Promoting Mechanistic Understanding of Lithium Deposition and Solid-Electrolyte Interphase (SEI) Formation Using Advanced Characterization and Simulation Methods: Recent Progress, Limitations, and Future Perspectives

Yaolin Xu, Kang Dong, Yulin Jie, Philipp Adelhelm, Yawei Chen, Liang Xu, Peiping Yu, Junghwa Kim, Zdravko Kochovski, Zhilong Yu, Wanxia Li, James LeBeau, Yang Shao-Horn, Ruiguo Cao, Shuhong Jiao,* Tao Cheng,* Ingo Manke,* and Yan Lu*

In recent years, due to its great promise in boosting the energy density of lithium batteries for future energy storage, research on the Li metal anode, as an alternative to the graphite anode in Li-ion batteries, has gained significant momentum. However, the practical use of Li metal anodes has been plagued by unstable Li (re)deposition and poor cyclability. Although tremendous efforts have been devoted to the stabilization of Li metal anodes, the mechanisms of electrochemical (re-)deposition/dissolution of Li and solid-electrolyte-interphase (SEI) formation remain elusive. This article highlights the recent mechanistic understandings and observations of Li deposition/dissolution and SEI formation achieved from advanced characterization techniques and simulation methods, and discusses major limitations and open questions in these processes. In particular, the authors provide their perspectives on advanced and emerging/potential methods for obtaining new insights into these questions. In addition, they give an outlook into cutting-edge interdisciplinary research topics for Li metal anodes. It pushes beyond the current knowledge and is expected to accelerate development toward a more in-depth and comprehensive understanding, in order to guide future research on Li metal anodes toward practical application.

1. Li Metal Anodes: Promises, Challenges, and Recent Advances in Fundamental Understanding

The rapidly developing electric vehicle (EV) industry demands advanced battery systems with high energy density, long operation lifespan, and low cost.[1] After 30 years' commercialization, lithium ion battery technology, which is based on Li-ion intercalation mechanism, achieves a specific energy density of ≈260 Wh kg^{-1} at the cell level and is approaching its theoretical limit (300 Wh kg^{-1}).[2] Unfortunately, such an energy density could not meet the increasing demand (≥500 Wh kg^{-1}) from the EV market. To fill the gap, high-energy-density battery systems such as Li-sulfur, Li-oxygen, and solid-state batteries (SSBs) have attracted overwhelming interest from both research and industrial fields.[3] Among these promising battery systems, Li metal anode is regarded as an essential component,

Y. Xu, Z. Kochovski, Z. Yu, Y. Lu
Department of Electrochemical Energy Storage (CE-AEES)
Helmholtz-Zentrum Berlin für Materialien und Energie
Hahn-Meitner-Platz 1, 14109 Berlin, Germany
E-mail: yan.lu@helmholtz-berlin.de

Y. Xu, P. Adelhelm
Department of Chemistry
Humboldt-Universität zu Berlin
Brook-Taylor-Str.2, 12489 Berlin, Germany

Y. Xu, P. Adelhelm
Joint Research Group Operando Battery Analysis (CE-GOBA)
Helmholtz-Zentrum Berlin für Materialien und Energie
Hahn-Meitner-Platz 1, 14109 Berlin, Germany

Y. Xu, J. Kim, Y. Shao-Horn
Research Laboratory of Electronics
Massachusetts Institute of Technology
Cambridge, MA 02139, USA

K. Dong, I. Manke
Institute of Applied Materials (CE-IAM)
Helmholtz-Zentrum Berlin für Materialien und Energie
Hahn-Meitner-Platz 1, 14109 Berlin, Germany
E-mail: manke@helmholtz-berlin.de

Y. Jie, Y. Chen, W. Li, R. Cao, S. Jiao
Hefei National Laboratory for Physical Science at Microscale
Department of Materials Science and Engineering
University of Science and Technology of China
Hefei, Anhui 230026, China
E-mail: jiaosh@ustc.edu.cn

L. Xu, P. Yu, T. Cheng
Institute of Functional Nano & Soft Materials (FUNSOM)
Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices
Joint International Research Laboratory of Carbon-Based Functional Materials and Devices
Soochow University
199 Ren'ai Road, Suzhou, Jiangsu 215123, China
E-mail: tcheng@suda.edu.cn

due to its ultrahigh capacity of 3860 mAh g^{-1} and the lowest electrochemical potential of -3.04 V (versus standard hydrogen electrode).[4] The adoption of metallic Li anode in Li metal batteries (LMBs) could boost the cell-level energy density to ≈450 Wh kg^{-1} when paired with a high-capacity cathode[2b] or to ≈600 Wh kg^{-1} in Li−S battery systems.[3a]

The first implementation of Li anode can be traced back to 1976,[5] but the practical use of Li metal anode in rechargeable batteries is still impeded by two main issues. First, Li^0 deposition occurs as a result of electrochemical reduction of Li$^+$ from the electrolyte on the anode, and it is accompanied with oxidation (i.e., delithiation) of active materials on the cathode side during battery operation. Li electrochemical plating is prone to be inhomogeneous or even dendritic, which is believed to be uncontrollable and to be rooted in the inhomogeneous distribution of Li-ions on the electrode.[6] Dendritic Li could penetrate a separator, short a cell, and thus bring about safety concerns.[7] Second, the intrinsic high chemical and electrochemical reactivity of Li metal makes it thermodynamically unstable when contacting organic electrolytes, leading to the decomposition of electrolyte and the formation of a solid electrolyte interphase (SEI) layer.[8] Locating at the reaction front of electrochemical Li deposition and dissolution, SEI is mechanically unstable due to repetitive expansion and shrinkage of the electrode during battery cycling. This unstable SEI brings about the continuous consumption of electrolytes and the formation of "dead" Li (electrically isolated Li) during stripping,[9] and eventually leads to poor cycle life. Although in the past years tremendous research and engineering efforts have been devoted to Li metal anodes, stable and highly efficient Li plating/stripping with beyond 99.9% Coulombic efficiency (CE) for long-term operation (≥1000 cycles) has not been realistic.[10]

To ultimately address the issues and eventually enable the commercialization of rechargeable LMBs, it is paramount to obtain insights into the underlying mechanism of Li plating and stripping. In addition, a comprehensive understanding of the formation and evolution processes and the composition-property–function relationship of SEI is crucial, which determines the energy kinetic landscape of the (electro-)chemical reactions occurring at the Li-electrolyte interface and thus plays a decisive role in the plating/stripping behavior.

