations of experiments and simulations or modeling are quite common.[10–13] However, reflecting upon the techniques, their interplay and the (communication) gap that is to be bridged is not done very often. And, of course, simulation just for the sake of simulating is absurd and potentially futile.

Anja Bielefeld is a junior group leader at the Center for Materials Research at JLU Giessen, Germany. Her research focuses on modeling electrochemical systems and exploring the impact of microstructure on battery cell properties. Through simulations and experiments, her group investigates these phenomena. Anja completed her Ph.D. at JLU, studying solid-state battery composite cathodes, while gaining expertise in battery research and concept development at Volkswagen AG. She holds a B.Sc. and M.Sc. in physics from TU Braunschweig, with part of her master's studies completed at the University of Oslo.

In the context of multi-scale modeling and numerical simulation in lithium-ion batteries (LIBs) Franco[14] visits general aspects in physical modeling and reflects upon the imperfectness of models. In their subsequent review, Franco[15] explain: "A model is a more or less lovely imperfect representation of a physical system.", a perception that we have come across in Section "Similarities and Differences".

In cell biology and biophysics, the research community has taken a similar direction: When the number of publications that include simulation increased by the mid 2010s, Berro[2] and Möbius and Laan[9] scrutinized when, how and and to which extent, simulations can and should be used, with the goal to provide guidelines for researchers from all involved disciplines and to facilitate communication and co-working.

Berro[2] even presented a tentative agenda containing nine points on how to develop useful models. A slightly modified version of this agenda is visualized in Figure 1. To exemplify what the agenda implies, each step is put in context with a percolation/conduction network study[16] that is intended to (among others) answer whether conductive carbon, such as Super C65, is required in ASSB-cathodes. From an experimental point of view, it would be favorable to build electrodes that do

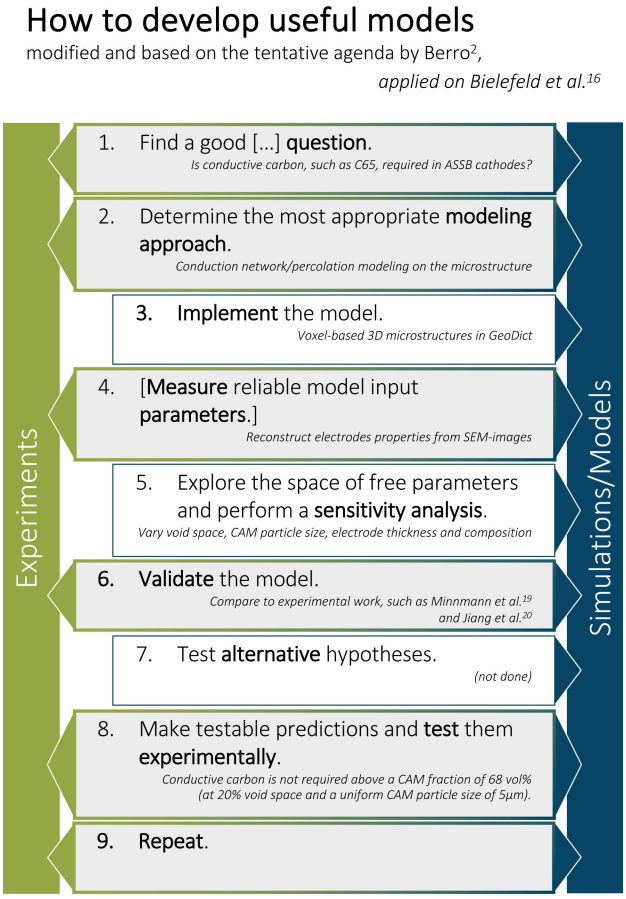

Figure 1. Agenda on how to develop useful models, originally proposed by Berro;[2] here step 1. is generalized and step 4. is modified. The agenda is applied on the question whether conductive carbon is required in ASSBs with the simulation study[16] in italic. The arrows sketch the interaction of experiments and simulations.

not contain conductive carbons, because these are known to degrade thiophosphates, such as $Li_{10}GeP_2S_{12}$[17] or β-Li_3PS_4,[10,18] and to lower the cell performance. Furthermore, in Figure 1 the linkage of the model with experiments is visualized by arrows.

Let us take a closer look at the tentative agenda:

1. Find a good […] question

Preliminary to building a model, it is essential to identify a research question of interest. One, that is non-trivial, has not been answered in multiple studies previously and that can be addressed by a model. If the question can better be answered by an experiment, there is no need for a model.[2] But if there is a chance for a model to become a shortcut for the experiments, it can still be a useful tool.

The "conductive carbon"-question provides a good example: The question can generally be answered by a well-chosen experiment that tests different electrode compositions for their electronic (and ionic) conductivity, such as the ones performed by Minnmann[19] and Jiang.[20] However, a wide screening of a variety of electrode design parameters would require a lot of time and effort and a model that provides guidelines on where to focus the experimental work can be a shortcut.

2. Determine the most useful model approach

A key to identify the most useful model approach is parsimony, or as Box[4] puts it: "simplicity illuminates, and complication obscures." The law of parsimony is also referred to as Occam's razor which implies that when confronted with two models, describing the phenomenon equally well, one should keep the simpler one.[6,21] This is not always straightforward, because simplicity is not well-defined and has to be put into context. If we want to quantify simplicity by the degrees of freedom, for example, a line might seem more simple to describe than a circle in a Cartesian system, because it requires only two points that mark the ends. But when transferring to polar coordinates, circles are just as easy to describe by a radius and a center.[21] Apart from the vague definition of simplicity, Occam's razor is regarded quite critically among scientists. The qualitative study of Riesch[21] indicates that while many scientists find simplicity useful and some believe that simplicity in theories actually mirrors the simplicity in nature, Occam's razor is not uncommon to be outright rejected.

Despite skepticism of Occam's razor, parsimony does not only make the modelers life easier, but also avoids overfitting. Or as John von Neumann is cited: "With four parameters I can fit an elephant, and with five I can make him wiggle his trunk."[22]

So, when setting up a model, it is recommended to either use a universal approach, because of its broad applicability and lower computation cost[9] or to focus on a specific phenomenon and stick with manageable degrees of freedom.

In the case of the "conductive carbon"-question, one could have simulated an entire ASSB cell including degradation phenomena, mechanics, temperature influences, etc. – The road of complexity is endless. However, with a rather simple approach of a network analysis in microstructure particle arrangements the research question was accessible at low computational cost and with few input parameters.

The modeling assumptions often originate from experiments, e.g. the negligible electronic conductivity in the solid electrolyte (SE) and the ionic conductivity in the cathode active material (CAM) had previously been shown in experiments.[23]

3. Implement the model

When implementing the model, one has to check in which environment the model will be represented and implemented best? Depending on the research question, the mathematical model and the available resources, the software choice may range from self implemented C-code to the use of predefined interfaces in a commercial software.

For the "conductive carbon"-question, I started implementing my own microstructure generation code and a version of the Hoshen-Kopelman algorithm[24] in Matlab,[25] until I realized the existence of a ready-to-use software available in my vicinity that did the job with less bugs and helped me to focus and concentrate on other steps in modeling.

