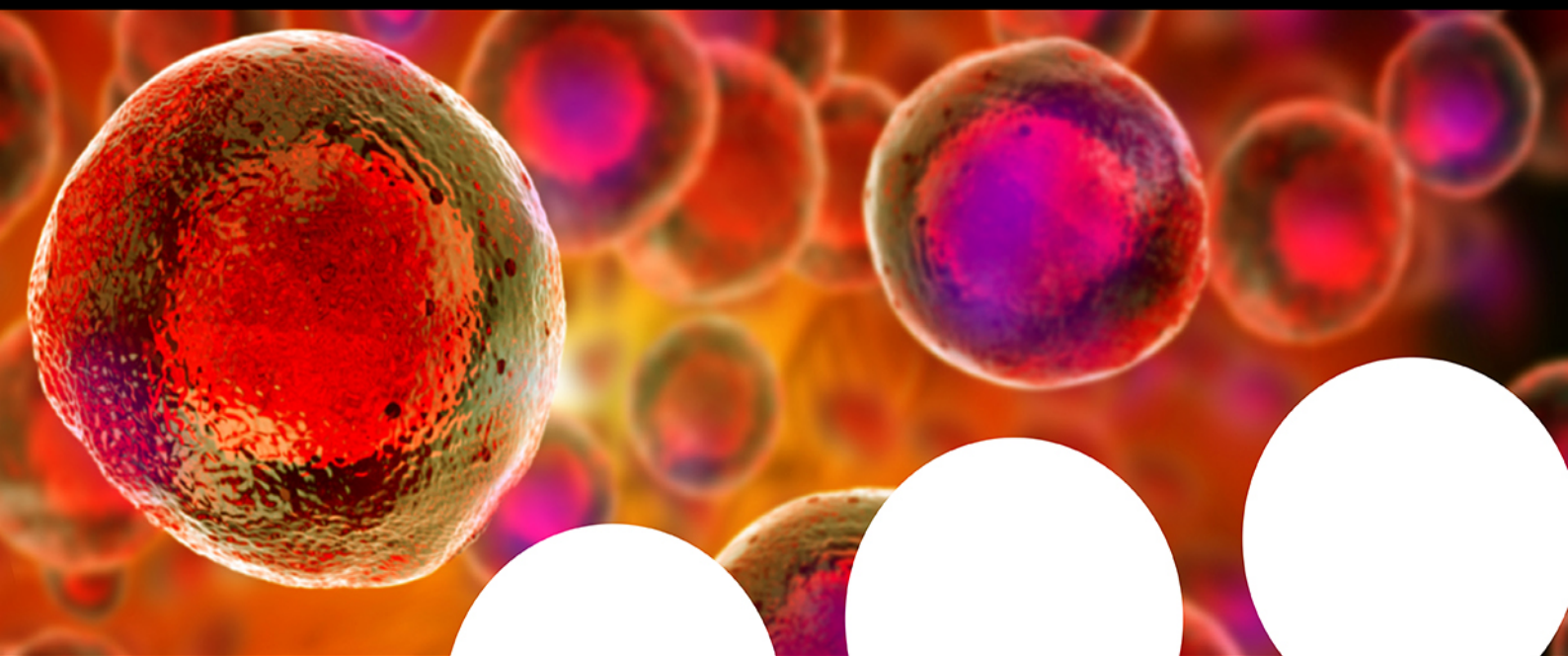


Your research is important and needs to be shared with the world



Benefit from the Chemistry Europe Open Access Advantage

- Articles published open access have higher readership
- Articles are cited more often than comparable subscription-based articles
- All articles freely available to read, download and share.

Submit your paper today.



www.chemistry-europe.org

Incorporating Diamondoids as Electrolyte Additive in the Sodium Metal Anode to Mitigate Dendrite Growth

Julian J. A. Kreissl,^[a, c] Daniel Langsdorf,^[a, c] Boryslav A. Tkachenko,^[b, c] Peter R. Schreiner,^[b, c] Jürgen Janek,^[a, c] and Daniel Schröder^{*[a, c]}

Owing to the high abundance and gravimetric capacity (1165.78 mAh g⁻¹) of pure sodium, it is considered as a promising candidate for the anode of next-generation batteries. However, one major challenge needs to be solved before commercializing the sodium metal anode: The growth of dendrites during metal plating. One possibility to address this challenge is to use additives in the electrolyte to form a protective solid electrolyte interphase on the anode surface. In this work, we introduce a diamondoid-based additive, which is incorporated

into the anode to target this problem. Combining operando and ex situ experiments (electrochemical impedance spectroscopy, optical characterization, and cycling experiments), we show that molecular diamondoids are incorporated into the anode during cycling and successfully mitigate the growth of dendrites. Furthermore, we demonstrate the positive effect of the additive on the operation of sodium-oxygen batteries by means of increased energy density.

Introduction

The leading electrochemical energy storage technology, the lithium-ion battery (LIB), provides a high energy density that can be released reversibly without significant energy loss for a large number of cycles. The continuous development of LIB materials strives to optimize this technology and to overcome its existing challenges, such as the high cost of the anode and cathode materials or capacity fading of the high-nickel materials.^[1] Furthermore, LIBs almost attain their theoretical limit in energy density on a cell level (584 Wh kg⁻¹).^[2] To overcome this limitation and to take the next step in technological advancement of Li-based batteries, it is necessary to use pure metal anodes that provide the highest possible theoretical energy density.^[3] In next-generation battery systems such as metal-

oxygen batteries, the utilization of metal anodes may facilitate significantly higher energy densities that cannot be reached with LIB technology ($W_{\text{theo}}(\text{Li}/\text{O}_2\text{-Batteries})$, discharge product: Li_2O_2) = 3456 Wh kg⁻¹; $W_{\text{theo}}(\text{Na}/\text{O}_2\text{-Batteries})$; discharge product: NaO_2) = 1105 Wh kg⁻¹).^[4] The use of metal anodes in battery cells brings new challenges, such as the high reactivity of the alkali metals towards the liquid electrolyte and limitations that come with electrolytes that degrade at high overpotentials during charge as well as dendrite growth.

The inhomogeneous plating of a metal on the metal anode surface and the resulting dendrite growth is one of the major challenges that complicate the commercial application of metal anodes. Short circuits of dendrites connecting the anode and cathode may result in battery death and create a serious safety risk by the formation of hot spots in the cell. Dendrites may either melt ("soft-shorts"), or heat up but remain intact ("hard-shorts").^[5] Both scenarios can lead to local overheating of the organic electrolyte up to its ignition temperature.^[6] To mitigate or suppress the growth of dendrites, a variety of strategies have been proposed in the past: 1) Specific cycling protocols (e.g., shallow cycling, pulsed charging) that only utilize a small amount of active material or allow for a higher ion concentration near the surface of the anode that is plated;^[6] 2) modification of the electrode (e.g., using intercalation electrodes, 3D-structured electrodes, liquid electrodes);^[7–20] 3) mechanical suppression (e.g., solid electrolytes, polymer-membrane)^[21–24] and 4) modification of the electrolyte (e.g., NaF, InF_3 , fluoroethylene carbonate (FEC), nanodiamond particles).^[6, 25–27]

The aim of most electrolyte modifications is to form a more stable solid electrolyte interphase (SEI) that alters the metal plating processes and slows or avoids dendrite growth. However, the formed SEI might still crack owing to its inhomogeneous

[a] J. J. A. Kreissl, Dr. D. Langsdorf, Prof. Dr. J. Janek, Dr.-Ing. D. Schröder
 Institute of Physical Chemistry
 Justus-Liebig-University Giessen
 Heinrich-Buff-Ring 17, 35392 Giessen (Germany)
 E-mail: daniel.schroeder@phys.chemie.uni-giessen.de

[b] Dr. B. A. Tkachenko, Prof. Dr. P. R. Schreiner
 Institute of Organic Chemistry
 Justus-Liebig-University Giessen
 Heinrich-Buff-Ring 17, 35392 Giessen (Germany)

[c] J. J. A. Kreissl, Dr. D. Langsdorf, Dr. B. A. Tkachenko, Prof. Dr. P. R. Schreiner,
 Prof. Dr. J. Janek, Dr.-Ing. D. Schröder
 Center for Materials Research (LaMa)
 Justus-Liebig-University Giessen
 Heinrich-Buff-Ring 16, 35392 Giessen (Germany)

Supporting Information and the ORCID identification number(s) for the author(s) of this article can be found under:
<https://doi.org/10.1002/cssc.201903499>.