Recently, the understanding of Li plating/stripping as well as SEI formation mechanism and its physicochemical properties have been profoundly promoted by ever-developing and newly-emerging advanced characterization methods (**Figure 1**a,b), especially in situ and operando analytical techniques.[11] These techniques, complementing each other, have revealed the 3D

structural evolution of Li deposition in real-time and at various length scales, and partially resolved the chemistry and structure of SEI on nanoscale at close-to-native state. In particular, imaging methods,[12] such as scanning electron microscopy (SEM),[13] liquid-cell transmission electron microscopy (liquid-cell TEM),[14] and optical microscopy (OM),[15] have been devoted to dynamically visualizing the evolution of Li plating and/or stripping at nanometer- or micrometer-scale, providing valuable dynamic information including initial Li nucleation and the subsequent growth and dissolution. Furthermore, Li et al.[16] have introduced cryogenic transmission electron microscopy (cryo-TEM) to reveal individual Li metal atoms of Li deposits and the chemical composition and structure information of the SEI layer thereon, having largely suppressed beam damage under cryogenic conditions. The advantages of cryogenic condition in probing Li deposition and SEI layers are rapidly acknowledged in the battery community, and cryogenic characterization probes have been expanded to other imaging methods, for example, cryogenic focus ion beam (cryo-FIB)[17] and cryogenic scanning transmission electron microscopy (cryo-STEM) based tomography.[18] Moreover, cryo-STEM based energy-dispersive X-ray spectroscopy (EDX) and electron energy loss spectroscopy (EELS) could provide not only element distribution but also chemical information and bonding environment. In 2018, Zachman et al.[17] have employed cryo-FIB tomography to reveal 3D and local structures of different types of Li dendrites on the nanoscale, and combined with cryo-STEM EELS mapping to identify the composition of intact SEI in LMBs. In 2021, Han et al.[19] have employed cryo-STEM tomography mapping to reveal 3D morphology and distribution of SEI as well as "dead" Li, which provides insights into the working mechanism of SEI in Li metal anodes. In addition, synchrotron X-ray computed tomography (SXCT)[7c,20] is proved to be a highly suitable technique to 3D unravel and track the Li microstructure evolution, particularly at the interface after or during electrochemical deposition. In 2019, Fang et al.[21] developed quantitative analysis tools such as titration gas chromatography (TGC) to quantify unreacted metallic Li^0 as well as Li$^+$ in SEI, which enables the identification of the small contribution from SEI and the dominant role of inactive Li among the factors that lead to low CE.

Experimental characterization means have difficulties achieving the resolution, on both temporal and spatial scales, needed to investigate Li dendrite growth, in particular the nucleation process. Theoretical simulation methods (Figure 1c) have the potential to become realistic in situ characterization technique. They could provide an accurate atomic picture of the formation process of electrogenic dendrites, offering a theoretical basis for understanding the physicochemical processes of dendrite formation and providing ideas for the subsequent inhibition of dendrite growth. In 2014, Aryanfar et al.[22] have employed Monte Carlo (MC) calculations to elucidate the mechanism of inhibited Li dendrite growth with a pulsed deposition mode. Specifically, Li$^+$ migration in the electric fields converging to dendrite tips generates extended depleted layers, which can be replenished by diffusion during the rest periods. In 2020, Tan et al.[23] have simulated cyclic Li dendrite growth at the electrode-electrolyte interface in lithium batteries over multiple cycles based on a reactive mass transport dendrite growth smoothed-particle hydrodynamics (SPH)

J. Kim, J. LeBeau, Y. Shao-Horn
Department of Material Science and Engineering
Massachusetts Institute of Technology
77 Massachusetts Avenue, Cambridge, MA 02139, USA
Y. Shao-Horn
Department of Mechanical Engineering
Massachusetts Institute of Technology
77 Massachusetts Avenue, Cambridge, MA 02139, USA
Y. Lu
Institute of Chemistry
Potsdam University
Karl-Liebknecht-Str. 24–25, 14476 Potsdam, Germany

2200398 (2 of 22)
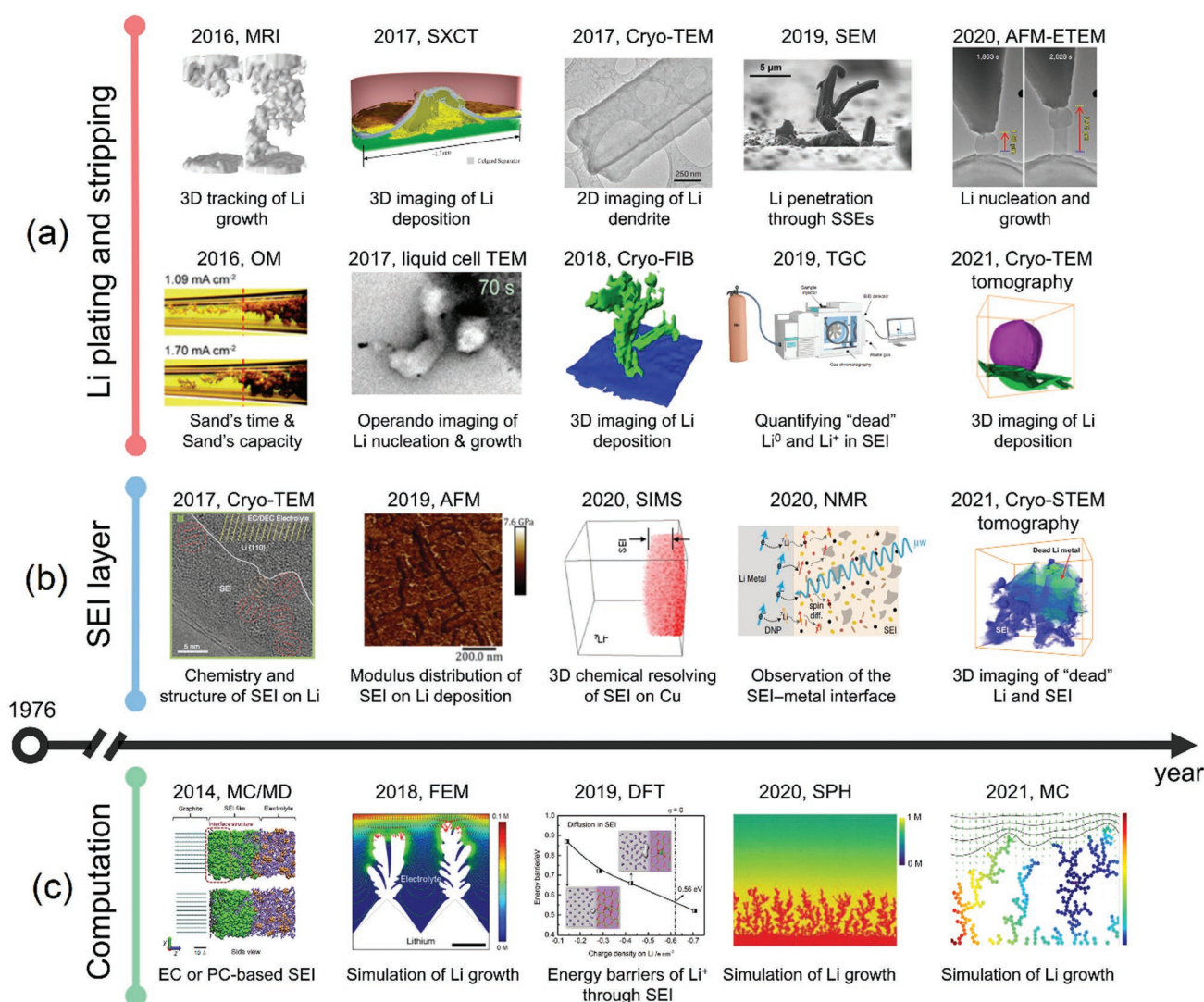
Figure 1. Recent advances in mechanistic understandings of Li deposition and SEI using advanced analytical techniques and theoretical modelling methods. a) Advanced characterization techniques for analyzing Li plating and stripping behaviors include Magnetic resonance imaging (MRI)[26] (Reproduced with permission.[26] Copyright 2016, National Academy of Sciences), SXCT[20a] (Reproduced with permission.[20a] Copyright 2017, American Chemical Society), Cryo-TEM[27] (Reproduced with permission.[27] Copyright 2017, The American Association for the Advancement of Science (AAAS)), SEM[13] (Reproduced with permission.[13] Copyright 2019, Elsevier), AFM-ETEM[28] (Reproduced with permission.[28] Copyright 2020, Springer Nature), OM[15a] (Reproduced with permission.[15a] Copyright 2016, The Royal Society of Chemistry), liquid-cell TEM[14] (Reproduced with permission.[14] Copyright 2017, Elsevier), Cryo-FIB[17] (Reproduced with permission.[17] Copyright 2018, Springer Nature), TGC[21] (Reproduced with permission.[21] Copyright 2019, Springer Nature), and Cryo-TEM tomography[18] (Reproduced with permission.[18] Copyright 2021, Elsevier). b) Analysis of SEI involves cryo-TEM[27] (Reproduced with permission.[27] Copyright 2017, The American Association for the Advancement of Science (AAAS)), AFM,[29] (Reproduced with permission.[29] Copyright 2019, Wiley-VCH), SIMS[30] (Reproduced with permission.[30] Copyright 2020, Springer Nature), NMR[31] (Reproduced with permission.[31] Copyright 2020, Springer Nature), and cryo-STEM tomography[19] (Reproduced with permission.[19] Copyright 2021, Elsevier). c) Theoretical modelling methods include MC/MD[32] (Reproduced with permission.[32] Copyright 2014, American Chemical Society), finite element method (FEM)[33] (Reproduced with permission.[33] Copyright 2018, American Chemical Society), DFT(B)[24a] (Reproduced with permission.[24a] Copyright 2019, The Royal Society of Chemistry), SPH[23] (Reproduced with permission.[23] Copyright 2020, Elsevier), and MC[34] (Reproduced with permission.[34] Copyright 2021, Elsevier) for calculation of the diffusion energy barriers and simulation of the Li deposition behavior and SEI structure.

model, which is able to qualitatively predict the morphologies of Li deposition and the effects of fast charging on the dendrite growth rate. At the same time, theoretical help is needed to resolve the property and nanostructure of SEI.[24] In 2019, Li et al.[24a] have developed combined density functional theory (DFT) and tight-binding (DFTB) calculations to derive that, at the electrochemical equilibrium or the experimentally defined zero-voltage for Li+/Li0, the Li metal surface is negatively

charged at the Li/SEI/electrolyte interface, which changes the electrolyte double-layer structure and impacts profoundly the charge transfer reaction kinetics. It reduces the overall Li+ ion desolvation energy barrier and facilitates the Li+ ion transport through the SEI during Li plating. In 2022, Liu et al.[24b] have revealed the SEI formation process based on in situ polymerization of 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropylether (TTE) on Li metal anode using hybrid ab initio and reactive

**ADVANCED
SCIENCE NEWS**

www.advancedsciencenews.com

**ADVANCED
ENERGY
MATERIALS**

www.advenergymat.de

molecular dynamics (HAIR), which involves the release of F atoms of TTE initiated by Li^0 and followed by C—O bond cleavages. Certainly, in the quest to achieve these goals, it is necessary to improve the computational accuracy and efficiency of the existing theoretical simulation methods. Apart from theoretical simulations, the classical nucleation theory has been adopted to interpret the initial Li nucleation but are limited to a certain extent. These limitations originate from the soaring complexity when, in a practical scenario, the local heterogeneous surface of deposition substrates and an electrically insulating and ionically conductive SEI layer composed of complex organic and inorganic compounds have to be considered. For the following Li dendrite formation, a space-charge model proposed by Chazalviel et al was developed,[25] which attributes the generation of Li dendrites to the large space charge and electric field induced by the anion depletion at the local surface of electrodes. In addition, originating from theoretical derivations, "Sand's time",[15a] which describes the time it takes in a binary electrolyte to deplete the concertation of cation at the electrode surface to zero, has been suggested. It provides a quantitative value to describe the time needed to trigger the formation of dendritic Li.

The past five years have seen revived interest and tremendous efforts devoted to the development of strategies for dendrite suppression and Li metal anode stabilization through electrode structure or surface/interface engineering.[35] These approaches are in general conceptualized based on the classical nucleation theory developed decades ago. Energetically, tuning the surface/interfacial energy[36] and promoting the affinity of substrate toward Li (i.e., lithophilicity)[37] have been proven to be effective in homogenizing Li nucleation and growth. Besides, the energy barriers related to desolvation and cation-anion de-association influence the overpotential for Li growth and hence the morphology of Li deposits. For instance, concentrated electrolytes (≥4 M Li salts)[38] attribute a decrease of solvation number per Li and hence reduction of Li-ion desolvation energy barrier, leading to reduced concentration overpotential and conformal Li growth. Kinetically, uniform Li-ion distribution and Li deposition can be facilitated through regulating Li-ion flux on the anode and accelerating Li-ion transfer through structural or materials innovations.[39] For instance, 3D conductive Li-host structures with large specific surface area (SSA),[39b] especially those based on carbonaceous nanomaterials,[40] reduce the local current density, delaying the "Sand's time" and the onset of Li dendrite growth. Other regulation methods include substrate structuring with nanochannels for facilitated Li-ion diffusion[41] and electrolyte modification, for example, using additives that result in electrostatic shielding for Li-ions[42] or that act as Li-ion carriers[43] for effective homogenization of Li-ions. Moreover, engineering the SEI also appears to be an imperative strategy to stabilize Li metal anodes.[44] The adoption of a uniform and Li-ion conductive artificial SEI layer on Li metal anode facilitates homogeneous Li deposition and accelerates Li-ion diffusion across the SEI.[45] An artificial interfacial layer with high mechanical strength/elasticity effectively protects Li and prevents continuous electrolyte decomposition and SEI formation.[46]

Despite the progress that has been made, currently there are no viable ways to completely avoid/eliminate Li dendrites to reach stable cyclability and long cycle life, especially when

cycling under harsh conditions (e.g., low temperature and high current density). In our view, it is mainly a consequence of nonideal or irrational cell design and operation based on inaccurate physical–chemical principles, due to the limitations of the classical nucleation theory (i.e., absence of SEI) and lack of mechanistic understanding of the whole process at the atomic scale. **Figure 2** highlights major processes during repetitive Li deposition/dissolution and limitations in the understanding of SEI formation, which calls for mechanistic insights into these processes in order to tailor the morphology of Li deposition toward dendrite-free.

This perspective highlights the recent, mostly in the last five years, mechanistic understandings and new observations on Li deposition and SEI formation processes that have been achieved with advanced characterization techniques and theoretical simulation methods. Next, we discuss the underlying mechanisms of Li initial nucleation, growth, and Li striping and their interplays that are poorly understood. Focus is also given to SEI, the "most important but least understood" component[47] in LMBs, in terms of its chemistry, structure, and physicochemical properties, and role in Li plating and stripping. Importantly, we point out the limitations of current understandings, identify remaining mysteries in these processes, and provide point-to-point perspectives on both advanced characterization and theoretical simulation aiming to solve the mysteries and to promote a more comprehensive and in-depth understanding of Li metal anodes. In addition, we provide an outlook into relevant research topics for future research, promoting the current understanding of the fundamental science of Li metal anodes and their eventual application in practice.

Though there are many review and perspective articles[4,35a,48] on Li metal anodes, the vast majority of them focus on various experimental strategies in stabilizing Li deposition and/or SEI. Only a couple of review articles[10,49] are available on the fundamental understanding of Li deposition/dissolution and/or SEI formation behaviors, and the limitations of current understanding have been rarely pointed out explicitly. In addition, there has been no specific review dedicated to the development of theoretical simulation methods for understanding Li deposition and Li-electrolyte interfaces. This article covers a mechanistic understanding of Li metal anodes in both liquid electrolyte-based LMBs and solid-state batteries (SSBs), and from both advanced characterization and simulation.

2. Mysteries in Li Deposition and Perspectives for Deeper Understanding

2.1. Mysteries during Li Deposition

2.1.1. Inaccessible Desolvation Pathway(s)

Prior to Li-ion reduction, driven by an electric field solvated Li-ions gather at the electrode surface, especially near areas where defects (e.g., surface cracks, pits, and subsurface impurities) are rich.[50] It has been realized that the solvation structure and the desolvation of metal-ion could largely impact the electrochemical interface (i.e., SEI) and electrode performance.[51]
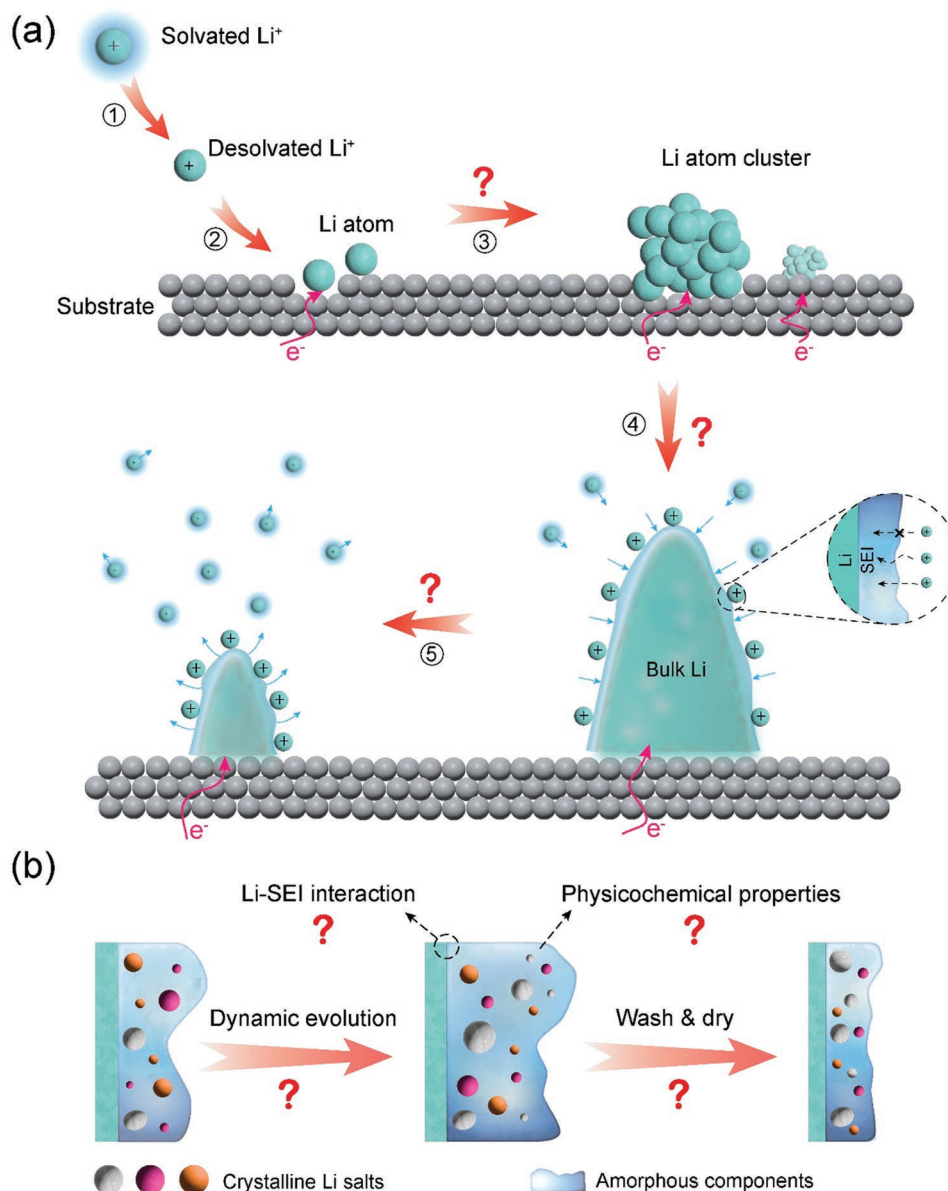
Figure 2. Mysteries in the Li deposition process and understanding of SEI. a) Electrochemical processes in Li deposition: 1) desolvation of Li-ions; 2) reduction of Li$^+$ to Li^0; 3) Li^0 atom clustering or nucleation; 4) morphological evolution of Li nucleus toward bulk deposits and influence of external factors, for example SEI; and 5) behaviors of Li dissolution and its relationship with Li deposition. b) Limitations in the understanding of SEI: 1) formation and dynamic evolution; 2) physicochemical properties; 3) natural state of SEI in batteries; and 4) interaction between SEI and Li deposition.

However, it remains challenging to elucidate the desolvation process of Li ions (as well as other ions), since the process is abstractive, dynamic, and non-quantitative.[52] Moreover, the structure of the Li-ion solvation and the electric double layer determine this dynamic process but could easily be altered if changing either the electrolyte concentration or composition (salts, solvents, and additives). A lack of feasible operando characterization tools further hinders an in-depth understanding of the Li-ions dynamics at the electrochemical interface. Recently, Zhang et al.[53] have proposed two competitive reaction pathways for the desolvation process of metal ions on graphite anode: i) the release of metal ions from a solvated structure, followed by the reduction of metal ions; and ii) the reduction

of the solvated structure, given a strong interaction between metal ions and solvents. The desolvation process of Li-ions in LMBs, though may share some similarities with these findings, remains mysterious and hardly approachable in experiments.

2.1.2. Elusive Li Nucleation Process and Inconclusive Influence of Li Nucleation on the Growth

Nucleation is thermodynamically driven by the Gibbs free energy for transformation from a supersaturated solution to a saturated one at the interface, and is in a tight relationship with the energy barrier for Li nucleation on the substrate.[54]

Therefore, regulating the affinity of the substrate toward Li (i.e., lithiophilicity) through, for example, hetero-atom doping[55] and lithiophilic coating with thin film deposition techniques such as chemical vapor deposition (CVD),[56] atomic layer deposition (ALD),[57] and molecular layer deposition (MLD)[58] have been popular to reduce the energy barrier for Li nucleation for more homogeneous Li deposition.[37]

The current understanding of the Li nucleation process is established upon the classical nucleation theory that involves a single-step nucleation, which results in inconsistencies between theoretical predictions and experimental results, suggesting that Li nucleation in liquid electrolytes may follow more complex routes. However, the mechanism of Li nucleation and early growth remains elusive, because of the small size of nuclei and the short time of the nucleation stage.

Recently, advanced characterization techniques have enabled observation of the nucleation process of many materials on the nanoscale and revealed different intermediated phases during nucleation.[59] For instance, Cao et al. have used in situ low-voltage aberration-corrected high-resolution TEM (AC-HRTEM) to capture the initial steps of nucleation of Fe/Au/Re metal crystal nucleus at the single-atom level, where three metals undergo three different nucleation pathways. Nevertheless, a two-step nucleation mechanism occurs in all three cases, in which a metastable amorphous precursor is necessary for the crystallite nucleation processes.[60] However, due to the high reactivity and electron beam sensitivity of Li, its nucleation details remain inaccessible with existing techniques.

Moreover, though Li nucleation is believed to be tightly related to the following growth process,[61] there is a lack of conclusive evidence on whether the initial nucleation is decisive for the morphological evolution of Li during the following growth process. It has been shown in literature that, regardless of the varying forms of Li nuclei formed in different substrate–electrolyte systems, they may eventually evolve toward dendrites at the growth stage, due to the inhomogeneous distribution of Li-ions and/or different nucleation energies. This can be caused by various reasons such as geometric roughness of the substrate crystallographic defects of Li deposits.[15a,62] The electrochemical cycling protocols could also significantly influence the Li deposition process. The higher the current densities, the larger the concentration gradients, and the easier the dendrite growth. Xu et al.[62a] reported that, when Li deposition happens in an ether-based electrolyte, the initially deposited Li appears dominantly spherical, which evolves toward bar/rod-like morphology as the capacity of Li deposition increases. When Li is deposited in a carbonate-based electrolyte, Bai et al.[15a] have demonstrated a mossy-to-dendritic transition of Li morphology. Besides, Dong and Xu et al.[62b] have revealed that the initially formed Li nuclei or early-stage deposits are spherical, which grow toward fiber-like dendrites during the following growth stage when the deposition current density is high. They also found that new Li nuclei tend to form at the kinks of Li dendrites rich in crystallographic defects and at the geometric defects/inhomogeneities of the substrate due to the altered electrical field and hence the Li-ion flux. This suggests that the morphological evolution of Li deposits at the growth stage may not decisively depend on the initially formed Li nuclei.

2.1.3. Complicated Morphological Evolution of Li Growth and Influencing Factors and Unclear Crosstalk between Stripping and Plating during Cycling

During Li growth, the initially formed nuclei evolve toward various types of morphologies, for example, balls, needles, columns, or a mixture of them, depending on the types of electrolytes and deposition conditions.[15a,62a,b,63] In particular, in the commonly used carbonate- and ether-based electrolytes, Li deposition appears to be needle-like and spherical/granular, respectively.[63b]

The morphological evolution of Li deposits is a complicated and dynamic process and governed by the real-time and local thermodynamic properties of the SEI layer, the reaction front and kinetic barrier for electrochemical Li deposition and dissolution, along the growth process.[49a] This could be rationalized because Li-ions have to migrate through the SEI layer and transfer charges to the substrate underneath to realize Li reduction to Li^0 atoms and growth of Li deposits. SEI is a complex and dynamically evolving layer (see Section 3.1.1). Li-ion diffusivity through the SEI may change with the chemical evolution of SEI, and the charge transfer kinetics may decrease as the SEI layer grows/thickens. Thus, how SEI shapes Li deposits in LMBs remains an open question.[49b,64]

Meanwhile, external factors such as working temperature and stacking pressure are noted to be of significant influence on the morphological evolution of Li deposits in LMBs: i) the Li-ion diffusivity and Li reduction reaction kinetics are temperature dependent, which is sluggish at low temperatures, resulting in reduced Li-ion flux and increased depletion region (i.e., space charge layer) near the surface of Li metal anode, especially at a high current density, leading to dendritic Li growth;[49a] 2) the chemistry and structure of SEI formed in different temperatures appear with discrepancies,[65] which also influence the Li diffusion kinetics and deposition morphology; and 3) the initial studies[66] have shown that the stacking pressure influences the Li plating and tripping processes as well as the SEI properties in different ways in both liquid and solid electrolytes based batteries. However, the effects of these factors on the morphological evolution of Li deposits are complicated and the understanding of their exact roles in LMBs remains underdeveloped.

Moreover, the past research has focused on the investigation of Li deposition behavior, with less attention paid to the understanding of dissolution and re-deposition processes. In particular, how Li dissolution is influenced by the previous Li deposition process and how it, in turn, shapes the redeposited Li remains unclear. The crosstalk of Li plating-stripping processes is particularly important when we look at the Coulombic efficiency and stability of Li metal anodes during long-term cycling. Even minor discrepancies in individual cycles may result in overwhelmingly different performance considering the accumulation of single-cycle variations. Li et al.[67] found that the order of Li deposition and dissolution could dramatically influence the morphological evolution of the Li electrode. Specifically, when the dissolving of Li happens first, large voids are formed and randomly distributed on the surface of the Li electrode. Dendritic Li preferentially fills these voids after the following deposition process. In comparison, when Li

deposition occurs first, granular-like Li deposits appear on the Li electrode, and, upon Li dissolution, voids are still formed on the surface, while most of the granular-like deposits remain. It is also important to note that whatever Li plating-stripping order, non-uniform and dendritic Li growth eventually takes place, and that the influence of the order on the long-term cycling stability and efficiency of Li metal anodes remains an open question.

As the SEI is believed to play a key role for Li deposition, it may also be the main factor determining the interplay between Li deposition and dissolution. Specifically, next to chemical reactions between Li and the electrolytes, the SEI formation during Li plating and stripping involves reductive and oxidative electrochemical reactions, respectively. Therefore, the Li plating-stripping crosstalk may also be related to the different SEI formation processes during Li deposition and dissolution. Future research should extend the research scope and pay attention to the fundamental relationship between Li deposition, dissolution, and re-deposition, and also correlate it with the concurrent SEI formation and evolution processes, in order to establish better Li deposition model(s).

2.1.4. Poor Understanding of Li Deposition Behaviors in SSBs

There is currently great enthusiasm in developing SSBs in which the liquid (highly flammable) electrolyte is replaced by a polymer or inorganic solid electrolyte.[68] In particular, the research field of inorganic solid electrolytes and their use for LMBs attracted a lot of attention in the last years. Several classes of inorganic solid electrolytes with high Li conductivity have been explored.[69] The most prominent ones include garnets,[70] NASICON-type materials[71] and perovskites[7a] (usually abbreviated as "oxides"), binary (P_xS_y) thiophosphates ("sulfides"[72]), halide-containing materials such as argyrodites[73] as well as rare-earth halides ("halides"[74]), and closo-borates ("hydrides"[75]). Some of these materials can have very high room temperature conductivities ($>10^{-3}$ S cm^{-1}) in the range of (organic) liquid electrolytes and Li-ion transference numbers close to unity, which makes them very appealing for LMBs.[76]

The Li-solid electrolyte interface is more difficult to describe as in reality it is not continuous and may be better described by point contacts due to the poor interfacial contact in between, and the understanding of Li deposition behaviors at such a non-continuous interface remains underdeveloped. There was hope that solid electrolytes are more "stable" in contact with Li metal but also in this case it was quickly realized that the stability window is quite limited in many cases, which requires, similar to liquid electrolytes, some sort of SEI, see Section 3.1.4. Meanwhile, as Li plating or stripping leads to a volume change at the interface,[77] it is immediately clear that for solid–solid interfaces, the electrochemical behavior will strongly depend on mechanical properties of the materials such as the yield strength or the shear modulus as well as on the applied pressure. Applying an external pressure can lead to plastic flow or creep which can effectively mitigate contact losses during cycling.[66c] Excessive pressures, however, lead to fracture of the solid electrolyte and short circuit.[66a] Stable

cycling may therefore be only obtained within a mechanical stability window as proposed by Tu and Ceder.[78] A comprehensive summary on the various aspects of Li plating/stripping at Li-solid electrolyte interfaces has been published by Krauskopf and Janek, which includes the physical and (electro-)chemical, mechanical, transport properties related to the stability and kinetic performance of the Li-solid electrolyte interface, and the effects of stacking pressure and temperature on the plating and stripping behaviors.[3b]

Research on solid electrolytes for LMBs is largely driven by the promise to make batteries safer and more compact and to realize a Li metal anode. Initially there was hope that the use of solid electrolytes will eliminate the problem of dendrite formation in contact with Li. However, it quickly became clear that dendrites can also grow through solid electrolytes. It has been widely acknowledged that polymer-based solid electrolytes have insufficient mechanical strength to inhibit the penetration of Li dendrites. The use of inorganic solid electrolytes, which have high shear modulus to mechanically inhibit dendrite propagation, seems more promising at first but also shows dendrite growth. Dendritic Li in SSBs preferably grows at the defects of the electrode and the solid electrolyte (e.g., cracks, impurities, grain boundaries, and voids).[79] The underlying mechanisms of Li dendrite formation and growth in SSBs remains poorly understood. Specifically, i) the Li nucleation and dendrite formation could happen at the Li-solid electrolyte interface, induced by the poor interfacial contact caused by geometric inhomogeneities, such as surface roughness, voids and defects; ii) Li dendrites could also form inside solid electrolytes induced by electrons from their residual electrical conductivity, oxygen framework, and pore surface; iii) grain boundaries inside solid electrolytes could induce Li propagation.[80] However, dendrite penetration and short-circuiting can still occur even when single-crystalline solid electrolytes are used. Swamy et al.[81] showed Li dendrite penetration through single-crystal $Li_6La_3ZrTaO_{12}$ garnets solid electrolytes, which occurred predominantly at the perimeter of the working electrode; and iv) it is noted that the stacking pressure of SSBs also plays an important role in the Li dendrite growth behavior.[82]

In contrast to LMBs with liquid electrolytes, the use of solid electrolytes enables different strategies for mitigating dendrite growth. One strategy for improving the Li plating/stripping is to introduce interlayers, for example, as shown by Samsung.[83] In their study, dendrite-free plating and stripping of Li between the current collector and an argyrodite solid electrolyte (Li_6PS_5Cl) was achieved by introducing an Ag−C nanocomposite interlayer. This interlayer prevented dendrite growth likely due to a combined effect of the carbon and the silver nanoparticles thereby leading to a more favorable behavior. While the exact mechanism remains unknown, the study is one example that the Li plating/stripping behavior in SSBs depends on many factors and can therefore be tailored by various approaches.

Probing and understanding Li dendrite growth in SSBs is challenging in general, because the Li/solid electrolyte interface is "buried" and inaccessible for most in situ analytical probes, and cannot be dismantled easily for ex situ characterization. Only limited techniques like XCT allow for in situ or operando characterization of SSBs, making it possible to uncover the structural and interfacial evolution in SSBs as well as the
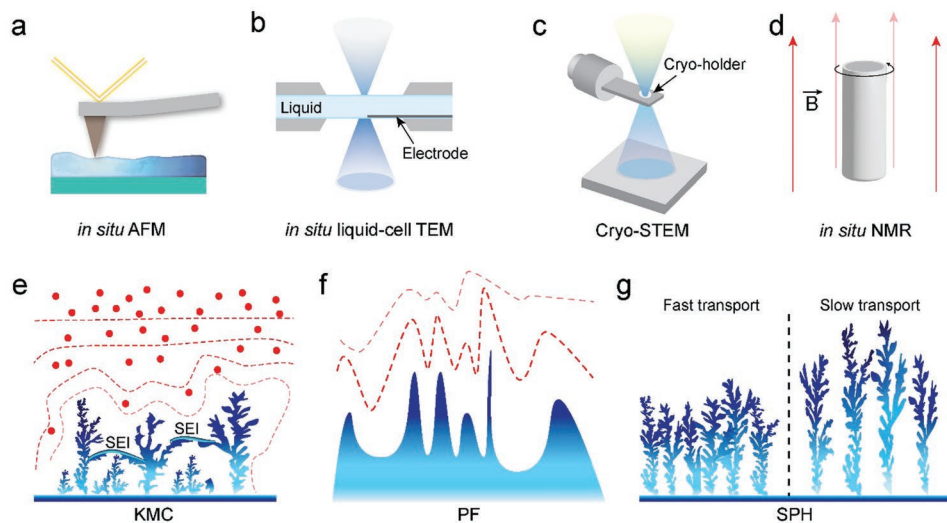
Figure 3. Advanced characterization (a–d) and theoretical methods (e–g) to obtain fundamental understanding of Li deposition. a) In situ EC-AFM, b) in situ liquid-cell TEM, c) cryo-STEM. d) In situ NMR. (e) shows that electric field and SEI can influence the Li dendrite growth, even electric potential distribution and SEI with high diffusion coefficient and Young's modulus will inhibit Li dendrite growth in a microscale. (f) shows that a stronger electric field results in easier Li dendrite growth in a mesoscale. (g) shows a fast mass transport will inhibit macroscale Li dendrite growth.

creep of Li within solid electrolytes.[77,84] It is also more difficult to implement a reference electrode that allows measurement of the real electrode potential rather than the cell voltage.

2.2. Perspectives for Deepening Understanding of Li Deposition

Due to the high reactivity and electron sensitivity, real-time visualization of the Li nucleation process, particularly Li atomic self-assembly and clustering before the formation of crystal nucleus (sub 10-nanometers), remains overwhelmingly challenging. In the past years, in situ probes such as OM,[15a] SEM,[85] and TXM,[86] have been used to study the growth process of Li deposits, but their spatial resolution is too limited to probe the initial Li nuclei. The development of in situ TEM,[14,87] particularly liquid-cell TEM,[14] has gained momentum for studying Li deposition in recent years, but tremendous technical challenges are still in place for capturing the initial form of Li nucleus, namely the high spatial- and tempo- resolution it requires and limited feasible operando setups that could provide a reaction environment close to practice. Therefore, we would like to emphasize that theoretical modelling at the reactive electrochemical interface of Li deposition at multiple temporal- and length-scales will be required for a fundamental understanding of the Li nucleation process, supported with atomic-resolution probes in real-time. Classical nucleation theory and simulations have been frequently adopted to elucidate the initial Li nucleation process. The thermodynamic driving force for Li nucleation is the presence of supersaturation $\Delta\mu$ defined as $\Delta\mu = \mu_s - \mu_b$, where μ_s and μ_b are the chemical potentials of Li in the electrolyte solution and in the bulk phase, respectively.[88] In electrochemistry, the supersaturation could be translated into overpotential of the involved electrochemical processes.[89] Kinetically, the Li nucleation is influenced by the Li-ion diffusion rate through the electrolyte and across the SEI layer, and the kinetics of electrochemical reactions.

To understand the influence of Li nucleation on the subsequent Li growth process, it would be necessary to operando monitor the ion flow and to visualize the morphological evolution of Li at various length-scales from sub-nanometer to millimeter throughout the Li deposition process. This could be achieved by in situ high-resolution microscopy, and examples include in situ scanning probe microscopy (SPM), such as, in situ electrochemical atomic force microscopy (EC-AFM, **Figure 3**a) with environmental control and fast scan rate, and in situ liquid-cell TEM (Figure 3b) with low-dose-/rate and rapid imaging. By varying the electrochemical Li deposition protocols (e.g., galvanostatic, potentiostatic, and sweeping voltage) and conditions (e.g., temperature, pressure, electrolyte type, and flow rate), energetic landscape and kinetic behaviors of Li deposition could be obtained, which helps understand the underlying physical–chemical principles governing Li deposition. These in situ probes could also potentially capture the very initial nucleation stage of Li deposition, and provide us with complementary information on the topographic, mechanical, and electro-/chemical properties of deposited Li throughout the deposition process.

To understand the Li growth mode, it would be imperative to upgrade the existing characterization techniques, such as combined low-dose cryo-STEM (Figure 3c) and cryo-FIB tomography to show the detailed structure of Li deposits at the close-to-native state and in situ solid-state nuclear magnetic resonance (ss-NMR, Figure 3d) to distinguish the dendritic and bulky Li deposits. XCT is a powerful method that can be leveraged to uncover the structural and mechanical evolution at the Li-solid electrolyte interface as well as the creep of Li within solid electrolytes that could induce the short-circuit in SSBs and that can hardly be uncovered by other microscopic techniques. Meanwhile, the classical nucleation theory should be modified to interpret the characterization result as well as to establish new Li deposition model(s), for example, by incorporating the

role of SEI, based on the recent observations and current understanding.

Multimodal theoretical simulations could also be developed to help support and interpret the experimental observations. Theoretical simulations can help in the resolution of TEMs. For example, image simulations play an important role in the interpretation of HRTEM images. Theoretically, theoretical simulations can also help in the resolution of cryo-TEM, which has been widely used in protein crystalline structure analysis.[90] Simulation techniques are actively under development. Furthermore, the underlying relationship between Li nucleation and growth should be further understood theoretically based on the established new electrodeposition model(s).

Simulation of the Li growth process requires macroscopic time and space scales. The current atomic level-based theoretical simulations are not able to meet such requirements. For instance, Message Passing Interface (MPI)–Graphics Processing Unit (GPU) can accelerate the numerically simulated process with existing software such as Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) and Multiphysics Object-Oriented Simulation Environment (MOOSE). However, these methods lack connections with atomic information. Accordingly, Kinetic Monte Carlo (KMC)[22,34,91] (Figure 3e), Phase-Field (PF)[92] (Figure 3f) and SPH[23,93] (Figure 3g) simulations have been developed to directly simulate the dendrite growth process. The results of these simulations clarify the effects of temperature, external field, physical segregation, etc., on dendrite growth. These simulations provide an important theoretical model for the dendrite growth process. However, we must also recognize the shortcomings of the existing models, which still lack an effective correlation between the existing macroscopic simulation methods and the atomic models: i) KMC typically simulates processes with known transition rates among states, which have to be obtained from diffusion experiments or MD (molecular dynamics) and DFT; and ii) PF is complex and costs more time compared to KMC. (iii) SPH has no connection with microscopic simulation methods and atomic models. To further improve our understanding of Li deposition, it is necessary to bridge the existing atomic and macroscopic simulations and establish a unified set of theoretical simulation models.

In short, the recent and emerging theoretical modeling and characterization methods that could deepen the understanding of Li deposition have been introduced. Theoretical modelling and simulation is anticipated to play a dominant role in understanding the formation of crystal Li nuclei (sub 10-nanometer) due to the tremendous challenges for in situ and operando characterization of Li nucleation, but has remained very much underdeveloped. Regarding the subsequent Li growth, complementary to modelling and simulation methods like KMC, PF, and SPH, various probes have been adopted for characterizing Li deposition, for example, in situ AFM, in situ liquid-cell TEM, XCT at nano- and micro-meter spatial resolution, cryo-EM, cryo-FIB tomography, second-ion mass spectroscopy (SIMS), and MRI. These methods enable characterization of Li deposition at different length scales, from nanometer to millimeter. The authors' view for the further development of relevant theoretical modelling and characterization methods is summarized in the Outlook section of this article.

3. Limitations and Challenges for Understanding SEI and Perspectives Solutions

3.1. Understanding of the Chemistry, Structure, and Physicochemical Properties of SEI

3.1.1. Elusive Chemistry and Structure of SEI

As the SEI is derived from reactions between Li and electrolyte, the chemical composition of SEI mainly depends on the type of electrolytes (including Li salts, solvents, and additives).[94] The chemistry of the SEI has been extensively investigated through X-ray photoelectron spectroscopy (XPS),[95] Fourier-transformed infrared spectroscopy (FTIR),[96] nuclear magnetic resonance (NMR),[31,97] SIMS,[97,98] etc. in recent years. It is widely accepted that the SEI is a mixture of inorganic Li salts and organic species so far, but its exact composition and distribution remain elusive. The inorganic Li salts mainly include Li_2O, LiF, Li_2CO_3, and possibly Li_2S, Li_3N depending on the types of solutes and solvents in electrolytes. In particular, LiF has been widely regarded to be "magic"—being greatly beneficial for the realization of stable Li metal anodes,[99] but its exact role in stabilizing the SEI and Li deposition is still a mystery. The organic species are thought to contain alkoxides in electrolytes with ethers, alkyl carbonates with carbonate esters, oligomers, and polymers.

The characterization of the structure of SEI has been very challenging, due to the small thickness (10–100 nm[8d]) of the SEI and the limited spatial resolution of many techniques as well as the sensitivity of SEI toward high-energy radiation. The accurate characterization of the SEI structure remained impossible until the application of cryo-electron microscopy recently.[17,100] Typically, the SEI is completely amorphous or composed of an amorphous framework distributed with crystalline inorganic Li salts like Li_2O and Li_2CO_3 when investigated under cryo-EM. The SEI with a multilayered structure composed of layers of different compounds has also been reported.[65,100d] It should be noted that this fragile film may decompose and collapse even under very low electron dosages (typically up to tens or hundreds of electrons per square angstrom depending on the chemical composition) at such a low temperature.[17] Upon beam damage, many components in the SEI decompose into more stable Li_2O under different electron doses depending on the composition, size, etc.[21] In particular, organic compounds are more susceptible to decomposition. The SEI with high content of organic compounds is very sensitive, aggravating the challenges of the acquisition of accurate nanometer-scaled structure. The electron beam damage is worse for STEM-EELS which requires an extended duration of exposure and hence total dosage. Though microscope resolution at low accelerating voltage has been improved considerably in recent years,[101] low-voltage cryo-EM has not been adopted in the analysis of sensitive battery materials.

Moreover, the SEI layer is subject to repetitive breakage and reparation along with Li plating and stripping, and thus evolves continuously in chemistry and structure. