Initial steps in the formation of the solid electrolyte interphase on alkaline metal anodes studied by ab initio simulations

Daniel Stottmeister *,† and Axel Groß *,†,‡

†Institute of Theoretical Chemistry, Ulm University,89069 Ulm, Germany
‡Helmholtz Institute Ulm (HIU) Electrochemical Energy Storage, Helmholtzstr. 11,89069
Ulm, Germany

E-mail: daniel.stottmeister@uni-ulm.de; axel.gross@uni-ulm.de

Abstract

The transition from lithium-based energy storage to post lithium systems plays a crucial part in achieving an environmentally sustainable energy infrastructure. Prime candidates for the replacement of lithium are sodium and potassium batteries. Despite being critical to battery performance, the solid electrolyte interphase (SEI) formation process for Na and K batteries remains insufficiently understood, especially compared to the well-established lithium systems. Using ab initio molecular dynamics (AIMD) simulations based on density functional theory (DFT) calculations, we study the first steps of SEI formation upon the decomposition of typical solvent molecules on lithium, sodium and potassium metal anodes. We find that two dominant products form during the early SEI formation of cyclical carbonates on alkali metal anodes, carbon monoxide and alkali-carbonate. The carbonate-producing reaction is thermodynamically favorable for all tested metals, however, Na and K exhibit a much stronger selectivity than Li towards carbonate formation. Furthermore, we propose a previously unknown reaction mechanism for the CO polymerization on metallic lithium.

Introduction

With the transition from fossil fuel-based energy production to environmentally sustainable methods, a strong need for safe and efficient energy storage has arisen. One well-established method is the electrochemical storage of energy in rechargeable batteries, with lithium-based batteries, in particular, having revolutionized energy storage for all sorts of electronic devices.^{1,2} Lithium-based batteries alone, however, will not solve today's energy storage problems as they face a variety of challenges, ranging from limited resource availability³ of crucial battery components over limited battery lifetimes⁴ to serious safety concerns.⁵ To combat the increasing resource shortages associated with lithium batteries and provide affordable and environmentally sustainable energy storage for the foreseeable future, research efforts with regards to alternative battery types have increased tremendously.⁶⁻¹³ Alternatives to the current generation of lithium batteries include other alkaline batteries, replacing lithium with sodium or potassium, as well as batteries using magnesium, calcium, or aluminum.

These new battery types also suffer from various problems, ranging from a limited energy density to aging and safety concerns similar to those found in lithium-based batteries. Especially for alternative alkaline batteries employing sodium or potassium, some very similar challenges remain compared to those known for lithium batteries.^{14,15} Commonly used electrolyte components like ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), and dimethoxyethane (DME), LiPF₆, LiBF₄, and LiTFSI, are known to be unstable in the presence of lithium-based battery anodes, leading to the formation of a passivation layer known as the solid electrolyte interphase (SEI).¹⁶ The SEI formation poses one of the main limitations in the insufficient cycling stability of the battery, leading either to a reduced battery capacity or, in the worst case, a catastrophic thermal runaway.¹⁰ At the same time, the SEI also acts as a protective layer preventing further electrolyte decomposition.¹⁷

Given this importance of the SEI, understanding the electrode/electrolyte interface has presented itself as a crucial part of improving battery performance and has been the focus of numerous studies, utilizing experimental and theoretical approaches.^{18–20} One established theoretical approach for investigating the SEI formation is ab initio molecular dynamic simulation (AIMD),^{18,21} which enables atomistic insights into reactions/interactions between electrolyte components and the battery anode. DFT-based AIMD simulations are generally limited by their comparatively high calculational cost, leading to short simulation times.²² However, thanks to improving computational power, the length and time scales accessible to AIMD simulations have increased considerably so that AIMD simulations have already provided insights into the electrolyte reduction reactions and predicted decomposition pathways for the well-established lithium battery systems,¹⁸ which were later confirmed by experimental measurements.²³ Recently these studies have been expanded upon and applied for other battery systems like hard carbon sodium anode batteries.²⁴ In this paper, we have utilized DFT-based AIMD simulations to simulate various common electrolyte component interactions with lithium, sodium, and potassium surfaces. We find spontaneous dissociative adsorption events^{25,26} which we carefully analyze. We compare the different decomposition pathways between the elements and identify similarities and differences concerning the solid electrolyte interphase formation.

Computational Details

The electrolyte decomposition reactions have been modeled using first-principles density functional theory (DFT) calculations within the plane-wave-based Vienna ab initio simulation package (VASP)²⁷ framework. To better account for chemisorption, the exchange-correlation was calculated using the revised Perdew-Burke-Ernzerhof functional (RPBE).²⁸



Figure 1: a) View of the simulation cell used for the AIMD simulation of EC on Li(100). b) Side view of the MD simulation cell for the EC decomposition.