© 2020 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA. This is an open access article under the terms of the Creative Commons Attribution Non-Commercial License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.

ous mechanical and physical properties, resulting in accelerated growth of dendrites owing to a channeled flux of metal ions into these cracks.^[6,28] As an alternative, Gogotsi's group recently proposed nanodiamond particles as an electrolyte additive to mitigate dendrite growth in lithium-metal-based batteries.^[27] They chose nanodiamond particles (a mixture of diamond-containing compounds with different sizes) because their addition to the electroplating bath leads to uniform metal films during electrodeposition.^[29,30] However, the influence of the nanodiamond particles during the co-deposition process is not well understood. Lee and Talbot simulated particle incorporation during electro-co-deposition. Their results showed that the local current density increased next to the incorporated particle.^[31] Therefore, a homogeneous distribution of particles may decrease the electric field effect on grown dendrites by creating nucleation germs.^[31,32] Based on DFT computations, Cheng et al. suggested that lithium ions adsorb on the surface of these nanodiamond particles in the liquid electrolyte during metal plating in the charging step. As a consequence, the additive is co-deposited and incorporated into the surface of the lithium metal electrode, leading to a more homogeneous plating process without dendrites.^[27]

Motivated by this concept, we tested a functionalized diamondoid (bis-*N,N'*-propyl-4,9-dicarboxamidediamantane (DCAD), 1) as an electrolyte additive to suppress the formation of dendrites in symmetric sodium/sodium cells and sodium–oxygen batteries. By using functionalized diamantane, our aim is to enhance several aspects of the co-deposition process: 1) The previously used nanodiamond particles^[27] were prepared by a detonation process and functionalized with octadecyl carboxamide. Small diamond particles of different sizes with a narrow particle size distribution were obtained through this route.^[33] However, in the electrolyte the size distribution significantly widens because of aggregation into clusters ranging from 300 to 700 nm in diameter.^[27] Additionally, the number of functional groups on the surface of these nanodiamonds remains undetermined.^[34–36] In contrast, diamantane has a well-defined diamond-type surface topology that can readily and uniformly be selectively functionalized at various positions, and very specific additives can be designed.^[34] The resulting material is chemically uniform and pure. 2) Higher solubility in the liquid electrolyte can be achieved through functionalization of the diamantane surface. 3) The small size of diamantane (≈ 0.5 nm) leads to a much larger sp^3 -surface area per mass of additive added to the electrolyte. 4) The size of the diamantane molecule enables the use of the additive in 3D-structured anodes with pore diameters below 100 nm.

In this work, we explored the use of functionalized diamantane as an additive in a liquid electrolyte to mitigate dendrite formation on the sodium metal anode. We applied a variety of operando and ex situ electrochemical and surface sensitive characterization methods to elucidate the influence of SEI formation and its composition as well as the co-deposition of the additive with sodium ions, which significantly influences the morphology of plated sodium. Based on the results, we propose a mechanism of sodium metal plating with and without additive that can be used to derive strategies for dendrite miti-

gation and enhancing the cycle life of next-generation battery systems that utilize sodium metal anodes.

Results and Discussion

Less short-circuiting in symmetric Na/Na cells with functionalized diamantane additive

Shallow cycling (0.2 mAh) was conducted at a current density of $356 \mu\text{A cm}^{-2}$ over 100 cycles in symmetric cells without and with additive (Figure 1 a,d). The behavior of the cell without additive was affected by several abrupt voltage drops from the third cycle onwards, which indicate short circuits in the symmetric cell that are probably caused by dendrite growth. These short-time drops are usually assigned as “soft” short circuits that quickly disappear owing to melting of the thin dendrites at locally high current densities.^[5,6] In contrast, no such voltage drops or fluctuations were detected if DCAD was used as an additive (Figure 1 d). Dendrite growth was not completely prevented, but the operating time until a short circuit emerges was significantly increased. This was also evidenced by longer stripping/plating experiments (Figure S1, Supporting Information).

To investigate the impact of the additive on the morphology of the deposited sodium, sodium electrodes were removed after 15 cycles and examined by SEM. The negatively polarized electrode, on which sodium was deposited in the final step, was imaged. The SEM images of the electrode surface of the cell cycled without additive is shown in Figure 1 b,c. The surface of the sodium electrode is rougher with more surface irregularities at the edge of the electrode (Figure 1 b). In comparison, the surface near the center of the electrode is smoother with only two distinct hillocks (Figure 1 c). In contrast to the rough surface of the electrode cycled without additive, the deposited sodium with DCAD in the electrolyte has a smoother surface (Figure 1 e,f) in both regions. This also indicates the effect of the additive and the resulting mitigation of dendrite growth.

To visualize the deposition of sodium in the presence of the additive, a symmetric Na/Na glass cell was used. The cathodically polarized electrode with a high applied current density of 1.27 mA cm^{-2} at different states of charge is shown in Figure 2. In the case of the glass cell without additive (Figure 2, left side) bush-like dendrites started to grow from a flown charge of 30 μAh onwards (see red circle). During the initial deposition of sodium, the growth of dendrites was more pronounced until they grew on the entire electrode at a flown charge of more than 90 μAh . At the end of the measurement (420 μAh), the entire electrode was covered with bush-like dendrites. In comparison with reports in the literature, the morphology of the dendrites remained bush-like and not tree-like at this high current density.^[6] In contrast, in a cell with additive, a smooth and planar surface on the sodium electrode was preserved throughout the experiment.

To show the impact of the initial surface morphology, additional experiments were performed with an intentionally roughened surface (Figure S3). The growth of dendrites should

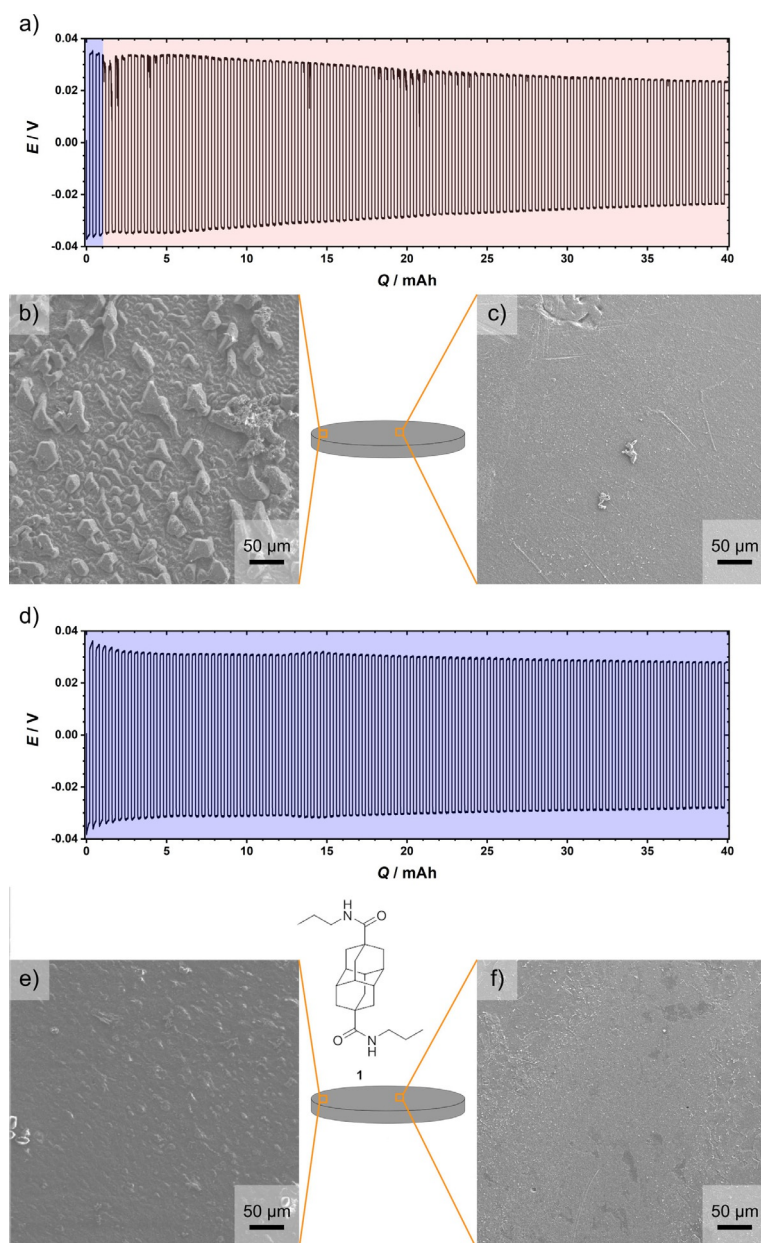


Figure 1. a, d) Shallow cycling (0.2 mAh) at $356 \mu\text{A cm}^{-2}$ of a symmetric cell with sodium electrodes, 0.5 M NaOTf in diglyme as electrolyte; a) without additive. Starting in the charging step of the third cycle, the cell potential occasionally decays and recovers to the initial value, which indicates short circuiting between the electrodes. d) With 1 mg mL^{-1} DCAD. The cell potential exhibits no sudden voltage decay during the entire period of cycling. b, c, e, f) Ex situ SEM images of sodium electrodes from cells corresponding to a) and d) after the 15th cycle. b, c) Cycled without additive. The growth of dendrites appears much more pronounced at b) the edge of the electrode compared with c) the center. e, f) Cycled with additive. The surface has a smoother morphology compared with the electrode cycled without additive.

be much accelerated on a roughened surface; in contrast, with DCAD in the electrolyte the growth of dendrites started much later. However, the growth of dendrites was only delayed. After a charge of $420 \mu\text{Ah}$ passed, small dendrites were visible even with DCAD in the electrolyte. The number of dendrites and their size compared with the results without DCAD in the electrolyte was much smaller.

Impact of functionalized diamantane additive on reactions at the cathode

The electrochemical stability of DCAD was evidenced by cyclic voltammetry in the voltage range from 1.3 to 3.4 V versus Na^+/Na (Figure S4). The investigated voltage range lies within the typical window in which sodium–oxygen batteries are cycled.^[6, 37–40]

To investigate the impact of the additive on the electrochemistry at the cathode, a combination of ex situ and operando techniques was used to analyze the discharge products and the reversibility of the redox reactions. Sodium superoxide was characterized as the sole crystalline discharge product by XRD and SEM (Figure S5a and S5b). A typical cubic NaO_2 morphology of the precipitated discharge product can be observed in the SEM image of a discharged cathode (Figure S5b). The edge length of the NaO_2 -cubes is approximately $12 \mu\text{m}$, which is in accordance with cycling results obtained without additive in the electrolyte.^[40]

Operando pressure monitoring and online electrochemical mass spectrometry (OEMS) were performed to analyze the gaseous reaction products. The results of the pressure monitoring during the galvanostatic cycling of a Na/O₂ cell with DCAD additive in the electrolyte are shown in Figure S5c; a summary of the calculated number of transferred electrons per oxygen molecule derived from monitoring the pressure change is shown in Table S1. These results prove a one-electron charge transfer process per oxygen molecule, which indicate that only superoxide was formed as an oxygen species. The OEMS results (Figure S5d) show that oxygen is the only gaseous product that was evolved during charge. In addition, the rate of oxygen formation of approximately 1.63 nmols^{-1} indicates that sodium superoxide electrochemically decomposed during charge as intended.

Elucidating the impact of the additive on dendrite formation in Na/O₂ batteries

The impact of DCAD on the formation of dendrites during battery operation was investigated by different ex situ and operando techniques. First, galvanostatic cycling was performed to investigate the influence of DCAD on the cycling stability. To achieve comparable charge capacities with comparable amounts of accumulated sodium for various batteries, shallow cycling was applied.

The obtained discharge and charge profiles of a cell without (Figure 3a) and with additive (Figure 3b) are shown in Figure 3. During the first discharge and charge, both cells showed stable voltages between 2.1 and 2.2 V during discharge or 2.3 and 2.4 V during charge. From the second charging step onwards, the voltage profiles cells with additive and

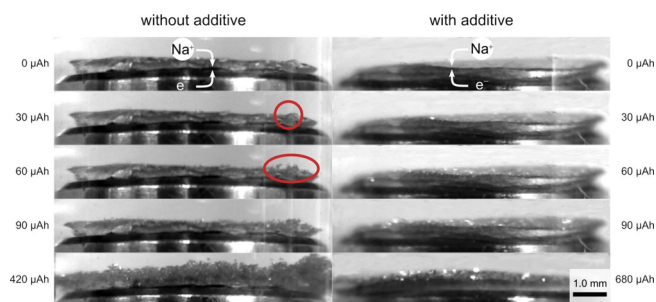


Figure 2. Visualizing the deposition of sodium metal in a symmetric Na/Na glass cell with and without DCAD (1.27 mA cm^{-2}). Bush-like dendrites formed without additive (left). A smooth surface was obtained if DCAD was used (right). The respective galvanostatic polarization curves are shown in Figure S2. Additional results for the glass cell obtained with various surface roughness are shown in Figure S3.

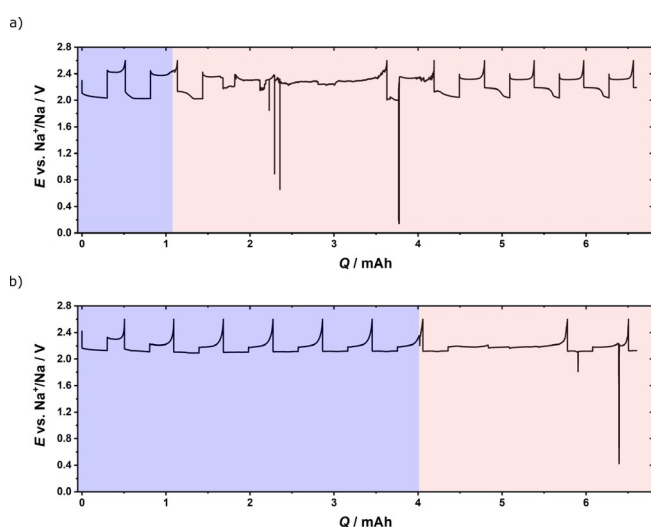


Figure 3. Shallow cycling (0.3 mAh during discharge) of a Na/O₂ battery at $200 \mu\text{A cm}^{-2}$. The cut-off voltage during discharge and charge was 1.8 and 2.6 V , respectively. 0.5 M NaOTf in diglyme was used as electrolyte: a) without additive. Starting in the charging step of the second cycle, the cell potential occasionally decays and recovers to the initial value, which indicates short circuiting between the electrodes. b) 2.5 mg mL^{-1} DCAD was used as additive in the electrolyte. The cell potential starts to fluctuate at approximately the seventh cycle.

without additive differed: Without additive in the electrolyte, the cell voltage started to fluctuate irregularly from the second charging step (Figure 3a). In addition, a coulombic efficiency higher than 100% was observed for cycles two to four (Figure S6a).

In contrast, the DCAD additive significantly improved the cycling stability of the Na/O₂ battery. The cell voltage started to fluctuate much later during the seventh charging step (Figure 3b). A coulombic efficiency of 68 to 97% was observed in the first six cycles and, simultaneously with the voltage drops that occurred from the seventh cycle onwards, coulombic efficiencies of more than 100% were observed (Figure S6b). The delayed voltage drops during cycling show that the growth of dendrites was less pronounced if DCAD was added to the electrolyte. A detailed discussion about the voltage fluctuation in

metal/oxygen batteries is provided in the Supporting Information (near Figure S6).

To obtain better insight into the formation of dendrites, operando galvanostatic electrochemical impedance spectroscopy (GEIS) measurements were performed. The insets in Figure 4a,b illustrate the chosen equivalent circuit model for a two-electrode measurement of our cell. This is a simplified version of the equivalent circuit model of Knudsen et al.,^[41] because our focus was on the processes involved at the anode. In comparison with the galvanostatic shallow cycling in Figure 3, two glass fiber separators were used instead of one to significantly increase the distance between the anode and cathode and ensure that the charging of the cell was not influenced by short circuits in the first two cycles.^[6]

The voltage, charge-transfer resistance ($R_{\text{CT, Na}}$), capacitance ($C_{\text{DL, Na}}$), and alpha (α_{Na}) as a function of capacity are shown in Figure 4. The voltage profiles of both cell types—with and without DCAD—are very similar. In each cycle, the cell potential remained almost constant, ranging from 2.0 to 2.1 V during discharge and at approximately 2.4 V during charge. Interestingly, the $R_{\text{CT, Na}}$ of the sodium anode increased from 5.93Ω up to 660Ω by the introduction of oxygen into the system (Figure S9a). Medenbach et al.^[6] and Abate et al.^[42] showed that this increase is caused by the continuous formation of a SEI mainly composed of NaOH, as investigated by Raman spectroscopy. The SEI grows during the first 24 h of contact between sodium and the electrolyte and the dissolved oxygen.^[6] We assume that by filling the gas reservoir, oxygen dissolves and diffuses to the anode and forms an oxide-based SEI, which inherently leads to the observed increase in $R_{\text{CT, Na}}$. The $R_{\text{CT, Na}}$ increased during the first discharge step in the case of the battery without additive (Figure 4a), which can be explained by a growing SEI layer. Furthermore, α_{Na} decreased during the first discharge step, which indicates increasing roughness of the surface of the electrode exposed to the electrolyte. The changing value of α_{Na} suggests that the SEI did not form as a homogeneous layer. $C_{\text{DL, Na}}$ slightly decayed at the beginning of the measurement but remained mostly constant after 0.2 mAh was reached.

At the start of the first charging step, $R_{\text{CT, Na}}$ dropped from 926 to 549Ω , followed by an increase to a value of 691Ω before it steadily decreased to 407Ω for the rest of the first charging between 0.60 and 0.89 mAh (Figure 4a). This trend can be explained by cracking of the SEI caused by inhomogeneous sodium deposition beneath the SEI.^[6] However, the initial drop of $R_{\text{CT, Na}}$ during the first charging and the subsequent increase might be explained by two simultaneous processes between 0.53 and 0.60 mAh . First, the SEI starts to crack, which leads to dendrite growth. As a consequence, freshly deposited sodium gets in contact with the electrolyte. Subsequently, a fresh SEI layer forms on the newly available sodium. Afterwards, dendrite formation is more pronounced than the formation of a new SEI, leading to the steady decrease of $R_{\text{CT, Na}}$ between 0.60 and 0.89 mAh .

During the second discharging step, $R_{\text{CT, Na}}$ strongly increased to a value of 931Ω between 0.89 and 1.05 mAh (Figure 4a). Subsequently, $R_{\text{CT, Na}}$ slowly increased to a value of 1014Ω be-

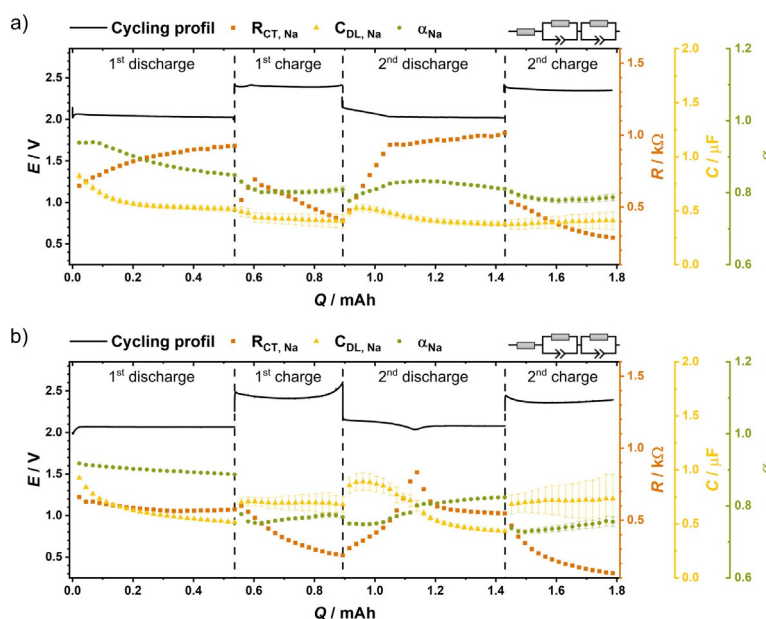


Figure 4. Galvanostatic cycling with superimposed GEIS analysis of Na/O₂ batteries to evaluate the changes of the cell potential (E), charge transfer resistance (R), capacitance (C) and α value (α) at the anode: a) without additive; b) with additive in the electrolyte. The charge-transfer resistance decreases during charge, which indicates that cracks in the SEI form and serve as nucleation sites for dendrites during sodium deposition. A result for an additional measurement under the same experimental conditions is shown in Figure S7. The respective Nyquist plots for the first cycle are shown in Figure S8 (without additive) and Figure S9 (with additive). Error bars indicate the fitting error for the mathematical fit routine for the equivalent circuit and the measured data.

tween 1.05 and 1.43 mAh. The increase of $R_{CT, Na}$ was caused by a new SEI layer that formed on the freshly deposited sodium. Once the entire sodium surface was covered, the slope flattened.

The trends for $R_{CT, Na}$, $C_{DL, Na}$ and α_{Na} of the first discharging step were quite similar in case of the cell with an additive in the electrolyte (Figure 4b). The only difference was the slight decrease of the $R_{CT, Na}$ during the first discharge. Between 0.53 and 0.89 mAh, $R_{CT, Na}$ steadily decreased from 575 to 256 Ω . Presumably, cracks formed inside the SEI and freshly deposited sodium was in contact with the electrolyte. Interestingly, $C_{DL, Na}$ increased from 0.51 to 0.70 μF at the beginning of the first charging step. Thus, it seems that the double layer formed during charge changed compared with the cell without additive. This observation indicates that DCAD was incorporated into the deposited sodium (also shown in Figure 2 by optical imaging).

The second discharge step differs the most compared with the cell without additive. A maximum $R_{CT, Na}$ of 833 Ω at 1.14 mAh was observed. Comparing the slope of $R_{CT, Na}$ with the slope of $C_{DL, Na}$ from 1.00 to 1.30 mAh, it is noticeable that at the maximum of the $R_{CT, Na}$ is a turning point in the slope of $C_{DL, Na}$. The maximum of R is not a clear proof of two different processes. One explanation for this maximum could be that new cracks formed in the SEI owing to inhomogeneous stripping of sodium. Therefore, we must consider several parameters. For the sake of simplicity, we assumed an ideal plate capacitor as a model for the double layer capacitance. Thus, it is defined by Equation (1) and is proportional to $A \cdot d^{-1}$ (A = surface area of the electrode; d = distance between the double layer).

We assumed that the relative permittivity (ϵ_r) and A were approximately constant during the measurement. Consequently, $C_{DL, Na}$ was mainly defined by d and therefore by the solvated ions. Therefore, it can be assumed that two different mechanisms might take place: We suggest that during the first part of the discharge the incorporated DCAD is stripped and afterwards only sodium is stripped. Then, the second charging step is very similar to the first.

$$C = \epsilon_0 \epsilon_r \frac{A}{d} \quad (1)$$

Both Medenbach et al.^[6] and Abate et al.^[42] concluded that the thickness of the SEI layer increases during discharge and resting, which leads to a continuously increasing value for $R_{CT, Na}$. Sodium is deposited on and inside the grain boundaries of the previously formed SEI layer during charge. This SEI layer can break apart owing to dendrite formation, leading to a decreased value for $R_{CT, Na}$.

By implication, the difference in $R_{CT, Na}$ at the end of discharge and at the end of charge (ΔR) is a good measure of the number and size of dendrites grown between the two cycling steps. Extracting the mean value ΔR of three different measurements per cell type yields the following (Table 1): The mean value for ΔR was much lower in the case of cycling a battery with additive than for the cell without an additive. This implies that the growth of dendrites in the Na/O₂ battery was mitigated by using DCAD in the electrolyte.

$R_{CT, Na}$ also decreased for batteries cycled with additive, which indicates that cracks also formed in the SEI. Similarly, the growth of dendrites would be a consequence, but the smaller

Table 1. Mean values of $R_{CT, Na}$ indicating the influence of the additive in Na/O₂ batteries.^[a]

Parameter	Without additive		With additive	
State of cycle	R [Ω]	ΔR [Ω]	R [Ω]	ΔR [Ω]
End of 1 st discharge	870 $\pm$ 40	337 $\pm$ 134	679 $\pm$ 73	207 $\pm$ 81
End of 1 st charge	532 $\pm$ 96		471 $\pm$ 153	
End of 2 nd discharge	989 $\pm$ 17	610 $\pm$ 101	742 $\pm$ 140	421 $\pm$ 13
End of 2 nd charge	379 $\pm$ 88		321 $\pm$ 140	

^[a] Generally, $R_{CT, Na}$ are always higher for cells without DCAD compared with cells with additive. In addition, the mean value of ΔR is smaller in the case of the battery with DCAD.

change in $R_{CT, Na}$ was attributed to significantly slower growth behavior.

To understand the dendrite growth mechanism when the additive was utilized, the anode surfaces from cycled batteries with and without additive were analyzed by SEM and energy-dispersive X-ray spectroscopy (EDS) after the first cycle (Figure 5).

In both cases, the anode surfaces were covered with small dendritic structures. Comparable dendrites with similar diameters of approximately 80 μm were observed in top-view SEM images (Figure 5a,b, and Figure 5e,f): In the absence of the additive, a bush-like dendrite formed and seems to be built by an interlaced wire-like sodium structure (Figure 5a) with a nanometer-sized filament-like substructure (Figure 5b).

In contrast, the dendrites in the cells with DCAD in the electrolyte have a significantly different morphology: The dendrite still has a wire-like structure, which can be observed in the cross section of the anode (Figure S11). However, the dendrite appears to be flattened and the interspace between the sodium wires is filled (Figure 5e). This could be observed even better at higher magnification (Figure 5f). However, the additive did not homogeneously flatten the dendrite surface, which indicates that the additive did not completely change

the dendrite growth, which is also corroborated by the cycling results in Figure 3.

Two processes seem to occur during the dendrite growth when the DCAD additive is available: the sodium wire-like growth and the co-deposition^[27] of the additive and sodium from the electrolyte in the void between the sodium wires. EDS measurements for these SEM images were conducted to shed light on the chemical nature of the dendrites. As expected, the anode surface of the cell with (Figure 5g) and without additive (Figure 5c) mainly consists of sodium. However, sodium is accumulated on top of the dendrite in the case of the cell cycled with additive (Figure 5g). Because the additive mainly consists of carbon, the presence of DCAD might be inferred from the EDS mapping of carbon as accumulation of carbon on top of the dendrite. However, owing to the uneven surface of the anode, the measurement resolution was too low to make a reliable quantification. Comparing the cross section of the anode cycled with (Figure S10) and without additive (Figure S11), we assumed that the material in the void (Figure 5e,f) was not formed as a result of a side reaction with the electrolyte. The mentioned nanometer-sized filamentous structure on the wire-like surface of the dendrite (Figure 5a,b) was also observed on the dendrite from the cell with additive at a magnification of 2500 $\times$ (Figure S11b). However, this nanometer-sized filamentous structure becomes smoother with increasing dendrite height. In the case of a side reaction with the electrolyte, the entire dendrite would be homogeneously covered.

The GEIS results and SEM images show that the formation of dendrites in Na/O₂ batteries was mostly influenced by the SEI, which is consistent with the literature.^[6,41,42] Because $R_{CT, Na}$ increased by a factor of 100 through the introduction of oxygen into the system (Figure 4b and Figure S9a) and visible formation of a grayish passivation film on the sodium electrode was observed (Figure S12b), we assumed that the SEI was mainly formed by oxide species. The GEIS results for symmetrical Na/

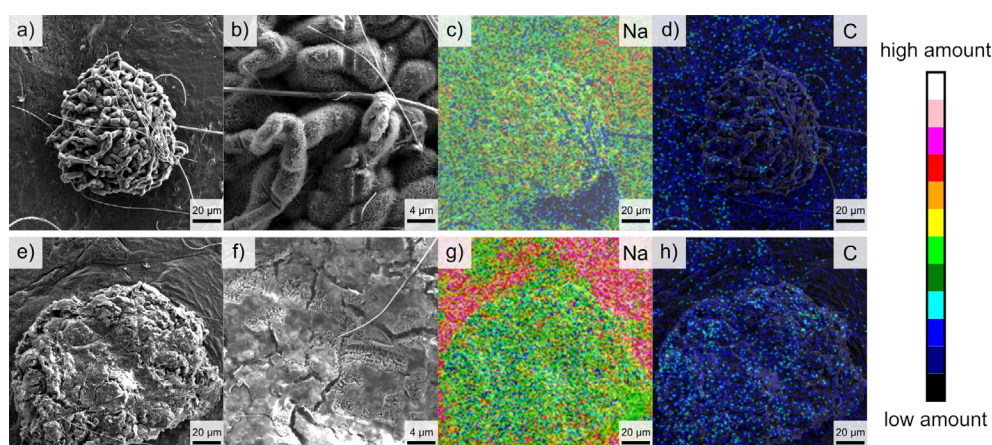


Figure 5. Analysis of the anode morphology after charge without additive (a–d) and with additive (e–h) in the electrolyte: a, b) SEM image after charge without additive. A bush-like dendrite formed of sodium wires is observed on the electrode surface. c, d) EDS mapping of sodium c) and carbon d). e, f) SEM image after charge with additive. A bush-like dendrite constructed of sodium wires is observed on the electrode surface but the interface between the sodium wires is filled with a substructure. g, h) EDS mapping of the sodium g) and carbon h). The thin fibers in the SEM images are residues of the glass fiber separator.

Na cells (Figure S13) also confirmed that the SEI formation was not as pronounced as for the Na/O₂ cells. Therefore, the positive influence of DCAD in full Na/O₂ cells was suppressed by the rapidly formed SEI, which was formed by mobile redox active species in the electrolyte (oxygen in our case). For this reason, we assumed that the use of DCAD in sodium metal-based full cells without mobile redox active species (e.g., sodium ion batteries) can lead to a significantly improved cycling performance. Consequently, the positive results in symmetrical cells do not directly indicate an equally positive effect in full cells. Especially if mobile redox-active compounds are present in the electrolyte.

Insight into the co-deposition of functionalized diamantane additive

A mechanism for dendrite growth on the sodium metal surface is proposed based on the data obtained in our work and the previously described co-deposition mechanism by Cheng et al. (Figure 6).^[27] However, in view of the importance of the formed SEI, we distinguished two cases in the following: symmetric Na/Na cells and Na/O₂ batteries. Based on the interactions between alkali metal ions and amides,^[43–46] we assumed that sodium ions bind to the functional amide groups of DCAD.

The working principle of a symmetric Na/Na cell with DCAD in the electrolyte is illustrated in the left panel in Figure 6. As the SEI is slowly formed, sodium and DCAD are co-deposited from the beginning. Therefore, a smooth sodium layer is obtained. In contrast, the SEI quickly forms in the case of the Na/O₂ battery, as shown in the right panel in Figure 6. From the obtained results, we deduced that the SEI in Na/O₂ batteries inhibits the direct co-deposition of DCAD during charge as a result of the electrochemical properties of the SEI, i.e., no ionic conductivity for the sodium-ion-DCAD complex whereas single sodium ions are still able to pass the SEI (Figure 6 bottom

right). Owing to inhomogeneous plating of sodium beneath the SEI, stress is induced on the SEI and cracks form. These cracks serve as nucleation sites for the dendrite growth. Because fresh sodium wire-like structures form and are in contact with the electrolyte, sodium and DCAD can also be co-deposited. This co-deposition process leads to the observed smooth surface of the dendritic structure in Na/O₂ batteries with additive (Figure 5e).

Another explanation for the strongly different effect of the additive on the cycle life of the symmetric Na/Na cell and the Na/O₂ battery could be the oxygen redox chemistry. Recently, the formation of a highly reactive singlet oxygen in alkali-metal batteries has been described and considered to be one of the major reasons for the degradation of additives such as redox mediators in metal/oxygen batteries.^[43] With the assumption that singlet oxygen formed in our Na/O₂ cell during discharging and charging, unwanted side reactions and degradation of our additive would occur. Over time, the concentration of available additive in the electrolyte would steadily diminish until its co-deposition effect during charging becomes irrelevant and dendrites grow solely by the plating of sodium.

Conclusions

Bis-*N,N'*-propyl-4,9-dicarboxamidodiamantane (DCAD) was investigated as an additive for a diglyme-based electrolyte to mitigate the formation of dendrites in batteries with a sodium metal anode. The successful application of the additive was evidenced by impedance spectroscopy during cycling, optical visualization of sodium deposition, and ex situ SEM/EDS analysis of the electrode surfaces. In particular, the number of stable charge and discharge cycles that can be obtained without short-circuiting considerably improved for symmetric Na/Na cells and slightly improved for Na/O₂ batteries. The fact that DCAD was less effective as an additive in Na/O₂ batteries is ex-

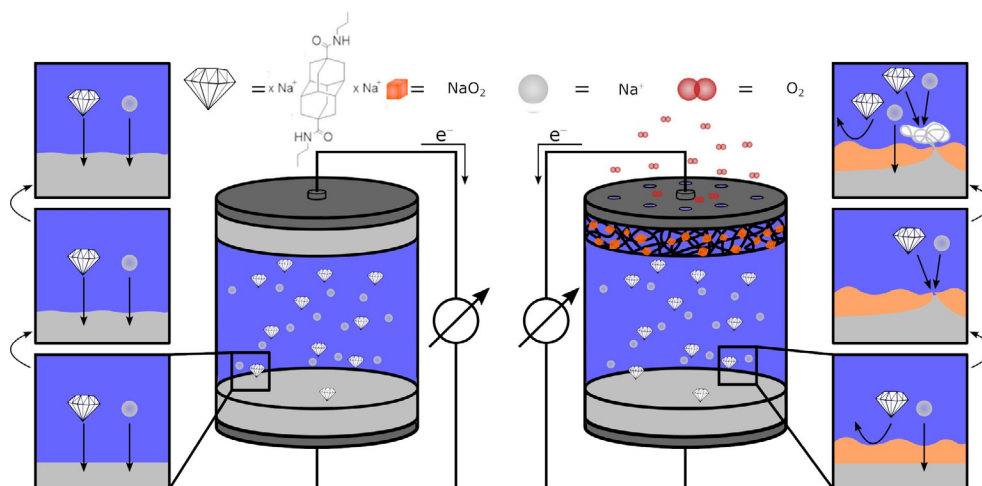


Figure 6. Illustration of the proposed working mechanism during charge of a symmetric Na/Na cell (left side) and a Na/O₂ battery (right side) when utilizing DCAD. In the case of the symmetric cell with sodium electrodes, the additive is directly incorporated into the deposited sodium. However, the pronounced formation of a SEI layer on the sodium anode in the Na/O₂ batteries inhibits the full positive impact of the additive. Cracks might form inside the SEI during sodium deposition owing to its inhomogeneous composition and physical properties. These cracks serve as nucleation sites for dendrite growth. DCAD is co-deposited into the freshly deposited sodium, which is in contact with the electrolyte.

plained by the more pronounced impact of the SEI layer, which had a different composition in the full cell that utilized oxygen at the cathode. As previously reported, the SEI in Na/O₂ batteries mainly forms from oxide species. This can explain the increase in the charge-transfer resistance of the sodium anode by a factor of 100 after the introduction of oxygen into the system. Based on an ex situ surface analysis, the co-deposition of the additive was elucidated and a mechanism for the growth of dendrites in Na/O₂ batteries was proposed, which includes the impact of the SEI as well as the functionality of the additive.

This study provides greater insight into the growth of dendrites in batteries with sodium metal anodes, especially Na/O₂ batteries. The knowledge can be transferred to other battery systems with metal anodes to maximize the practical energy density of the next battery generation. Our results also highlight that the properties of metal anodes in full cells can strongly vary from those in symmetric transference cells, which indicates that only full cell measurements allow proper conclusions about the stability and kinetics of metal anodes under realistic conditions.

Experimental Section

Synthesis of bis-*N,N'*-propyl-4,9-dicarboxamidediamantane (DCAD)

Diamantane-4,9-dicarboxylic acid^[47,48] (2.76 g, 10.0 mmol), SOCl₂ (16.31 g, 10 mL, 137.1 mmol), dimethylformamide (0.28 g, 0.30 mL, 3.9 mmol), and dry benzene (60 mL) were stirred and heated to reflux for 1 h. Upon cooling to room temperature, the solvent and excess SOCl₂ were evaporated to form a light-orange residue. The residue was dissolved in dry benzene (30 mL) and the solvent was again evaporated. This procedure was repeated one more time to remove traces of SOCl₂. Afterwards, CH₂Cl₂ (2 mL) was added to the orange solid and the supernatant solution was removed with a pipette. The remaining solid was dried under reduced pressure to obtain colorless crystals of diamantane-4,9-dicarboxylate dichloride (3.04 g, 9.7 mmol, 97%). To a stirred solution of this dichloroanhydride in dry benzene (60 mL), a mixture of propylamine (1.48 g, 2.06 mL, 25 mmol) and triethylamine (2.53 g, 3.48 mL, 25 mmol) in dry benzene (20 mL) was added dropwise. The resulting mixture was stirred overnight at room temperature. The colorless precipitate was filtered off and washed on the filter with benzene (3 × 15 mL) and H₂O (3 × 15 mL). Drying under reduced pressure yielded pure DCAD (3.31 g, 9.22 mmol, 95%) as a colorless solid (Figure 7). m.p. = 259.0–266.6 °C, dec. (chloroform). ¹H NMR (400 MHz, CDCl₃): δ = 5.64 (t, 2H, *J* = 5.8 Hz), 3.25–3.17 (m, 4H), 1.86 (s, 18H), 1.52 (sext, 4H, *J* = 7.4 Hz), 0.92 ppm (t, 6H, *J* = 7.4 Hz); ¹³C NMR (101 MHz, CDCl₃): δ = 177.5 (C), 41.0 (CH₂), 39.5 (CH₂), 38.6 (C), 36.5 (CH), 22.9 (CH₂), 11.3 ppm (CH₃); IR (KBr): $\tilde{\nu}$ = 3450, 2892, 1630, 1527, 1438, 1383, 1323, 1242, 1049, 614 cm⁻¹; MS: *m/z* (%) = 358 (41), 330 (3), 272 (100), 230 (4), 187 (5), 185 (5), 131 (4), 129 (4), 105 (5), 91 (6), 79 (4). HRMS (ESI) *m/z*: [*M*+Na]⁺

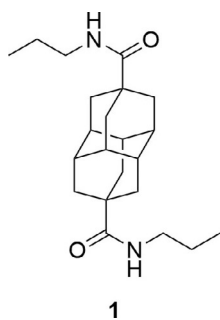


Figure 7. Bis-*N,N'*-propyl-4,9-dicarboxamidediamantane (1); DCAD.

calcd for C₂₂H₃₄N₂O₂Na 381.2512; found 381.2513. anal. calcd for C₂₂H₃₄N₂O₂: C, 73.70; H, 9.56; N, 7.81. found: C, 73.19; H, 9.57; N, 7.76. The reaction sequence starting from diamantane and NMR spectra are available in Figures S14–S16.

Cell assembly

The Na/O₂ battery tests were conducted in two different cell setups: 1) A modified Swagelok design (Giessen cell)^[39] was used in all cell tests except for the pressure monitoring and OEMS measurement. 2) A modified cell setup reported by Liang et al.^[49] was used. Pure sodium (Sigma–Aldrich, ≥ 99% stored under mineral oil (pressure monitoring/OEMS)), BASF SE pure sodium ((Swagelok cell), diameter: 12 mm) was used as anode material. Glass fiber filters (Whatman GF/A; diameter: 16 mm (pressure monitoring/OEMS) or 12 mm (all other electrochemical cell test)) were used as separator material. They also served as an electrolyte reservoir for 0.5 M NaOTf (Sigma–Aldrich; 98%) in Diglyme (Sigma–Aldrich; anhydrous 99.5%) with or without DCAD (2.5 mg mL⁻¹) as an additive. Diglyme was dried over molecular sieves (pore diameter 3 Å, for 1 week), NaOTf under reduced pressure at 120 °C for 24 h and 1 under reduced pressure at 100 °C for 24 h. The water content of the electrolytes was determined by the Karl-Fischer titration technique (Metrohm) and was below 50 ppm (mass fraction). A binder-free gas diffusion layer (GDL, Freudenberg, H2315, Quintech; diameter: 10 mm) was used as cathode material. Before the electrochemical cell tests, the gas reservoir of the cells were flushed with oxygen (1 bar overpressure) for 10 s. Subsequently, the gas reservoir was opened for less than one second to reduce the overpressure inside the cell to atmospheric pressure.

The symmetric Na/Na cells were also built in two different cell setups: 1) A modified Swagelok design ("Giessen cell")^[39] was used in all electrochemical cell tests instead of the glass cell tests to visualize the dendrite growth. 2) A cell designed by Medenbach et al.^[6] was used. Sodium metal (BASF SE, diameter: 8 mm (glass cell), 10 mm (galvanostatic cycling), 12 mm (GEIS)) was used as the electrode material. Glass fiber filters (Whatman GF/A; diameter: 12 mm (GEIS)) or polypropylene (Celgard 2325; diameter: 12 mm (galvanostatic cycling)) sheets were used as separator material. 0.5 M NaOTf (Sigma–Aldrich; 98%) in Diglyme (Sigma–Aldrich; anhydrous 99.5%) with or without DCAD (1.0 mg mL⁻¹) as an additive was used as the electrolyte. The solvent, conducting salt, and additive were dried as described above. The water content of the electrolytes was controlled by the Karl-Fischer titration technique (Metrohm) and determined to be below 50 ppm (mass fraction).

All cells were assembled in an argon-filled glove box with water content below 0.5 ppm in Ar and oxygen content below 2.5 ppm in Ar.

Electrochemical testing

The cyclic voltammetry measurements were performed in a gas-tight glass cell with two valves for gas supply. The glass cell was equipped with a glassy carbon working electrode (ALS, diameter: 3 mm), a platinum wire as counter electrode (ALS), and activated carbon^[50] or sodium metal as reference electrode. For the CV measurements, 1 mL of 0.5 M NaOTf in diglyme or 0.5 M tetrabutylammonium tetrafluoroborate (TBABF₄) in diglyme with a small amount of decamethylferrocene (DMFc) added to the TBA⁺-containing electrolyte as an inner reference were used as electrolyte. For the measurements with additive, 0.5 mg mL⁻¹ DCAD was added to the electrolyte. All cells were assembled in an argon-filled glovebox. First, CV measurements under argon atmosphere were

conducted using a SP300 potentiostat (BioLogic). Subsequently, the glass cells were transferred out of the glovebox and purged for 10 min with pure oxygen (Praxair, purity 5.0). Afterwards, additional CVs were measured under an oxygen atmosphere using a SP150 potentiostat (BioLogic). All CVs were started at the open circuit voltage (OCV). The scan rate was 20 mV s^{-1} with a voltage window between 1 and 4 V versus Na^+/Na .

The Swagelok cells and pressure monitoring/OEMS cell were investigated galvanostatically in a temperature chamber at 25°C (298.15 K) with a battery cycler system 4300 from Maccor or VMP3 electrochemical testing unit (BioLogic). A current density between 100 and $400 \mu\text{A cm}^{-2}$ was used for these experiments. The specific current, current density, cut-off voltage, and fixed capacity for the cycling procedure are provided in the result sections.

All electrochemical impedance spectroscopy (EIS) measurements were performed with a SP200 potentiostat (BioLogic). In the case of the Na/O_2 batteries, potentiostatic electrochemical impedance spectroscopy (PEIS) was performed at OCV using an AC amplitude of 20 mV in the frequency range from 3 MHz to 1 Hz with 10 points/decade and 5 periods/frequency. GEIS was performed at a DC current of $157 \mu\text{A}$ ($200 \mu\text{A cm}^{-2}$) and with an AC amplitude of $15.7 \mu\text{A}$. The frequency was varied from 100 kHz to 390 mHz with 10 points/decade and 5 periods/frequency. A DC step of 6 min and 48 s with applied constant current was performed before each GEIS measurement. 24 GEIS measurements were performed during each discharge and 16 GEIS measurements were performed during each charge. A capacity of 0.53 mAh was achieved during discharge and 0.36 mAh during charge. For the Na/Na cells, potentiostatic electrochemical impedance spectroscopy (PEIS) was performed at the OCV using an AC amplitude of 20 mV that was varied from 1 MHz to 650 mHz with 15 points/decade and 5 periods/frequency. GEIS was performed at a DC of $226 \mu\text{A}$ ($200 \mu\text{A cm}^{-2}$) and with an AC amplitude of $113 \mu\text{A}$. The frequency was varied from 1 MHz to 650 mHz with 10 points/decade and 5 periods/frequency. One step of 2 min and 30 s with applied constant current was performed before each GEIS measurement. 30 GEIS measurements were performed during each charge and 30 GEIS measurements were performed during each discharge. A capacity of 0.61 mAh was achieved during charge and discharge. EIS data fitting to equivalent circuit models was performed by means of the software RelaxIS software package (rhd instruments, Version 3). The sodium-deposition experiments inside the glass cell were performed by using a SP200 potentiostat (Bio-Logic) and applying a current of 0.360 mA (1.27 mA cm^{-2}).

Pressure monitoring and OEMS measurements

One valve on the oxygen reservoir of the pressure monitoring/OEMS cell was connected through a 316SS capillary (diameter: 0.16 mm) to the online electrochemical mass spectrometry and pressure monitoring system. Two SS316 tubes with ball valves were connected to the top of the cell. These valves allowed the connection of the pressure transducer (GB-3000HK, Ganbei Zhongtian Tech.) for pressure monitoring during discharge or the connection to the mass spectrometer (QMS 200, Stanford Research Systems) during charge. The evolved gas during charge was transported into the mass spectrometer by a steady flux of an argon carrier gas. A standard gas mixture of oxygen, carbon dioxide, carbon monoxide, hydrogen, and water (5000 ppm each, balanced by argon, Linde HKO) was used to calibrate the mass spectrometer and quantify the MS signals during the OEMS measurements. The cell was flushed with oxygen for 5 min before discharge and with argon for 20 min before charge.

Optical characterization

SEM and EDS investigations were performed with a Merlin high-resolution Schottky field emission electron microscope (Zeiss SMT) equipped with a X-MAX EDS detector (Oxford Instruments). The samples were removed from the cells, washed three times with $50 \mu\text{L}$ of diglyme followed by drying under reduced pressure at room temperature, and subsequently transferred to the SEM systems. A high vacuum transfer module (Leica) was used to transfer the samples into the SEM system without exposure to the atmosphere. Optical images of the samples were taken with a 12 megapixel camera (iPhone 8, Apple) and the sodium deposition inside the glass cells was monitored with a 2.4 megapixel camcorder (Canon, Legria HFM 46).

Structural characterization

The X-ray diffraction measurements were conducted with a powder X-ray diffractometer (X'Pert Pro, Panalytical). A CuK_α X-ray source with a voltage of 40 kV and a current of 40 mA was used for this purpose. To protect the air-sensitive samples, a self-made gas-tight sample holder was used, which was sealed with Kapton foil. The respective electrodes were removed from the cells and washed three times with $50 \mu\text{L}$ pure diglyme followed by drying under vacuum at room temperature before measurements.

Acknowledgements

J.K. gratefully acknowledges financial support by the Chinese University of Hong Kong during his three months of exchange during this work. We also acknowledge fruitful scientific discussions with Prof. Dr. Yi-Chun Lu from CUHK. In addition, D.L., J.J., and D.S. gratefully acknowledge financial support by the BMBF (Federal Ministry of Education and Research) within the projects "BenchBatt" (03XP0047D) and "MeLuBatt" (03XP0110A). B.A.T. and P.R.S. have been, in part, supported by the U.S. Department of Energy (Contract No. DE-AC02-76SF00515). The authors thank Dr. Anja Henss for fruitful discussions on surface analytics and ToF-SIMS measurements during the revision.

Conflict of interest

The authors declare no conflict of interest.

Keywords: sodium batteries • electrolytes • additives • dendrites

- [1] O. Gröger, H. A. Gasteiger, J.-P. Suchsland, *J. Electrochem. Soc.* **2015**, *162*, A2605–A2622.
- [2] M. M. Thackeray, C. Wolverton, E. D. Isaacs, *Energy Environ. Sci.* **2012**, *5*, 7854.
- [3] D. Linden, T. B. Reddy, *Handbook of Batteries*, McGraw-Hill, New York, **2001**, chapter 34.
- [4] P. Adelhelm, P. Hartmann, C. L. Bender, M. Busche, C. Eufinger, J. Janek, *Beilstein J. Nanotechnol.* **2015**, *6*, 1016–1055.
- [5] X. Zhang, E. Sahraei, K. Wang, *Sci. Rep.* **2016**, *6*, 32578.
- [6] L. Medenbach, C. L. Bender, R. Haas, B. Mogwitz, C. Pompe, P. Adelhelm, D. Schröder, J. Janek, *Energy Technol.* **2017**, *5*, 2265–2274.
- [7] B. Jache, P. Adelhelm, *Angew. Chem. Int. Ed.* **2014**, *53*, 10169–10173; *Angew. Chem.* **2014**, *126*, 10333–10337.

- [8] U. von Sacken, E. Nodwell, A. Sundher, J. R. Dahn, *J. Power Sources* **1995**, *54*, 240–245.
- [9] T.-T. Zuo, X.-W. Wu, C.-P. Yang, Y.-X. Yin, H. Ye, N.-W. Li, Y.-G. Guo, *Adv. Mater.* **2017**, *29*, 1700389.
- [10] Y. Liu, D. Lin, Z. Liang, J. Zhao, K. Yan, Y. Cui, *Nat. Commun.* **2016**, *7*, 10992.
- [11] F. Farmakis, C. Elmasides, P. Fanz, M. Hagen, N. Georgoulas, *J. Power Sources* **2015**, *293*, 301–305.
- [12] M. Hagen, E. Quiroga-González, S. Dörfler, G. Fahrer, J. Tübke, M. J. Hoffmann, H. Althues, R. Speck, M. Krampfert, S. Kaskel, et al., *J. Power Sources* **2014**, *248*, 1058–1066.
- [13] M. Chamoun, B. J. Hertzberg, T. Gupta, D. Davies, S. Bhadra, B. Van Tasell, C. Erdonmez, D. A. Steingart, *NPG Asia Mater.* **2015**, *7*, e178.
- [14] D. Stock, S. Dongmo, K. Miyazaki, T. Abe, J. Janek, D. Schröder, *J. Power Sources* **2018**, *395*, 195–204.
- [15] C. L. Bender, B. Jache, P. Adelhelm, J. Janek, *J. Mater. Chem. A* **2015**, *3*, 20633–20641.
- [16] G. Weddigen, *J. Electrochem. Soc.* **1980**, *127*, 1225–1227.
- [17] L. Xue, H. Gao, W. Zhou, S. Xin, K. Park, Y. Li, J. B. Goodenough, *Adv. Mater.* **2016**, *28*, 9608–9612.
- [18] B. Sun, P. Li, J. Zhang, D. Wang, P. Munroe, C. Wang, P. H. L. L. Notten, G. Wang, *Adv. Mater.* **2018**, *30*, 1801334–1801342.
- [19] Y.-J. Kim, H. S. Jin, D.-H. Lee, J. Choi, W. Jo, H. Noh, J. Lee, H. Chu, H. Kwack, F. Ye, et al., *ChemElectroChem* **2018**, *5*, 3169–3175.
- [20] T.-T. Zuo, Y.-X. Yin, S.-H. Wang, P.-F. Wang, X. Yang, J. Liu, C.-P. Yang, Y.-G. Guo, *Nano Lett.* **2018**, *18*, 297–301.
- [21] R. Pinedo, D. A. Weber, B. Bergner, D. Schröder, P. Adelhelm, J. Janek, *J. Phys. Chem. C* **2016**, *120*, 8472–8481.
- [22] B. J. Bergner, M. R. Busche, R. Pinedo, B. B. Berkes, D. Schröder, J. Janek, *ACS Appl. Mater. Interfaces* **2016**, *8*, 7756–7765.
- [23] L. Porz, T. Swamy, B. W. Sheldon, D. Rettenwander, T. Frömling, H. L. Thaman, S. Berendts, R. Uecker, W. C. Carter, Y. M. Chiang, *Adv. Energy Mater.* **2017**, *7*, 1701003.
- [24] X. Bi, X. Ren, Z. Huang, M. Yu, E. Kreidler, Y. Wu, G. Girishkumar, B. McCloskey, A. C. Luntz, S. Swanson, et al., *Chem. Commun.* **2015**, *51*, 7665–7668.
- [25] Q. Pang, X. Liang, I. R. Kochetkov, P. Hartmann, L. F. Nazar, *Angew. Chem. Int. Ed.* **2018**, *57*, 9795–9798; *Angew. Chem.* **2018**, *130*, 9943–9946.
- [26] R. Mogi, M. Inaba, S.-K. Jeong, Y. Iriyama, T. Abe, Z. Ogumi, *J. Electrochem. Soc.* **2002**, *149*, A1578–A1583.
- [27] X. Cheng, M. Zhao, C. Chen, A. Pentecost, K. Maleski, T. Mathis, X.-Q. Zhang, Q. Zhang, J. Jiang, Y. Gogotsi, *Nat. Commun.* **2017**, *8*, 336.
- [28] Y. S. Cohen, Y. Cohen, D. Aurbach, *J. Phys. Chem. B* **2000**, *104*, 12282–12291.
- [29] V. Medeliené, V. Stankevič, G. Bikulčius, *Surf. Coat. Technol.* **2003**, *168*, 161–168.
- [30] I. Petrov, P. Detkov, A. Drovosekov, M. V. Ivanov, T. Tyler, O. Shenderova, N. P. Voznecova, Y. P. Toporov, D. Schulz, *Diam. Relat. Mater.* **2006**, *15*, 2035–2038.
- [31] J. Lee, J. B. Talbot, *J. Electrochem. Soc.* **2005**, *152*, C706.
- [32] C.-P. Yang, Y.-X. Yin, S.-F. Zhang, N.-W. Li, Y.-G. Guo, *Nat. Commun.* **2015**, *6*, 8058.
- [33] A. Krüger, Y. Liang, G. Jarre, J. Stegk, *J. Mater. Chem.* **2006**, *16*, 2322–2328.
- [34] M. A. Gunawan, J.-C. Hierso, D. Poinot, A. A. Fokin, N. A. Fokina, B. A. Tkachenko, P. R. Schreiner, *New J. Chem.* **2014**, *38*, 28–41.
- [35] V. N. Mochalin, O. Shenderova, D. Ho, Y. Gogotsi, *Nat. Nanotechnol.* **2012**, *7*, 11–23.
- [36] H. Schwertfeger, A. A. Fokin, P. R. Schreiner, *Angew. Chem. Int. Ed.* **2008**, *47*, 1022–1036; *Angew. Chem.* **2008**, *120*, 1038–1053.
- [37] P. Hartmann, C. L. Bender, J. Sann, A. K. Dürr, M. Jansen, J. Janek, P. Adelhelm, *Phys. Chem. Chem. Phys.* **2013**, *15*, 11661.
- [38] C. Xia, R. Black, R. Fernandes, B. Adams, L. F. Nazar, *Nat. Chem.* **2015**, *7*, 496–501.
- [39] C. L. Bender, P. Hartmann, M. Vračar, P. Adelhelm, J. Janek, *Adv. Energy Mater.* **2014**, *4*, 1301863–1301862.
- [40] D. Schröder, C. L. Bender, M. Osenberg, A. Hilger, I. Manke, J. Janek, *Sci. Rep.* **2016**, *6*, 24288.
- [41] K. B. Knudsen, J. E. Nichols, T. Vegge, A. C. Luntz, B. D. McCloskey, J. Hjelm, *J. Phys. Chem. C* **2016**, *120*, 10799–10805.
- [42] I. I. Abate, L. E. Thompson, H. C. Kim, N. B. Aetukuri, *J. Phys. Chem. Lett.* **2016**, *7*, 2164–2169.
- [43] D. S. Gill, J. P. Singla, R. C. Paul, S. P. Narula, *J. Chem. Soc. Dalton Trans.* **1972**, 522.
- [44] D. V. S. Jain, B. S. Lark, S. P. Kochar, V. K. Gupta, *Indian J. Chem.* **1969**, *7*, 256–259.
- [45] D. Balasubramanian, A. Goel, C. N. R. Rao, *Chem. Phys. Lett.* **1972**, *17*, 482–485.
- [46] D. Balasubramanian, R. Shaikh, *Biopolymers* **1973**, *12*, 1639–1650.
- [47] N. A. Fokina, B. A. Tkachenko, A. Merz, M. Serafin, J. E. P. Dahl, R. M. K. Carlson, A. A. Fokin, P. R. Schreiner, *Eur. J. Org. Chem.* **2007**, 4738–4745.
- [48] N. A. Fokina, B. A. Tkachenko, J. E. P. Dahl, R. M. K. Carlson, A. A. Fokin, P. R. Schreiner, *Synthesis* **2012**, *44*, 259–264.
- [49] Z. Liang, Y.-C. Lu, *J. Am. Chem. Soc.* **2016**, *138*, 7574–7583.
- [50] D. Weingarth, A. Foelske-Schmitz, A. Wokaun, R. Kötz, *Electrochem. Commun.* **2012**, *18*, 116–118.

Manuscript received: December 20, 2019
 Revised manuscript received: February 28, 2020
 Accepted manuscript online: March 2, 2020
 Version of record online: April 2, 2020