When modeling microstructures, one should also keep in mind that the FEM and voxel-based methods might not be equally suited for the task.[26]

4. Measure reliable model input parameters

This is, where a different focus is proposed. Berro,[2] suggests to "Identify model parameters that fit the data." and that screening parameters until the model output fits the experimental data is the general practice. He warns that a parameter set which produces a good fit is not necessarily the only parameter set that does.

And while this procedure might be fine in other fields, there have been different studies on the parametrization of electrochemical models for conventional LIBs; all conclude that a reliable simulation result can only be obtained when the input parameters are reliable,[27–29] which is quite intuitive, just like the adage: Garbage in, garbage out.

Therefore, the suggestion for the fourth step is to measure reliable model input parameters on the materials (and material combinations) that are to be simulated. Adopting previously measured data sets to the own simulation should be done with caution and only if the materials are the same. Ecker et al.[29] point out, that the lithium diffusion coefficient in the active material is a critical parameter in particular, as the values reported in the literature vary widely and the coefficient has to be implemented including its dependence on the lithiation degree of the active material. In layered structures, such as $LiNi_xCo_yMn_{1-x-y}O_2$ (NCM), the diffusion of lithium is affected by a multitude of influences: From the lithium vacancy concentration, the *c* lattice expansion/contraction, the valance of

transition metal cations to the different electron affinities between transition metal cations, all change upon (de-)lithiation of the host material.[30,31]

Furthermore, Lee et al.[32] compare different measurement techniques for the chemical diffusion coefficient and the exchange current density in a P2D-model simulation and illustrate that the reliability of input parameters is crucial. When the model parameter set is not complete and experimental measurements are not possible, models can either be simplified, e.g. instead of simulating a full electrochemical cell, relying on a flux-based simulation of the effective conductivity, or to factor out the specific parameter by making a sophisticated guess that assures this parameter will not affect the simulation result. Of course, such a step must be explained in detail and with a discussion of the consequences.

5. Explore the space of free parameters and perform a sensitivity analysis

Even with a reliable input parameter set, one has to be aware that all input data are limited by their accuracy and precision. To get an impression how robust the simulation is with respect to the input parameters, a sensitivity analysis is appropriate. If small changes in a parameter result in large deviations in the results, the particular parameter should be elaborated on.

In the electrode microstructure model of the percolation study[16] this meant, screening the electrode design parameters: void space, CAM particle size, electrode thickness and composition. Due to the model simplicity, the parameter space was comparably small.

6. Validate the model

Once the model is all set up, it is important to check whether it actually describes the processes in the target system, usually by comparing the simulation results to experimental data that is measured under controlled and comparable conditions.

In pseudo-2-dimensional (P2D) Newman-type electrochemical battery models, new model implementations[33] are also validated numerically by comparison with an existing well-established implementation of the P2D model, such as COMSOL[34] or DUALFOIL.[35]

In simulations that rely on complex geometries, like electrode microstructures, one has to make sure that the chosen mesh (for FEM-based simulations), voxel size, etc. is adequately representing the structure. This means testing different discretizations and mesh refinements. In the FEM, the h-method describes the refinement of linear or parabolic mesh elements and apart from that one should also consider to use the p-method that relies on elements with a variable polynomial order.[36]

For the work on conductive carbon in ASSB cathodes, the main comparison to experimental data was later done by Minnmann et al.[19] However, the effect of the CAM particle size on the electronic conduction network and its utilization degree had already been shown experimentally by Strauss et al.,[37] previously and helped to assure the model suits the intended purpose. Still, technically, this is rather a qualitative agreement than a full validation.

7. Test alternative hypotheses

If a phenomenon can be explained by different mechanisms, one should test the alternative as well to distinguish which hypothesis is most likely to be true. This may require the design of adequate experiments that discard one of the possibilities.

8. Make testable predictions and test them experimentally

Apart from the direct validation and the test of alternative hypotheses, simulations can advance to experimentally unexplored regions and predict the systems behavior. However, the best prediction is useless, if it is not experimentally verifiable. – Another argument to keep it simple. – If the model becomes excessively complex, its predictions are unlikely to be concrete, distinguishable and verifiable.

For the question of conductive carbons in ASSB cathodes, the work predicts: "Conductive carbon is not required above a CAM fraction of 68 vol%."[16] A statement that was later supported by Minnmann et al.[19] who tested cathode compositions between 25 to 61 vol% NCM622 as CAM and observed that the electronic tortuosity factor goes down to 4.3 for the highest CAM fraction, compared to 120 at 25 vol% NCM622. They conclude that high CAM fractions could enable sufficient electron percolation and supersede carbon additives. This is not the exact same conclusion, but considerably close. Jiang et al.[20] who further include different CAM particle sizes confirm the model predictions on electronic and ionic percolation.

9. Repeat

Scientific questions reproduce. Answering one, usually evokes several new questions.

Therefore, refining the model, revisiting its assumptions and implementation and expanding its scope can be useful to touch upon newly arising questions.

Interactions of Simulations and Experiments

We have scratched the interaction of experiments and simulations already in the previous section. With 3., 5. and 7. there are only a few steps in the modeling agenda that do not involve experiments. From the obvious aspects that simulations have to be validated with experimental data to the experimentally obtained insight that is the basis for fundamental model assumptions or the availability of reliable input parameters for the simulation. Experiments are an integral part of simulations

providing the motivation for simulations as well as the foundation and the credibility.

But despite all similarities and common goals, simulations and experiments generally involve different viewpoints on problems and may also lead to diverging perceptions, definitions and/ or use of language. A situation that is natural to arise in interdisciplinary environments. For example in biophysics, where Bentovim et al.[38] depict the different understanding of the term "precision" among biologists and physicists and attempt to dissolve it. Due to the complexity of all the disciplines involved, complete all-round-knowledge is impossible to obtain. This leaves a gap which becomes all the worse, when the interaction of simulations and experiments is impeded by deficient communication or ignorance of the simulation/experiment counterpart.

Möbius and Laan[9] suggest to bridge the inter-disciplinary gap by adapting the explanation degree and language use to the audience. Berro[2] depicts that the simplistic assumptions used by mathematicians and physicists in modeling biological processes are occasionally not sufficiently explained. He encourages to switch the perspective by role reversal, arguing that switching the perspective does not only widen the horizon, but also helps understanding the methods, assessing the data accuracy and proposing expedient experiments. Modelers in the lab building battery cells and measuring cycle data and experimenters who test different time discretizations, … – Not the worst vision, is it?

Communication is the key. Only well-explained models are graspable for other scientists and when they understand the model, they can think it through, question it and, eventually, gain trust in the model and its predictions. Once this trust is established, those conducting scientific experiments will be more likely to draw conclusions for their own work, to eventually test the simulations' predictions in practice or to develop suggestions for further model sophistication.

Notwithstanding all gaps between specialists, epistemologically, simulations can be regarded as a particular kind of experiment, also called in-silico experiments.[8,39] Franco et al.[15] point out that "experimentalists are, indeed, theorists as well", portraying their use of mathematical models and underlying assumptions in their day-to-day data analysis. These are, inherently, not different to the approaches of theorists. For Frigg and Reiss[40] simulations create parallel worlds that represent the target system, but this does not distinguish them from experiments or models of all kinds. They further highlight the capability of simulations to mediate between theories and experiments and Morgan[41] pictures models as "artificial worlds built to represent the real world" and experiments as "versions of the real world captured within an artificial laboratory experiment". Consequently, simulations could join this perception as "versions or approximations of an artificial world built to represent the real world".

And because this is quite abstract and not straightforward to grasp, communication is essential for inter-disciplinary work.

Battery Models

From the methodological background and the epistemological understanding of models and simulations in general, let us proceed to their application in battery research, particularly in ASSB cathodes.

The Newman Model

The state-of-the-art model to describe the electrochemical processes in a battery with liquid electrolyte is based on the early works by the group of John Newman.[42,43] It is widely known as the Newman model or the P2D-model and has been simplified, as well as extended in various directions over the years from single-particle models to multi-scale models including aging and/or mechanical effects (for a detailed overview, see Falconi,[28] chapter 1.4 or Ramadesigan et al.[44]).

Generally, to model a battery cell, one has to account for the charge transport, namely diffusion and migration, in the relevant materials and reactions at the interfaces, e.g. the intercalation of lithium ions into the graphite host structure at the anode. From the original works of Doyle[42] and Fuller et al.[43] to more recent publications,[28,33,45] the P2D-model has been explained at length, so this section is limited to the main line of thoughts.

The crux of the P2D-model is to break the complex 3-dimensional microstructure down to a computationally convenient 2-dimensional system in two steps:

Effective microstructure parameters

Newman and co-workers developed the idea of describing the complex electrode microstructure by three characteristics: porosity, tortuosity and active surface area. The underlying assumption is that the electrode microstructures are sufficiently homogeneous for this purpose.

- The porosity, ε, represents the electrode composition, particularly the volume fraction that is available for the liquid electrolyte. In conventional LIBs the porosity is usually around 30 %.[46]
- The tortuosity, τ, describes how intertwined a path is, as illustrated in Figure 2. So when the charge carriers travel through the electrode, the idea is to account for the microstructural influences by a factor that elongates the way they have to travel.

$$\tau = \frac{l_{\text{eff}}}{l}, \tag{1}$$

with the direct path length l and the effective path length l_{eff}. The effective diffusion coefficient D_{eff} is then described by:

$$D_{\text{eff}} = \frac{\varepsilon}{\tau^2} D_{\text{bulk}}, \tag{2}$$

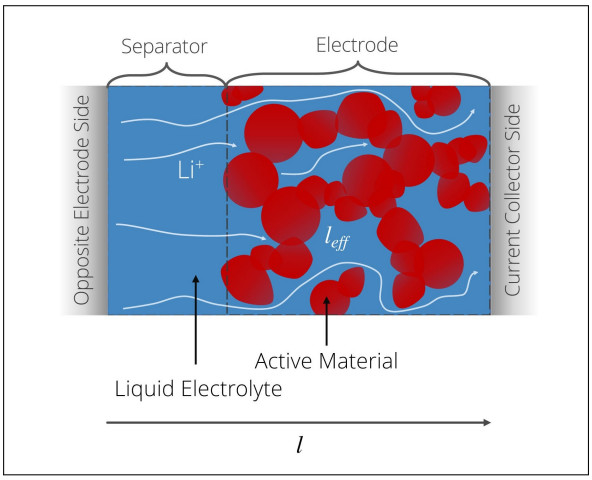

Figure 2. Schematic representation of ion pathways in a liquid electrolyte cell.

where the diffusion coefficient in the bulk material is denoted as D_{bulk}^{ion}. This concept is employed for both, the effective ion transport and the effective electron transport.

In three-dimensional (3D)-microstructures that offer a variety of transport pathways, different in size and length, the description via the effective pathlength is not sufficient. For better distinction, one frequently refers to the tortuosity factor κ in 3D and defines $D_{eff} = \frac{\varepsilon}{\kappa} D_{bulk}$, accordingly. Both, τ and κ as well as their common assessment by the Bruggeman relation(s)[47] are controversially discussed.[48–51] Commercial LIB cathodes possess tortuosity factors around 4.[52]

- The active surface area A_s is the surface area that is available for insertion and extraction of lithium ions to/from the active material (AM).

The introduction of these parameters allows to describe the battery cell, the charge transport in the liquid electrolyte and the (de-)intercalation of lithium into/from the AM in just one dimension, x that runs from the anode current collector through the electrodes and separator to the cathode current collector. However, this dimension is not well-suited to describe the diffusion of lithium inside the AM particles. Therefore, Newman and co-workers extended the model with a second dimension.

Spherical coordinates in the AM

Once lithium ions havereached the interface of the liquid electrolyte and the AM they will intercalate into the latter (if the local electric field is sufficiently large). Common electrode AMs, such as NCM or graphite are mixed electron-ion-conductors whose electronic conductivity is by orders of magnitude larger than the ionic conductivity.[23] This implies that the electrons are much faster and follow the ions without delay. In theory, the chemical lithium diffusion coefficient $\tilde{D}_{Li}$ (of neutral Li) is the geometric mean of both the electronic diffusion coefficient $\tilde{D}_{e^-}$ and its ionic equivalent $\tilde{D}_{Li^+}$:

$$\tilde{D}_{Li} = \frac{\tilde{D}_{e^-} \cdot \tilde{D}_{Li^+}}{\tilde{D}_{e^-} + \tilde{D}_{Li^+}}. \tag{3}$$

Due to the faster electron transport, the ion diffusion inside the AM particle is limiting the charge transport, a lithium concentration gradient forms and the ions diffuse into the particle center according to Fick's law. In the P2D-model, one chooses the radius of the AM particles r_p to be the second dimension in the model. Assuming spherical AM particles, the ion mass balance can be described by:

$$\frac{\partial c_{Li}}{\partial t} = D_s \left(\frac{\partial^2 c_{Li}}{\partial r^2} + \frac{2}{r} \frac{\partial c_{Li}}{\partial r} \right), \tag{4}$$

with the local lithium concentration c_{Li} the chemical lithium diffusion coefficient in the AM $\tilde{D}_{Li}$ and the spherical coordinate, the radius r. In the particle center, there is no flux:

$$-\tilde{D}_{Li} \frac{\partial c_{Li}}{\partial r}\bigg|_{r=0} = 0 \tag{5}$$

and at the outer AM particle boundary the current density j_n is given by the reaction at the interface:

$$-\tilde{D}_{Li} \frac{\partial c_{Li}}{\partial r}\bigg|_{r=r_p} = j_n. \tag{6}$$

These two assumptions facilitate the modelers life and enable fast simulations.

Naturally, the assumptions narrow the applicability of the model, e.g. not all AMs are spherical particles. The particle shape of natural graphite, for example, is flake-like, while synthetic graphite features a random particle shape.[53]

NCM single-crystals are also shaped rather octahedral or tetradecahedral,[54,55] but secondary NCM particles possess a spherical form.[56]

The homogenization assumption that supports the use of effective parameters is also limited in its applicability. Real electrodes in conventional LIBs are more complicated than homogeneously distributed AM and the remaining space (the porosity) filled with liquid electrolyte (as sketched in Figure 2). Mass-produced anodes and cathodes feature polymeric binders, such as polyvinylidene fluoride (PVDF) or nitrile butadiene rubber (NBR) that provide mechanical support for the porous AM structure. In cathodes, carbon additives, namely Ketjen-black, Super C65, vapor grown carbon fibers (VGCFs) or others, ensure sufficient electronic conduction. Both components make only a small weight fraction, but, depending on the density ($\rho_{PVDF} = 1.78\ g\,cm^{-3}$,[57] $\rho_{NBR} = 1\ g\,cm^{-3}$,[58] $\rho_{VGCF} = 1.8\ g\,cm^{-3}$,[59] compared to $\rho_{NCM} = 4.76\ g\,cm^{-3}$), the volume they take may not be negligible.

Further, scanning electron microscopy (SEM) images show that the production process influences the distribution of binders and the agglomeration of carbons.[60–62] Apart, it is unknown to which extent binders and carbons are nanoporous and may be penetrated by the liquid electrolyte.[63,64] This is

where the P2D-model reaches its limits and FEM- or voxel-based simulations are used to address the effect of binders and carbons.[26]

Apart from the P2D-model and its derivatives, various other modeling techniques from the atomistic scale to the battery system scale are used and combined in multi-scale approaches for LIBs.[14,15] For ASSBs, the modeling landscape has been less diverse for now with a focus on microstructures.

All-Solid-State Battery Models

In ASSBs the above mentioned issues are supplemented by another component in the electrodes: Voids.

Other than in conventional cells, the electrolyte cannot wet and penetrate the pores. In ASSBs that feature ceramic or glassy electrolytes, the SE has a particle morphology, even if it is a rather soft material, like the thiophosphate SEs.[65,66] The assumption that all volume that is not filled with CAM contains electrolyte no longer applies. This is shown schematically in Figure 3. The volume taken up by voids is around 15 %[13,19,20,67] in pressed cells with thiophosphate SEs. This fraction can be reduced to 6–8 % by sophisticated manufacturing techniques,[68] but an entire elimination is unlikely. Therefore, the microstructure is suspected to play a decisive role in the performance of ASSBs, especially in composite electrodes. As a result, representative microstructures are the basis for the simulation: One approach to obtain such microstructures involves directly importing data from μ-computed tomography (CT)[69] or using focused-ion beam-SEM (FIB-SEM).[10,12,70,71] Another method involves reconstructing the microstructure fromSEM cross sections[16,72–74] and/or reconstructing the particle arrangement by DEM.[11,75,76] These techniques enable the extraction of information such as particle size distributions, particle shapes, and material distributions. Additionally, fully synthetic microstructures[11,16,73,75,77–79] are employed to analyze the influence of specific design parameters, such as the composition which may include residual void space, binder and/or carbon additive content. An overview of the issues that have been addressed and their commonly used computation techniques is shown in Table 1. A more detailed explanation of the particular modeling approaches is given below.

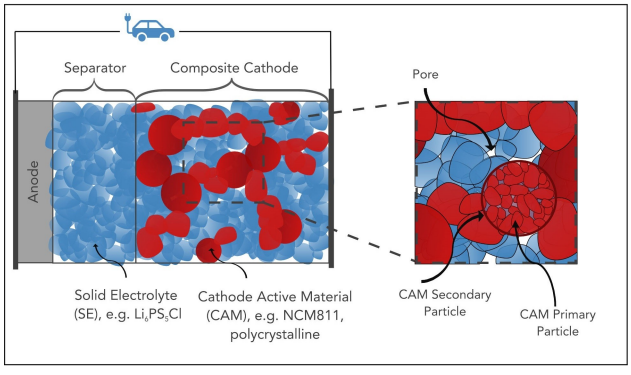

Figure 3. Schematic representation of an ASSB with a zoom on the voids at the CAM/SE-interface.

Similar to a recent review,[83] Figure 4 shows the ASSB simulation landscape with a focus on composite cathodes and their microstructure. Likewise, there are issues and open questions on the anode side for both high-energy cell concepts, silicon and lithium (or reservoir-free) anodes.[84] These range from the growth of a solid-electrolyte interface (SEI) at the anode-thiosphosphate SE-interface[85] to mechanical and morphological issues. For lithium, metal dendrite growth upon plating and void formation upon stripping are the major obstacles to be overcome.[86,87] Some of these might counteract with cathode issues, but to date, the simulation strategy is rather to separate issues and keep it as simple as possible, just like step 2 in the tentative agenda suggests. The x-axis of Figure 4 is inspired by the model classification of Möbius and Laan[9] who distinguish between universal models that feature general principles and are broadly applicable and highly complex, specific models that are theoretically more sophisticated, but usually act as a spotlight on a very specific topic rather than illuminating the overall picture. This is not supposed to be a grading as in good/bad, but shows the various model approaches for ASSB simulations and the clusters that form.

On the universal end … Braun et al.[80] assess the general design of ASSBs in a 1-dimensional homogenized transmission line impedance model that simulates discharge curves for various separator thicknesses and temperatures. The electrode microstructure is represented by the effective parameters, porosity and tortuosity, that were introduced in the Newman Model and the SE does not posses a specific morphology. The model exhibits flaws at elevated C-rates, because it simulates the cell behavior in equilibrium state and parameters, like the specific charge-transfer resistance at the interfaces are rough estimates. Yet, its Ragone diagrams sketch the overall development for ASSB design.

Conduction network models do not simulate discharge curves or model the chemical processes, but focus on the electronic and/or ionic conduction clusters. They are geometrical rather than physical models. The implementation of the cathode microstructures is either based on voxel particle arrangements[16,77,81] or the discrete element method (DEM) with spherical particles.[11,75] In ASSB modeling, DEM models have been limited to spherical particles, but more realistic and complex particles shapes have recently been demonstrated for porous NCM111-cathodes.[88]

Laue et al.[77] and Sangrós-Giménez et al.[75] both investigate $LiFePO_4$(LFP)/polymer-SE (e. g. polyethylene oxide:lithium bis(trifluoromethanesulfonyl)imide (PEO:LiTFSI))/carbon black composites and are particularly interested in a homogeneous distribution of the carbon black to ensure sufficient electron conduction. While LFP-containing composites require carbon additives to compensate the low electronic conductivity, this question is open for debate in NCM-containing ASSB cathodes and part of the percolation model.[16] The conduction network models do not require a plurality of input parameters and rely solely on the particle sizes, distributions and shapes. Despite

Table 1. Overview of ASSB model approaches with focus on the cathode composite; input is marked as "(i)", output as "(o)".

goal	modeling approach	input/output (excerpt; for detailed info see references)	refs.
power and energy density assessment	1D homogenized transmission line impedance model	(i) effective microstructure properties (i) charge transport properties (i) charge transfer properties (i) cell and electrode dimensions (o) Ragone plot	[80]
electrode design: percolation	conduction network model: SE: ion conductor; CAM/carbon: electron conductor	(i) microstructure properties (o) utilization levels (o) active surface area	[11,16,75,77,81]
electrode design: conduction efficacy	flux-based simulation limited to Ohmic losses	(i) microstructure properties (i) charge transport properties (o) effective conductivity and tortuosity (o) microstructure-resolved current distribution	[71–74]
prediction of cell performance	charge/discharge simulation	(i) microstructure properties (i) charge transport properties (i) charge transfer properties (i) cell and electrode dimensions (i) open circuit voltage (i) cycling conditions (o) charge/discharge profiles (o) microstructure-resolved current distribution (o) microstructure-resolved lithium concentration in AM	[10,12,69,70,72,74,82]
…	other approaches	…	

input type	examples
microstructure properties	particle distribution/arrangement/agglomeration, particle sizes, particle size distributions, particle shapes, composition, void space and distribution
charge transport properties	chemical lithium diffusion coefficient in CAM, partial ionic and electronic (bulk) conductivities
charge transfer properties	exchange current densities at interfaces, charge transfer coefficients

their low level of complexity, conduction networks turn out useful for general issues.

Flux-based simulations are a stationary approach to approximate effective conductivities[71–74] that we got to know as an auxiliary property from the microstructure homogenization approach in the Newman model. Although the porosity and the tortuosity are not able to fully describe the microstructure of ASSB electrodes, they are still noteworthy characteristics to study the effect of different electrode design parameters. Park et al.[72] and Bielefeld et al.[73] both study the influence of binders in a flux-based simulation.

Still not reflecting other processes than the transport of charge carriers in an electric field, these models are single-physics models as oppose to multi-physics models. They require the bulk conductivites as additional input compared to the pure network models. The bulk conductivities are commonly measured to characterize materials and are, consequently, straightforward to obtain for modelers.

The analysis of Park et al.[72] and Lee et al.[74] also simulate discharge curves, which leads us over to the largest cluster:

Electrochemical cell simulations – The general idea is not far off the Newman model with a mathematical description of lithium diffusion inside the AM particle, ion transfer at the AM/SE-interfaces denoted by the Butler-Volmer equation and charge and energy conservation. Coupling electrochemistry and charge transport, these models are multi-physics models.[14] What is different in ASSBs is that single ion conductors can be modeled as (ionic) Ohmic conductors (for a detailed explanation, see Ref. [82]) and that the homogenization approach is not applicable. Instead, FEM[76,82] or voxel-based methods[10,12,69,70] are used to approximate the system of partial differential equations on the particle microstructure. The cell simulations provide charge or discharge voltage curves and information about the lithium distribution and the current density in every discretized geometry part. These simulations are closer to actual cell cycling than the approaches to the left in Figure 4, but that inherits challenges: Besides the higher model complexity and the resulting computational cost, the input parameters needed for this kind of simulation are various and not straightforward to obtain. As described in the tentative agenda the reliability of the input strongly affects the reliability of the output.

Finally, this model type is quite specific compared to the conduction network models, where the outcome was broadly applicable. In the context of electrode cell charge or discharge simulations the conditions are tightly defined. In predicting anything from these models, one has to reflect upon the underlying assumptions and always remember the validity limits.

Perspective
doi.org/10.1002/batt.202300180
Chemistry Europe
European Chemical Societies Publishing

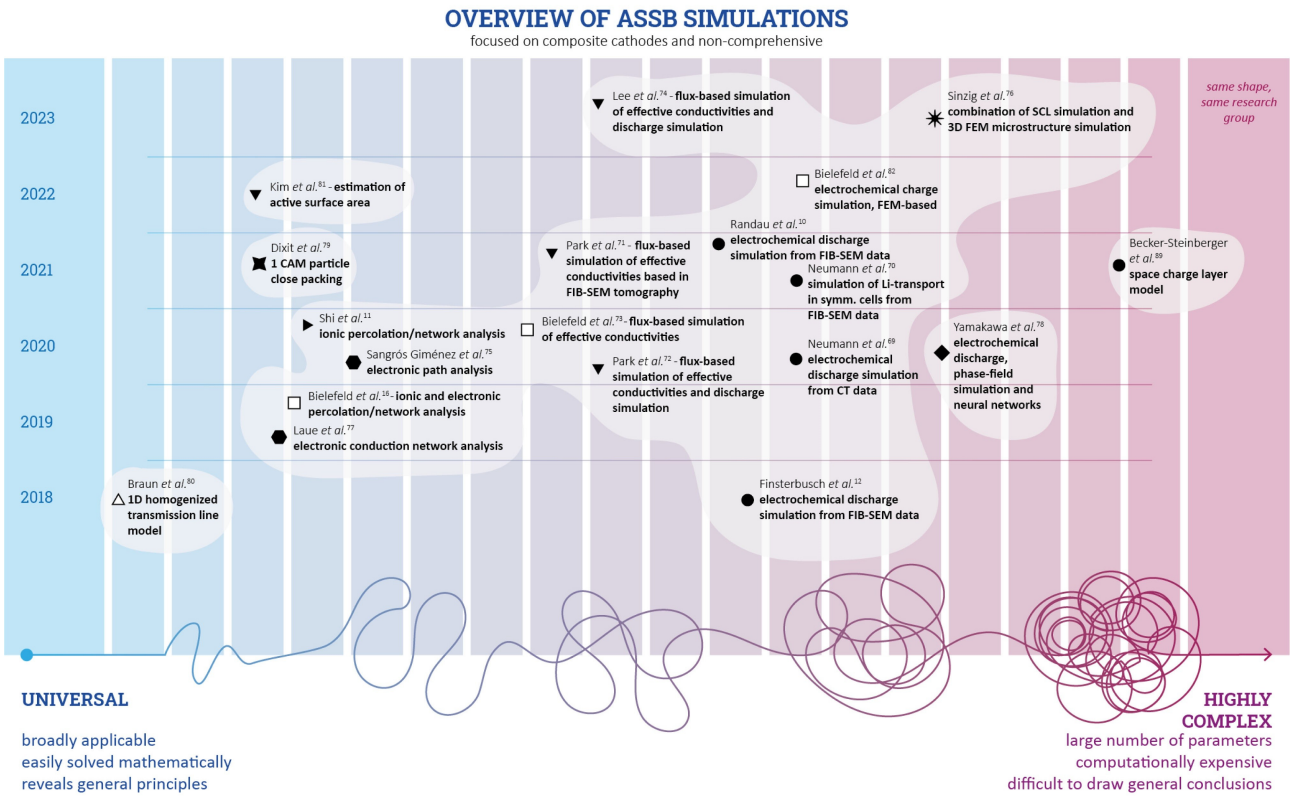

Figure 4. Cutout of the ASSB simulation landscape focusing on composite cathodes with schematic representations of selected models. Credit: Elisa Monte/ JLU Giessen.

… further down the road of specific models are space charge layer models, such as the one by Becker-Steinberger et al.[89] who focus on the SE and its interfaces with the anode and the cathode. The controversy about the significance of the build-up of lithium depleted layers that result in a space charge is still ongoing for SEs[90–92] and the models have the potential to provide insight that is hardly ever extracted experimentally.

Of course, this is not the actual end of the road and the model landscape in Figure 4 is not the full picture, but rather a cutout. Apart from the work of Becker-Steinberger et al.,[89] there are other approaches with elevated complexity, such as density functional theory-based simulations.[93] To bridge the gap between highly complex local space charge layer modeling and microstructure-resolved electrode/cell modeling, Sinzig et al.[76] propose a combination of the former which assumes that the space charge layers are one-dimensional and develop solely at the SE-electrode interfaces. They therefore split the SE into the charge neutral bulk region and the space charge region, introducing a multi-physical, multi-scalar model.

To date, the landscape of simulation studies for ASSBs contains comparably few studies overall. While multi-scale and multi-physics modeling is common for conventional LIBs,[15] these approaches are yet to come for ASSBs: There are many chemo-mechanical issues to be addressed and coupled electrochemical-mechanical models are a prospect to point out where the comfort zone for the cell, in terms of external pressure and cycling conditions, is. This is especially important, when proceeding towards practical application in electric vehicles with the integration of the cells into the battery pack and the design of the battery module that comprises cell stacks. The field of mechanical modeling that had been in its fledgling stage[94] is developing quite quickly[95–98] with phase-field models entering the stage. Coupling of thermal and electrochemical multi-physics models is a blind spot for ASSBs. Meanwhile, generally, multi-physics models are situated at the right side of the landscape and one major challenge will be to extract general guidelines from these models with elevated complexity. Furthermore, the validation of microstructure-resolved electro-chemo-mechanical models also requires precise microstructure information from (FIB-)SEM or CT data at different states of charge and degradation stages.

So, has the SSB-research passed the simple conduction network and flux-based models? Will the models get more and more complicated from now on with multiple coupled effects and scales?

Not necessarily. Instead, the strategy should be to build models according to the agenda suggested previously (section tentative agenda) and not to forget about step 2: “Determine

the most useful model approach." To be parsimonious with the model complexity, and if needed, to focus on a specific effect rather than building the all-in-one model suitable for every purpose that is difficult to implement, to understand, to interpret and to explain.

Conclusions

As pointed out above, the extent to which ASSBs are studied in simulations is moderate and that, for sure, is not the result of too few research questions. For instance, further studies of the CAM/SE/void-interface that account for the morphology of the SE could advance the insight to this interface. Coupling electrochemical charge/discharge models to a mechanical models is of interest to understand the local stresses that arise due to the volume changes of the CAM upon cycling.

Overall, the number of publications on mechanical models are increasing and they are needed to proceed towards the integration of ASSBs in electric vehicles. Therein the construction of the surrounding component parts requires a sophisticated understanding of the cell (and cell pack) behavior on electrical, thermal and mechanical level.

Also, degradation, both electrochemical and (chemo-) mechanical, will be a major upcoming topic, once ASSBs become more mature and advance toward practical application.

Coupling these aspects to microstructure-resolved models will not go without computational cost. And while computational power is still increasing and solvers are improved to handle larger problems, I do not believe that infinitely increasing the model complexity is the best answer. An extended effective representation of the electrode microstructure, similar to the crux of the Newman model, might be feasible. One way to go could be to study the evolution of the porosity, tortuosity and specific surface area upon cycling in order to implement these in a modified Newman model. But these studies also require an experimental basis that is rock-solid, which leads to another aspect. One that is not restricted to ASSB simulations: Measure and use reliable input parameter sets for simulations.

One example for a vital input parameter is the chemical diffusion coefficient of lithium in the CAM whose state-of-charge-dependence is significant, but still widely neglected in simulations. Parameter sets that can be extracted from literature, may be convenient, but is it essential to look into their origin and reflect upon the ramifications that these sets imply.

Modelers and experimental experts should feel encouraged to get into contact and cooperate. Apart from the specific study, the interaction of modelers with specialists for experiments and their measuring techniques is likely to widen the horizon of everyone involved. Discussion with those who experiment helps to understand the parameters themselves, the underlying experiments and their limitations and assumptions better. It may also motivate a novel simulation study. Communication is the key.

And finally, as alternative and/or supplement to physics-based electrochemical models, machine learning techniques are evolving in battery research. From materials discovery via microscopy image analysis to cycling optimization,[99,100] these introduce new perspectives and new scientists in the field, enhancing its diversity and calling for interdisciplinary cooperation.

Acknowledgements

I want to thank Jürgen Janek und Doreen Mollenhauer for the support and discussion and especially Philip Minnmann, Raffael Ruess and Dominik A. Weber for introducing the world of experiments to me. A special thanks goes to Elisa Monte for her graphical support in Figure 4 and the TOC graphic. Finally, I want to thank the reviewers for their valuable remarks! Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interests

I declare no conflict of interest.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

Keywords: battery models · epistemology · experiments · modeling philosophy · solid-state batteries

[1] P. Albertus, V. Anandan, C. Ban, N. Balsara, I. Belharouak, J. Buettner-Garrett, Z. Chen, C. Daniel, M. Doeff, N. J. Dudney, B. Dunn, S. J. Harris, S. Herle, E. Herbert, S. Kalnaus, J. A. Libera, D. Lu, S. Martin, B. D. McCloskey, M. T. McDowell, Y. S. Meng, J. Nanda, J. Sakamoto, E. C. Self, S. Tepavcevic, E. Wachsman, C. Wang, A. S. Westover, J. Xiao, T. Yersak, *ACS Energy Lett.* **2021**, *6*, 1399.
[2] J. Berro, *Biophys. Rev. Lett.* **2018**, *10*, 1637.
[3] A. Bielefeld, *At the Interface of Simulation and Experiment in Composite Cathodes for All-Solid-State Batteries*, Phd thesis, Justus-Liebig University Giessen **2022**.
[4] G. E. P. Box, Robustness in the Strategy of Scientific Model Building, in R. L. Launer, G. N. Wilkinson (Editors), *Robustness in Statistics*, pages 201–236, Academic Press **1979**.
[5] J. von Neumann, *The Neumann Compendium*, chapter Method in the Physical Sciences, pages 627–635, World Scientific Series In 20th Century Mathematics, World Scientific **1995**.
[6] P. Truran, Models: Useful but Not True, in *Practical Applications of the Philosophy of Science: Thinking about Research*, pages 61–67, Springer International Publishing, Heidelberg **2013**.
[7] Comsol, The Finite Element Method (FEM), https://www.comsol.com/multiphysics/finite-element-method **2016**.
[8] E. Winsberg, *Science in the Age of Computer Simulation*, University of Chicago Press, Chicago, United States **2010**.
[9] W. Möbius, L. Laan, *Cell* **2015**, *163*, 1577.
[10] S. Randau, F. Walther, A. Neumann, Y. Schneider, R. S. Negi, B. Mogwitz, J. Sann, K. Becker-Steinberger, T. Danner, S. Hein, A. Latz, F. H. Richter, J. Janek, *Chem. Mater.* **2021**, *33*, 1380.
[11] T. Shi, Q. Tu, Y. Tian, Y. Xiao, L. J. Miara, O. Kononova, G. Ceder, *Adv. Energy Mater.* **2020**, *10*, 1902881.

[12] M. Finsterbusch, T. Danner, C.-L. Tsai, S. Uhlenbruck, A. Latz, O. Guillon, *ACS Appl. Mater. Interfaces* **2018**, *10*, 22329.
[13] D. Hlushkou, A. E. Reising, N. Kaiser, S. Spannenberger, S. Schlabach, Y. Kato, B. Roling, U. Tallarek, *J. Power Sources* **2018**, *396*, 363.
[14] A. A. Franco, *RSC Adv.* **2013**, *3*, 13027.
[15] A. A. Franco, A. Rucci, D. Brandell, C. Frayret, M. Gaberscek, P. Jankowski, P. Johansson, *Chem. Rev.* **2019**, *119*, 4569.
[16] A. Bielefeld, D. A. Weber, J. Janek, *J. Phys. Chem. C* **2019**, *123*, 1626.
[17] W. Zhang, T. Leichtweiß, S. P. Culver, R. Koerver, D. Das, D. A. Weber, W. G. Zeier, J. Janek, *ACS Appl. Mater. Interfaces* **2017**, *9*, 35888.
[18] F. Walther, S. Randau, Y. Schneider, J. Sann, M. Rohnke, F. H. Richter, W. G. Zeier, J. Janek, *Chem. Mater.* **2020**, *32*, 6123.
[19] P. Minnmann, L. Quillman, S. Burkhardt, F. H. Richter, J. Janek, *J. Electrochem. Soc.* **2021**, *168*, 040537.
[20] W. Jiang, X. Zhu, R. Huang, S. Zhao, X. Fan, M. Ling, C. Liang, L. Wang, *Adv. Energy Mater.* **2022**, *12*, 2103473.
[21] H. Riesch, *THEORIA. An International Journal for Theory, History and Foundations of Science* **2010**, *25*, 75.
[22] F. Dyson, *Nature* **2004**, *427*, 297.
[23] R. Amin, Y.-M. Chiang, *J. Electrochem. Soc.* **2016**, *163*, A1512.
[24] J. Hoshen, R. Kopelman, *Phys. Rev. B* **1976**, *14*, 3438.
[25] MATLAB, *R2016a (9.0.1)*, The MathWorks Inc., Natick, Massachusetts **2016**.
[26] B. L. Trembacki, A. N. Mistry, D. R. Noble, M. E. Ferraro, P. P. Mukherjee, S. A. Roberts, *J. Electrochem. Soc.* **2018**, *165*, E725.
[27] V. Laue, F. Röder, U. Krewer, *J. Appl. Electrochem.* **2021**, *51*, 1253.
[28] A. Falconi, *Electrochemical Li-Ion Battery Modeling for Electric Vehicles*, Thesis, Communauté Université Grenoble Alpes **2017**.
[29] M. Ecker, T. K. D. Tran, P. Dechent, S. Käbitz, A. Warnecke, D. U. Sauer, *J. Electrochem. Soc.* **2015**, *162*, A1836.
[30] A. Van der Ven, J. Bhattacharya, A. A. Belak, *Acc. Chem. Res.* **2013**, *46*, 1216.
[31] K. Märker, P. J. Reeves, C. Xu, K. J. Griffith, C. P. Grey, *Chem. Mater.* **2019**, *31*, 2545.
[32] H. Lee, S. Yang, S. Kim, J. Song, J. Park, C.-H. Doh, Y.-C. Ha, T.-S. Kwon, Y. M. Lee, *Curr. Opin. Electrochem.* **2022**, *34*, 100986.
[33] M. Torchio, L. Magni, R. B. Gopaluni, R. D. Braatz, D. M. Raimondo, *J. Electrochem. Soc.* **2016**, *163*, A1192.
[34] COMSOL AB, Comsol Multiphysics 5.4 **2019**.
[35] J. Newman, FORTRAN Programs for the Simulation of Electrochemical Systems **1998**, http://www.cchem.berkeley.edu/jsngrp/fortran.html.
[36] P. Fröhlich, *FEM-Anwendungspraxis: Einstieg in die Finite Elemente Analyse Zweisprachige Ausgabe Deutsch/Englisch*, Studium Technik, Vieweg + Teubner Verlag, 1 edition **2005**, pp. 74.
[37] F. Strauss, T. Bartsch, L. de Biasi, A.-Y. Kim, J. Janek, P. Hartmann, T. Brezesinski, *ACS Energy Lett.* **2018**, *3*, 992.
[38] L. Bentovim, T. T. Harden, A. H. DePace, *Development* **2017**, *144*, 3855.
[39] E. Winsberg, Computer Simulations in Science, in E. N. Zalta (Editor), *The Stanford Encyclopedia of Philosophy*, Metaphysics Research Lab, Stanford University **2019**.
[40] R. Frigg, J. Reiss, *Synthese* **2009**, *169*, 593.
[41] M. S. Morgan, *J. Econ. Methodol.* **2005**, *12*, 317.
[42] C. M. Doyle, *Design and Simulation of Lithium Rechargeable Batteries*, Ph.D. thesis, Lawrence Berkeley Laboratory. University of California **1995**.
[43] T. F. Fuller, M. Doyle, J. Newman, *J. Electrochem. Soc.* **1994**, *141*.
[44] V. Ramadesigan, P. W. C. Northrop, S. De, S. Santhanagopalan, R. D. Braatz, V. R. Subramanian, *J. Electrochem. Soc.* **2012**, *159*, R31.
[45] S. Erhard, *Mehrdimensionale Elektrochemisch-Thermische Modellierung von Lithium-Ionen-Batterien*, Dissertation, Technische Universität München, München **2017**.
[46] M. Singh, J. Kaiser, H. Hahn, *J. Electrochem. Soc.* **2015**, *162*, A1196.
[47] D. A. G. Bruggeman, *Ann. Phys. (Berlin)* **1935**, *416*, 636.
[48] M. F. Lagadec, R. Zahn, S. Müller, V. Wood, *Energy Environ. Sci.* **2018**, *11*, 3194.
[49] T.-T. Nguyen, A. Demortière, B. Fleutot, B. Delobel, C. Delacourt, S. J. Cooper, *NPJ Comput. Mater.* **2020**, *6*, 123.
[50] B. Tjaden, D. J. L. Brett, P. R. Shearing, *Int. Met. Rev.* **2018**, *63*, 47.
[51] K. S. Mayilvahanan, Z. Hui, K. Hu, J. Kuang, A. H. McCarthy, J. Bernard, L. Wang, K. J. Takeuchi, A. C. Marschilok, E. S. Takeuchi, A. C. West, *J. Electrochem. Soc.* **2021**, *168*, 070537.
[52] J. Landesfeind, J. Hattendorff, A. Ehrl, W. A. Wall, H. A. Gasteiger, *J. Electrochem. Soc.* **2016**, *163*, A1373.
[53] J. Asenbauer, T. Eisenmann, M. Kuenzel, A. Kazzazi, Z. Chen, D. Bresser, *Sustain. Energy Fuels* **2020**, *4*, 5387.
[54] G.-L. Zhu, C.-Z. Zhao, J.-Q. Huang, C. He, J. Zhang, S. Chen, L. Xu, H. Yuan, Q. Zhang, *Small* **2019**, *15*, 1805389.
[55] J. Li, H. Li, W. Stone, R. Weber, S. Hy, J. R. Dahn, *J. Electrochem. Soc.* **2017**, *164*, A3529.
[56] Z. Xu, Z. Jiang, C. Kuai, R. Xu, C. Qin, Y. Zhang, M. M. Rahman, C. Wei, D. Nordlund, C.-J. Sun, X. Xiao, X.-W. Du, K. Zhao, P. Yan, Y. Liu, F. Lin, *Nat. Commun.* **2020**, *11*, 83.
[57] Sigma-Aldrich, Safety Data Sheet according to Regulation (EC) No. 1907/2006: Poly(vinylidene fluoride) **2018**, version 6.3, accessed 2019-12-02.
[58] Sigma-Aldrich, Safety Data Sheet according to Regulation (EC) No. 1907/2006: Poly(acrylonitrile-cobutadiene) **2018**, version 6.2, accessed 2019-12-02.
[59] S. R. Dhakate, R. B. Mathur, T. L. Dhami, *J. Mater. Sci.* **2006**, *41*, 4123.
[60] D. Schmidt, M. Kamlah, V. Knoblauch, *J. Energy Storage* **2018**, *17*, 213.
[61] M. Bolsinger, M. Weller, S. Ruck, P. Kaya, H. Riegel, V. Knoblauch, *Electrochim. Acta* **2020**, *330*, 135163.
[62] W. Bauer, D. Nötzel, V. Wenzel, H. Nirschl, *J. Power Sources* **2015**, *288*, 359.
[63] L. Zielke, T. Hutzenlaub, D. R. Wheeler, C.-W. Chao, I. Manke, A. Hilger, N. Paust, R. Zengerle, S. Thiele, *Adv. Energy Mater.* **2015**, *5*, 1401612.
[64] S. R. Daemi, C. Tan, T. Volkenandt, S. J. Cooper, A. Palacios-Padros, J. Cookson, D. J. L. Brett, P. R. Shearing, *ACS Appl. Energ. Mater.* **2018**, *1*, 3702.
[65] A. Sakuda, A. Hayashi, M. Tatsumisago, *Sci. Rep.* **2013**, *3*, 2261.
[66] Z. Deng, Z. Wang, I.-H. Chu, J. Luo, S. Ong, *J. Electrochem. Soc.* **2016**, *163*, A67.
[67] R. Ruess, S. Schweidler, H. Hemmelmann, G. Conforto, A. Bielefeld, D. A. Weber, J. Sann, M. T. Elm, J. Janek, *J. Electrochem. Soc.* **2020**, *167*, 100532.
[68] D. H. Kim, D. Y. Oh, K. H. Park, Y. E. Choi, Y. J. Nam, H. A. Lee, S.-M. Lee, Y. S. Jung, *Nano Lett.* **2017**, *17*, 3013.
[69] A. Neumann, S. Randau, K. Becker-Steinberger, T. Danner, S. Hein, Z. Ning, J. Marrow, F. H. Richter, J. Janek, A. Latz, *ACS Appl. Mater. Interfaces* **2020**, *12*, 9277.
[70] A. Neumann, T. R. Hamann, T. Danner, S. Hein, K. Becker-Steinberger, E. Wachsman, A. Latz, *ACS Appl. Energ. Mater.* **2021**, *4*, 4786.
[71] J. Park, K. T. Bae, D. Kim, W. Jeong, J. Nam, M. J. Lee, D. O. Shin, Y.-G. Lee, H. Lee, K. T. Lee, Y. M. Lee, *Nano Energy* **2021**, *79*, 105456.
[72] J. Park, K. T. Kim, D. Y. Oh, D. Jin, D. Kim, Y. S. Jung, Y. M. Lee, *Adv. Energy Mater.* **2020**, *10*, 2001563.
[73] A. Bielefeld, D. A. Weber, J. Janek, *ACS Appl. Mater. Interfaces* **2020**, *12*, 12821.
[74] J. Lee, S. Byun, H. Lee, Y. Roh, D. Jin, J. Lim, J. Song, C. B. Dzakpasu, J. Park, Y. M. Lee, *Battery Energy* **2023**, *2*, 20220061.
[75] C. Sangrós Giménez, L. Helmers, C. Schilde, A. Diener, A. Kwade, *Chem. Eng. Technol.* **2020**, *43*, 819.
[76] S. Sinzig, T. Hollweck, C. P. Schmidt, W. A. Wall, *J. Electrochem. Soc.* **2023**, *170*, 040513.
[77] V. Laue, N. Wolff, F. Röder, U. Krewer, *Energy Technol.* **2019**, *8*, 1801049.
[78] S. Yamakawa, S. Ohta, T. Kobayashi, *Solid State Ionics* **2020**, *344*, 115079.
[79] M. B. Dixit, A. Parejiya, N. Muralidharan, R. Essehli, R. Amin, I. Belharouak, *Energy Storage Mater.* **2021**, *40*, 239.
[80] P. Braun, C. Uhlmann, M. Weiss, A. Weber, E. Ivers-Tiffée, *J. Power Sources* **2018**, *393*, 119.
[81] J. Y. Kim, S. Jung, S. H. Kang, M. J. Lee, D. Jin, D. O. Shin, Y.-G. Lee, Y. M. Lee, *J. Power Sources* **2022**, *518*, 230736.
[82] A. Bielefeld, D. A. Weber, R. Ruess, V. Glavas, J. Janek, *J. Electrochem. Soc.* **2022**, *169*, 020539.
[83] M. Alabdali, F. M. Zanotto, V. Viallet, V. Seznec, A. A. Franco, *Curr. Opin. Electrochem.* **2022**, *36*, 101127.
[84] J. Janek, W. G. Zeier, *Nat. Energy* **2023**, *8*, 230.
[85] S.-K. Otto, L. M. Riegger, T. Fuchs, S. Kayser, P. Schweitzer, S. Burkhardt, A. Henss, J. Janek, *Adv. Mater. Interfaces* **2022**, *9*, 2102387.
[86] T. Krauskopf, F. H. Richter, W. G. Zeier, J. Janek, *Chem. Rev.* **2020**, *120*, 7745.
[87] M. J. Wang, R. Choudhury, J. Sakamoto, *Joule* **2019**, *3*, 2165.
[88] J. Xu, A. C. Ngandjong, C. Liu, F. M. Zanotto, O. Arcelus, A. Demortière, A. A. Franco, *J. Power Sources* **2023**, *554*, 232294.
[89] K. Becker-Steinberger, S. Schardt, B. Horstmann, A. Latz, *arXiv e-prints* **2021**, https://ui.adsabs.harvard.edu/abs/2021arXiv210110294B.
[90] N. de Klerk, M. Wagemaker, *ACS Appl. Energ. Mater.* **2018**, *1*, 5609.
[91] M. W. Swift, Y. Qi, *Phys. Rev. Lett.* **2019**, *122*, 167701.
[92] R. Usiskin, J. Maier, *Adv. Energy Mater.* **2021**, *11*, 2001455.

[93] M. W. Swift, J. W. Swift, Y. Qi, *Nat. Comput. Sci.* **2021**, *1*, 212.
[94] D. Bistri, A. Afshar, C. Leo, *Meccanica* **2021**, *56*, 1523–1554.
[95] J. Tian, Z. Chen, Y. Zhao, *ACS Omega* **2022**, *7*, 6455.
[96] S. Sun, C.-Z. Zhao, H. Yuan, Y. Lu, J.-K. Hu, J.-Q. Huang, Q. Zhang, *Materials Futures* **2022**, *1*, 012101.
[97] Y. Zhao, R. Wang, E. Martínez-Pañeda, *J. Mech. Phys. Solids* **2022**, *167*, 104999.
[98] W. Ai, B. Wu, E. Martínez-Pañeda, *J. Power Sources* **2022**, *544*, 231805.
[99] T. Lombardo, M. Duquesnoy, H. El-Bouysidy, F. Årén, A. Gallo-Bueno, P. B. Jørgensen, A. Bhowmik, A. Demortière, E. Ayerbe, F. Alcaide, M. Reynaud, J. Carrasco, A. Grimaud, C. Zhang, T. Vegge, P. Johansson, A. A. Franco, *Chem. Rev.* **2021**, *122*, 10899.
[100] C. Ling, *npj Comp. Mater.* **2022**, *8*, 33.

Manuscript received: April 29, 2023
Revised manuscript received: June 14, 2023
Version of record online: July 20, 2023