The electron-core interactions were described via the projector augmented wave (PAW) method.^{29,30} The alkali anode surfaces were modeled using a 6-layer slab with a 4x4 geometry and a vacuum region of > 20 Å, using the (100) surface termination. A Γ centered 5 x 5 x 1 k-point grid was used to calculate the energies. Total energies were converged up to 10^{-5} eV using the Methfessel-Paxton smearing scheme³¹ with a width of 0.2 eV, with the ionic geometry being converged to energetic differences below 10^{-4} eV. Note that all calculations were performed for charge-neutral systems. Although we also consider the interaction of ions with the metal surfaces, upon adsorption these ions become coupled to the electron reservoir of the metal anodes, so that it is more appropriate to consider the adsorbate system as being overall charge-neutral.

To include dispersion effects, the DFT-D3 vdW correction of Grimme³² was applied. The molecular dynamics simulations have been performed within a canonical ensemble using the Nose thermostat with a Nose-frequency of 10¹⁴ Hz at a temperature of 300K. A typical cell setup for the MD simulations is shown in Fig. 1. The simulations included between 2-6 electrolyte molecules explicitly, further electrolyte molecules were neither explicitly nor implicitly considered, which is a simplification since, in an actual cell, there is no vacuum following the first electrolyte molecules but rather a solution of various components. The ab-

sence of solvent molecules means that the performed simulations cannot catch any solvation effects and might overestimate the interactions between the electrolyte molecules and the surface. There is, however, one advantage of neglecting of solvation effects since, without any attractive interaction between different electrolyte layers, the adsorbed molecules are expected to be more reactive concerning the surface. This increased reactivity is beneficial because of the limited simulation timeframe of just a few picoseconds, which otherwise would make any observation of surface reactions very costly.

Results and Discussion

Due to the dominance of lithium-based batteries, the lithium SEI is by far the most studied and consequently best understood of the alkaline metal SEIs.^{33–35} The decomposition reactions of cyclic carbonates, such as ethylene carbonate (EC), propylene carbonate (PC), or vinylene carbonate (VC), in particular, have been studied extensively and have been shown to play a critical role in the formation of the SEI.^{36–38} Cyclic carbonates decompose in oneelectron and two-electron processes, 36 at the electrode surface, 37 allowing for a variety of decomposition products to form. The number of possible reaction products for EC alone could account for many observed electrolyte decomposition products.³⁸ Depending on the location of the bond cleavage, EC is expected to produce ethylene or carbon monoxide gas¹⁸. Both the generation of ethylene gas³⁹ and of CO have been found experimentally.⁴⁰Further, AIMD simulations for the lithium metal surface have shown that the spontaneous EC decomposition occurs at a picosecond timescale.⁴¹ First-principles electronic structure calculations have suggested a rapid decomposition of ethylene carbonate and propylene carbonate on a lithium metal surface,⁴² along the reaction pathways depicted in Fig. 2. When examining these reduction reactions, which were also observed on different surfaces such as LiSi,⁴³ one question arises: Is this purely a reduction process, or is this reaction element/site specific? In order to answer this question, a direct comparison between the decomposition reactions



Figure 2: Observed decomposition pathways for EC on alkali metal surfaces.

on Li, Na, and K was made in this study.

We have studied the interaction of some of the most common electrolyte molecules used in alkali metal batteries, including ethylene carbonate (EC), propylene carbonate (PC) and dimethoxyethane (DME), with well-defined lithium, sodium, and potassium surfaces in order to derive chemical trends among these alkali metals. In addition, to validate our calculations we compare their results with corresponding experimental studies.⁴⁴ Further simulations for two electrolyte salts, alkali-hexafluorophosphate (MPF_6) and alkali-perchlorate $(MClO_4)$ have been performed. Note that due to their still high computational demand, AIMD simulations are usually not well-suited to explore reaction mechanisms, in particular those of activated reactions. However, for several of the considered electrolyte-anode combinations, we have directly observed decomposition reactions within a simulation timeframe of $5-50 \,\mathrm{ps}$ which means that these reactions basically occur spontaneously at the electrolyte/electrode interface. This is a first indication of the high reactivity of the alkali metal electrodes. Note furthermore, that we only considered the interaction of single molecules with the anode surfaces without really simulating the liquid nature of the electrolytes. By neglecting the interaction of the molecules with the surrounding electrolyte, we might overestimate the reactivity as the presence of solvation shells will probably weaken the molecular interaction with the metal electrode. Still our simulations will provide valuable insights into the



Figure 3: Snapshots of the ClO_4 decomposition simulation on Li(100) a) Initial physisorption step, b) concerted dissociation of two oxygen atoms from one ClO_4 resulting in ClO_2 formation, c) addition of two additional perchlorate moities to the system d) completed decomposition with chlorine atoms adsorbed on the surfaces and the formation of local lithium-oxide subsurface structures.

electrolyte-electrode interaction as eventually the decomposition reactions at such interfaces will be dominated by the direct electrode-molecule interactions.

Simulations addressing the interaction of counter ions with alkali metal surfaces

First we address the interaction of hexafluorophosphate and perchlorate with alkali metal surfaces. Along the AIMD simulations, both perchlorate and hexafluorophosphate decomposed within a few ps. Details of the ClO_4 decomposition on Li(100) are illustrated in



Figure 4: Final structures of the ClO_4 simulation run a) ClO_4 on Na(100) after 15 ps b) ClO_4 on K(100) after 3 ps.

Fig. 3. The initial physisorption step, depicted in Fig. 3a, is then followed by a concerted dissociation of two oxygen atoms, resulting in the formation of ClO_2 and two oxygen atoms (Fig. 3b). We further observed the dissociation into adsorbed ClO_3 and one oxygen atom. Both pathways lead to the formation of Li-Cl structures at the surface while oxygen penetrates deeper into the lithium metal, creating structures that locally resemble oxide configurations (Fig. 3d).^{45,46} The formed Li-Cl structures loosely resemble a Li₃Cl(100) surface, with the nearest neighbor distance of Cl atoms averaging at about 4 Å. We also performed AIMD runs with two additional perchlorate moities per unit cell (Fig. 3c). Even for this higher perchlorate concentration, a complete separation into chloride surface and oxide subsurface structures occurred.

The final outcome of the AIMD runs when the lithium surface is replaced by sodium and potassium is depicted in Fig. 4. On the sodium surface, we observed a similar behavior as on the lithium surface. After approximately 7.5 ps, one ClO_4 ion fully decomposed in two concerted oxygen dissociation reactions. This decomposition leads to the formation of sodium oxide structures within the sodium surface, while the chloride atom remained adsorbed on the surface. While the lithium reaction occurred within less than 1.5 ps, the onset of the sodium reaction only started after 4ps.

In contrast, no reaction could be observed for the potassium surface. However, this could

be a consequence of the limited simulation timeframe of the computationally demanding potassium calculations, resulting in a total runtime of under 3 ps. It is therefore likely that the simulation time was insufficient to observe the ClO_4 decomposition on potassium.

We now turn to the interaction of PF_6 with the alkaline metal anodes. Typical reaction steps of the PF_6 decomposition are illustrated in Fig. 5. On the lithium surface, the PF_6 simulation started with a concerted dissociation of three fluorine atoms, resulting in the formation of LiF and PF_3 (Fig. 5b). Following this initial step, a fast reorientation of the produced PF_3 from a P-surface to an F-surface orientation occured(Fig. 5c). A second concerted reaction involving three fluorine atoms followed with fluorine and phosphorous atoms sinking into the lithium surface, forming a stable Li-P-F surface. The second PF_6 molecule followed a 6-F concerted dissociation, leading to the same stable surface as the two-step reaction (Fig. 5d). Similar to the CIO_4 runs, the PF_6 decomposition on the sodium surface followed the same scheme as the lithium run. While it took only three ps to fully decompose both PF_6 on the lithium surface, even after 12 ps, only one of the PF_6 molecules within the sodium run decomposed.

In contrast to the clear separation between oxide and chloride structures during the ClO_4 decomposition, no separation between fluoride and phosphate was observed upon their interaction with the Li and Na surfaces. In both cases a fluoride surface formed, with the phosphate acting as a defect within the structure. A slightly different reaction was observed for the potassium simulation, depicted in Fig. 6, where the two PF₆ molecules initially penetrated the potassium surface, sinking almost entirely into the surface and decomposing into two PF₂ moieties. Due to the limited runtime of the potassium simulations (5 ps), it is unclear whether PF₂ would further decompose or remain adsorbed on the surface.



Figure 5: Reaction steps observed for the PF_6 decomposition on Li(100) a) initial physisorption step, b) PF_3 formation, c) PF_6 surface adsorption d) concerted fluorine dissociation of six F, e) PF_3 adsorption f) LiF formation.

Simulations addressing the interaction of solvent molecules with alkali metal surfaces

The cell setup for the ethylene carbonate reaction consisted of two EC molecules in a 4x4 Li(100) supercell with six Li layers. The topmost three lithium layers and the EC molecules were allowed to relax fully. The initial placement of the EC molecules has been arbitrary since the finite temperature results in sufficient molecular movement causing rather random conditions. According to the simulations, the decomposition of ethylene carbonate proceeds in two steps on the lithium metal surface, an initial ring-opening after adsorption followed by carbon monoxide formation.

Typical reaction steps of the EC decomposition are illustrated in Fig. 7, where after just 30 fs of simulation time, the first EC molecule underwent decomposition via a ring-opening process (Fig. 7b). In this process, the two ring oxygen atoms became coordinated by one surface lithium atom each, while the terminal oxygen penetrated the surface and assumed a two-fold coordinated position. The newly exposed carbon and oxygen atoms each form a



Figure 6: Snapshot of the PF_6 decomposition on K(100), a) PF_6 sinking into the K(100) surface b) PF_2 formation.

bond with a separate surface lithium atom. This step is followed by a decarbonylation of the terminal C-O group, leaving a carbon monoxide and a de-protonated ethylene glycol molecule as reaction products (Fig. 7c). This reaction is analogous to the hydrolysis of ethylene carbonate in ethylene glycol synthesis. It was also observed for propylene carbonate (PC) on lithium after 345 fs of simulation time using a similar cell setup. An alternative two-electron reaction was occurred in another AIMD run in which a carbon monoxide molecule split apart from the EC molecule in a single step, resulting in the same decomposition products.

Further reactions between the decomposition products occurred after the decomposition of EC on lithium. One follow-up reaction was the splitting of carbon monoxide, which resulted in the formation of carbon on the lithium surface. Such a formation of carbon on lithium metal as a consequence of CO splitting has indeed been observed via photoelectron spectroscopy.⁴⁷ As illustrated in Fig. 8, the two carbon monoxide molecules can also penetrate the lithium surface and form a C-C bond resulting in a glycol-like product. In fact, the CO molecule sinking into the Li metal surface has previously been documented⁴⁸.

The final observed reaction is illustrated in Fig. 8d, wich involved the separation of one oxygen atom, resulting an almost linear C-C-O chain (C-C-O angle of 175°). This reaction could be interpreted as the initial polymerization step, which polymerizes carbon monox-



Figure 7: Reaction steps observed for the EC decomposition on Li(100) a) initial physisorption step, b) Ring-opening of first EC molecule, c) Decarbonylation d) Ring-opening of second EC molecule.

ide. This reaction is similar to the proposed reaction mechanisms of the Fischer–Tropsch process, which polymerizes carbon monoxide into hydrocarbons⁴⁹, with the difference being the substitution of hydrogen by lithium, resulting in lithium-bonded carbon chains and lithium oxides. CO polymerization using lithium has in fact previously been recorded using molecular lithium.⁵⁰

The polymerization product remained submerged in the lithium surface for the remainder of the simulation. These simulation results agree with previous results, which also found both one-electron and two-electron reduction reactions³⁶. No decomposition could be observed for dimethoxyethane (DME) within the simulation timeframe of 48 ps. However, the



Figure 8: a) CO molecules adsorbed on Li(100) after EC decomposition, all Li atoms are scaled down. b) C-C bond formation inside Li surface, c) side view of C-C bond formation. d) O dissociation.

molecules strongly preferred an adsorption configuration via an oxygen-lithium connection and remained almost stationary during the entire MD run. These findings support previous simulations, which DME observed as being "stable" on lithium metal surfaces.⁵¹ Of course it has to be taken into account that the time scale of the AIMD simulations is much too short to really speculate about the stability of the adsorbed moities.

The decomposition of EC on the Na(100) surface followed the same ring-opening pathway observed on the lithium surface. No formation of carbon monoxide was observed within the 30 ps simulation time. The carbonate split-off reaction, previously found on lithium surfaces for the EC molecule³⁶, was observed for PC, leading to sodium carbonate and



Figure 9: a) Decomposition products of two EC molecules on K(100) after 3 ps simulation time. b) Decomposition products of two PC molecules on K(100) after 3 ps simulation time.

propene gas formation. Analogous to the Li simulation, DME did not show any reactivity during the Na simulation run and preferred an O-Na-O orientation. Still, in contrast to the adsorption scenario of DME on lithium, on Na(100) the DME molecules alternated between two configurations, one being based on coordinating one sodium surface atom with both oxygen atoms, leading to a compressed molecular structure, and the other being a stretched position, where each oxygen atom coordinates a different Na surface atom. For lithium, the stretched configuration was dominant during the entire simulation run. This difference in configurational preference can be explained by the larger lattice constant of sodium, leading to longer distances between the surface metal atoms and demanding a more significant molecular deformation for the stretched orientation, when compared to lithium. Note that the observation that the decomposition reactions of EC/PC on lithium and sodium metal anodes are similar is supported by experimental IR spectroscopy, which found a very similar SEI composition for both lithium and sodium under OCV conditions.⁴⁴

As depicted in Fig. 9, the EC/PC AIMD runs on K(100) yielded similar results as those on Na(100). No carbon monoxide formation was observed, and the molecule underwent the ring opening pathway only in the case of propyleneoxide (Fig 9b). For EC, carbonate formation under the release of ethylene gas was observed within the first 3 ps. Analogous



Figure 10: a) Initial setup of the EC, PF_6 mixed calculation. b) Formation of organic chains after inclusion of PF_6 in the EC decomposition simulation on a Li(100) surface.

to lithium and sodium, DME on potassium was found to be unreactive within the limited timeframe of 3 ps. Further, no clear adsorption site preference could be identified during the short simulation run.

So far, all simulations only considered the interaction between the metal surface and one type of electrolyte component. In any actual cell, however, different components are mixed to form the electrolyte solution. Therefore, a cell setup containing more than one species was employed to make the simulations more realistic. For this simulation, two electrolyte solvent (EC) and two counterion (PF₆) molecules were considered per (4×4) Li(100) surface unit cell. The reactions observed in this mixed setup (see Fig. 10), were the same as with the pure simulation setups, suggesting that as long as there is still an exposed lithium surface, the decomposition mechanisms are independent of each other for this specific combination. Still, while the initial reduction reaction was seemingly independent of the presence of PF₆, the change in surface composition, namely the LiF formation, led to the formation of chain-like structures, which may influence possible follow up reactions.

Up to here, the molecular dynamics simulations have indicated that, in contrast to lithium, sodium and potassium surface behave rather similarly. The decomposition of both investigated counter ions on Na(100) and K(100) showed only minor differences, with only

the PF_2 formation on K being a potential difference. DME was stable throughout all simulations on all surfaces and showed only variations in its mobility, being less mobile on lithium than sodium and potassium. Both ethylene carbonate and propylene carbonate adsorption consistently resulted either in carbon monoxide or carbonate surface structure formation, with the exception that no carbon monoxide formation was observed on potassium surface. To understand whether this was just a consequence of the limited simulation timescale or a real difference, we investigated the two decomposition reactions for both PC and EC more closely. Due to the consistently small timeframes on which the observed reactions occur (<20 ps), it seems unlikely that the observed reactions exhibit high reaction barriers. Low kinetic barriers would imply that any relevant difference between the two possible reaction paths is thermodynamic, not kinetic (the preexponential factor for a monomolecular decomposition should be dependent on the entropy of activation). We, therefore, calculated the reaction energies for the complete decomposition of both EC and PC on Li, Na, and K as follows:

$$E_{reaction} = E_{products} - E_{educt} \tag{1}$$

Here $E_{products}$ and E_{educt} are the respective energies of the adsorbed molecules on the alkali metal surface. The calculated reaction energies are listed in table 1, Fig. 11 provides a visual representation of the decomposition thermodynamics for EC. No frequencies were calculated within the scope of this work, therefore we did not consider the influence of the zero point energy on the reaction energies.

 CO_3 formation is favorable for all investigated surfaces for both EC and PC. There is,

Table 1: Calculated reaction energies for the EC/PC decomposition pathways on Li,Na and K.

	EC, CO Path	PC, CO Path	EC, CO_3 Path	PC, CO_3 Path
Li	-3.05 eV	-4.10 eV	-4.50 eV	-4.32 eV
Na	-1.18 eV	-1.80 eV	-3.60 eV	-3.67 eV
Κ	+1.53 eV	+1.06 eV	-4.00 eV	-3.89 eV



Figure 11: Visualization of the EC decomposition thermodynamics, the CO_3 producing reaction is found to be favorable for all tested metal surfaces.

however, a substantial difference with respect to the preference of the CO_3 vs CO formation between the alkali metals. While the energetic difference between the two paths is relatively small for lithium, for sodium and potassium CO formation is energetically much more unfavorable, as illustrated in Fig. 12. CO formation even becomes endothermic on potassium, thus explaining the absence of CO in the potassium simulations.

This much more pronounced preference for the CO_3 formation on sodium and especially potassium would likely have further consequences for the formation of the solid electrolyte interphase. Within our simulations, any CO_3 formed on the metals during the decomposition reaction would lead to an MCO_3 surface structure. At the same time, the organic byproducts do not adsorb on the metal surface, but leave it instead. However, the CO decomposition paths lead to follow-up reactions with the organic byproducts, thus leading to vastly different interface structures.



Figure 12: Comparison of the energetic preference of the CO_3 forming reaction between the tested metal surfaces.

Conclusion

Performing ab initio molecular dynamics simulations, we have compared the initial decomposition reactions of common electrolyte components on lithium, sodium, and potassium surfaces. At room temperature, the reactions occurred almost spontaneously within picoseconds on all investigated surfaces. While the decomposition of electrolyte salts did not exhibit any significant differences between lithium and sodium, leading to metal-oxide and metalhalide structures, the formation of PF_2 was observed on the potassium surface. We further found a clear separation between an oxygen-rich surface structure and a chloride surface layer for the decomposition of perchlorate on sodium and lithium. DMC was found to be non-reactive within the simulation timeframe. The initial cyclic carbonate decomposition results in two sets of products, yielding either carbon monoxide or leading to carbonate formation. The carbonate-forming reaction was found to be energetically favorable on all considered alkali metal surfaces, though the difference in reaction energies between the two reactions increased from less than 1 eV for PC on lithium to over 5 eV for EC on potassium. This indicates a strong selectivity towards the formation of K_2CO_3 in the case of the potassium surfaces. The selectivity of initial decomposition reactions is expected to strongly influence the formation of the solid electrolyte interphase since the formation of organic compounds was not observed in the carbonate reaction. In contrast, multiple secondary reactions involving carbon monoxide were observed, including the formation of C-C bonds along a Fischer-Tropsch process-like mechanism. While sodium and potassium overall were found to behave rather similarly to lithium in most situations, we were still able to identify key differences in the initial decomposition processes. Understanding and controlling these initial decomposition reactions and their products - the building blocks of the SEI - might be a pathway to stabilize the SEI in post-lithium batteries.

Acknowledgements

This work contributes to the research performed at CELEST (Center for Electrochemical Energy Storage Ulm-Karlsruhe) and was funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany's Excellence Strategy – EXC 2154 – Project number 390874152. The authors furthermore acknowledge computer time supplied by the state of Baden-Württemberg through the bwHPC project and the Germany Research Foundation (DFG) through grant number INST 40/467-1 FUGG (JUSTUS cluster).

References

Björn, N.; Måns, N. Rapidly falling costs of battery packs for electric vehicles. *Nature Climate Change* 2015, 5, 329–332.

- (2) Ishikawa, M.; Kanemoto, M.; Morita, M. Control of lithium metal anode cycleability by electrolyte temperature. J. Power Sources 1999, 81-82, 217–220.
- (3) Martin, G.; Rentsch, L.; Höck, M.; Bertau, M. Lithium market research global supply, future demand and price development. *Energy Storage Mater.* 2017, 6, 171 – 179.
- (4) Pender, J. P.; Jha, G.; Youn, D. H.; Ziegler, J. M.; Andoni, I.; Choi, E. J.; Heller, A.; Dunn, B. S.; Weiss, P. S.; Penner, R. M.; Mullins, C. B. Electrode Degradation in Lithium-Ion Batteries. ACS Nano 2020, 14, 1243–1295.
- (5) Chen, Y.; Luo, Y.; Zhang, H.; Qu, C.; Zhang, H.; Li, X. The Challenge of Lithium Metal Anodes for Practical Applications. *Small Methods* **2019**, *3*, 1800551.
- (6) Khudyshkina, A. D.; Morozova, P. A.; Butzelaar, A. J.; Hoffmann, M.; Wilhelm, M.; Theato, P.; Fedotov, S. S.; Jeschull, F. Poly(ethylene oxide)-Based Electrolytes for Solid-State Potassium Metal Batteries with a Prussian Blue Positive Electrode. ACS Appl. Poly. Mater. 2022, 4, 2734–2746.
- (7) Hasa, I.; Adelhelm, P.; Cao, G.; Mai, L. Batteries & Supercaps: Beyond Lithium-Ion Batteries. Batteries Supercaps 2021, 4, 1036–1038.
- (8) Walter, M.; Kovalenko, M. V.; Kravchyk, K. V. Challenges and benefits of post-lithiumion batteries. New J. Chem. 2020, 44, 1677–1683.
- (9) Lv, S.; Yuan, J.; Chen, Z.; Gao, P.; Shu, H.; Yang, X.; Liu, E.; Tan, S.; Ruben, M.; Zhao-Karger, Z.; Fichtner, M. Copper Porphyrin as a Stable Cathode for High-Performance Rechargeable Potassium Organic Batteries. *ChemSusChem* **2020**, *13*, 2286–2294.
- (10) Jäckle, M.; Helmbrecht, K.; Smits, M.; Stottmeister, D.; Groß, A. Self-diffusion barriers: possible descriptors for dendrite growth in batteries? *Energy Environ. Sci.* 2018, 11, 3400–3407.

- (11) Pfeifer, K.; Greenstein, M. F.; Aurbach, D.; Luo, X.; Ehrenberg, H.; Dsoke, S. Interaction between Electrolytes and Sb2O3-Based Electrodes in Sodium Batteries: Uncovering the Detrimental Effects of Diglyme. *ChemElectroChem* **2020**, *7*, 3487–3495.
- (12) Euchner, H.; Vinayan, B. P.; Reddy, M. A.; Fichtner, M.; Groß, A. Alkali metal insertion into hard carbon – the full picture. J. Mater. Chem. A 2020, 8, 14205–14213.
- (13) Ma, Y.; Ma, Y.; Euchner, H.; Liu, X.; Zhang, H.; Qin, B.; Geiger, D.; Biskupek, J.; Carlsson, A.; Kaiser, U.; Groß, A.; Indris, S.; Passerini, S.; Bresser, D. An Alternative Charge-Storage Mechanism for High-Performance Sodium-Ion and Potassium-Ion Anodes. ACS Energy Lett. 2021, 6, 915–924.
- (14) Sawicki, M.; Shaw, L. L. Advances and challenges of sodium ion batteries as post lithium ion batteries. RSC Advances 2015, 5, 53129–53154.
- (15) Rajagopalan, R.; Tang, Y.; Ji, X.; Jia, C.; Wang, H. Advancements and Challenges in Potassium Ion Batteries: A Comprehensive Review. Adv. Funct. Mater. 2020, 30, 1909486.
- (16) Zachman, M.; Choudhury, S.; Archer, L.; Kourkoutis, L. Cryo-STEM mapping of solid–liquid interfaces and dendrites in lithium-metal batteries. *Nature* 2018, 560, 345–349.
- (17) Han, J.; Euchner, H.; Kuenzel, M.; Hosseini, S. M.; Groß, A.; Varzi, A.; Passerini, S. A Thin and Uniform Fluoride-Based Artificial Interphase for the Zinc Metal Anode Enabling Reversible Zn/MnO₂ Batteries. ACS Energy Lett. 2021, 6, 3063–3071.
- (18) Leung, K.; Budzien, J. L. Ab initio molecular dynamics simulations of the initial stages of solid–electrolyte interphase formation on lithium ion battery graphitic anodes. *Phys. Chem. Chem. Phys.* 2010, *12*, 6583–6586.

- (19) Aiping, W.; Sanket, K.; Hong, L.; Yue, Q. Review on modeling of the anode solid electrolyte interphase (SEI) for lithium-ion batteries. *npj Comp. Mater.* 2018, 4.
- (20) Forster-Tonigold, K.; Kim, J.; Bansmann, J.; Groß, A.; Buchner, F. Model Studies on the Formation of the Solid Electrolyte Interphase: Reaction of Li with Ultrathin Adsorbed Ionic-Liquid Films and Co₃O₄(111) Thin Films. *ChemPhysChem* **2021**, 22, 441–454.
- (21) Euchner, H.; Groß, A. Atomistic modeling of Li- and post-Li-ion batteries. Phys. Rev. Mater. 2022, 6, 040302.
- (22) Groß, A.; Sakong, S. Ab Initio Simulations of Water/Metal Interfaces. Chem. Rev. 2022, 122, 10746–10776.
- (23) Li, T.; Balbuena, P. B. Theoretical studies of the reduction of ethylene carbonate. *Chem. Phys. Lett.* 2000, 317, 421–429.
- (24) Soto, F. A.; Marzouk, A.; El-Mellouhi, F.; Balbuena, P. B. Understanding Ionic Diffusion through SEI Components for Lithium-Ion and Sodium-Ion Batteries: Insights from First-Principles Calculations. *Chem. Mater.* **2018**, *30*, 3315–3322.
- (25) Groß, A.; Scheffler, M. Influence of molecular vibrations on dissociative adsorption. Chem. Phys. Lett. 1996, 256, 417.
- (26) Groß, A.; Eichler, A.; Hafner, J.; Mehl, M. J.; Papaconstantopoulos, D. A. Unified picture of the molecular adsorption process: O₂/Pt(111). Surf. Sci. 2003, 539, L542.
- (27) Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* 1996, 54, 11169.
- (28) Hammer, B.; Hansen, L. B.; Nørskov, J. K. Improved adsorption energetics within density-functional theory using revised Perdew-Burke-Ernzerhof functionals. *Phys. Rev.* B 1999, 59, 7413–7421.

- (29) Blöchl, P. E. Projector augmented-wave method. Phys. Rev. B 1994, 50, 17953.
- (30) Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmentedwave method. *Phys. Rev. B* 1999, 59, 1758.
- (31) Methfessel, M.; Paxton, A. T. High-precision sampling for Brillouin-zone integration in metals. *Phys. Rev. B* 1989, 40, 3616.
- (32) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. J. Chem. Phys. 2010, 132, 154104.
- (33) Cheng, X.-B.; Zhang, R.; Zhao, C.-Z.; Zhang, Q. Toward Safe Lithium Metal Anode in Rechargeable Batteries: A Review. *Chem. Rev.* 2017, 117, 10403–10473.
- (34) Horstmann, B.; Single, F.; Latz, A. Review on multi-scale models of solid-electrolyte interphase formation. *Curr. Opin. Electrochem.* 2019, 13, 61–69.
- (35) He, X. et al. The passivity of lithium electrodes in liquid electrolytes for secondary batteries. Nat. Rev. Mater. 2021, 6, 1036–1052.
- (36) Wang, Y.; Nakamura, S.; Ue, M.; Balbuena, P. B. Theoretical Studies To Understand Surface Chemistry on Carbon Anodes for Lithium-Ion Batteries: Reduction Mechanisms of Ethylene Carbonate. J. Am. Chem. Soc. 2001, 123, 11708–11718.
- (37) Hammer, N. I.; Hinde, R. J.; Compton, R. N.; Diri, K.; Jordan, K. D.; Radisic, D.; Stokes, S. T.; Bowen, K. H. Dipole-bound anions of highly polar molecules: Ethylene carbonate and vinylene carbonate. J. Chem. Phys. 2004, 120, 685–690.
- (38) Jin, Y.; Kneusels, N.-J. H.; Magusin, P. C. M. M.; Kim, G.; Castillo-Martínez, E.; Marbella, L. E.; Kerber, R. N.; Howe, D. J.; Paul, S.; Liu, T.; Grey, C. P. Identifying the Structural Basis for the Increased Stability of the Solid Electrolyte Interphase Formed

on Silicon with the Additive Fluoroethylene Carbonate. J. Am. Chem. Soc. 2017, 139, 14992—15004.

- (39) Campion, C. L.; Li, W.; Lucht, B. L. Thermal Decomposition of LiPF[sub 6]-Based Electrolytes for Lithium-Ion Batteries. J. Electrochem. Soc. 2005, 152, A2327.
- (40) Onuki, M.; Kinoshita, S.; Sakata, Y.; Yanagidate, M.; Otake, Y.; Ue, M.; Deguchi, M. Identification of the Source of Evolved Gas in Li-Ion Batteries Using [sup 13]C-labeled Solvents. J. Electrochem. Soc. 2008, 155, A794.
- (41) Yu, J.; Balbuena, P. B.; Budzien, J.; Leung, K. Hybrid DFT Functional-Based Static and Molecular Dynamics Studies of Excess Electron in Liquid Ethylene Carbonate. J. Electrochem. Soc. 2011, 158, A400.
- (42) Ebadi, M.; Brandell, D.; Araujo, C. M. Electrolyte decomposition on Li-metal surfaces from first-principles theory. J. Chem. Phys. 2016, 145, 204701.
- (43) Hankins, K.; Soto, F. A.; Balbuena, P. B. Insights into the Li Intercalation and SEI Formation on LiSi Nanoclusters. J. Electrochem. Soc. 2017, 164, E3457–E3464.
- (44) Iermakova, D. I.; Dugas, R.; Palacín, M. R.; Ponrouch, A. On the Comparative Stability of Li and Na Metal Anode Interfaces in Conventional Alkyl Carbonate Electrolytes. J. Electrochem. Soc. 2015, 162, A7060–A7066.
- (45) Rogal, J.; Reuter, K.; Scheffler, M. CO oxidation at Pd(100): A first-principles constrained thermodynamics study. *Phys. Rev. B* 2007, 75, 205433.
- (46) Didar, B. R.; Yashina, L.; Groß, A. First-Principles Study of the Surfaces and Equilibrium Shape of Discharge Products in Li–Air Batteries. ACS Appl. Mater. Interf. 2021, 13, 24984–24994.
- (47) Zhuang, G.; Chen, Y.; Ross, P. N. The reaction of lithium with carbon dioxide studied by photoelectron spectroscopy. *Surf. Sci.* **1998**, *418*, 139–149.

- (48) Camacho-Forero, L. E.; Smith, T. W.; Bertolini, S.; Balbuena, P. B. Reactivity at the Lithium–Metal Anode Surface of Lithium–Sulfur Batteries. J. Phys. Chem. C 2015, 119, 26828–26839.
- (49) de Klerk, A. Kirk-Othmer Encyclopedia of Chemical Technology; American Cancer Society, 2013; pp 1–20.
- (50) Wang, B.; Luo, G.; Nishiura, M.; Luo, Y.; Hou, Z. Cooperative Trimerization of Carbon Monoxide by Lithium and Samarium Boryls. J. Am. Chem. Soc. 2017, 139, 16967– 16973.
- (51) Camacho-Forero, L. E.; Smith, T. W.; Bertolini, S.; Balbuena, P. B. Reactivity at the Lithium–Metal Anode Surface of Lithium–Sulfur Batteries. J. Phys. Chem. C 2015, 119, 26828–26839.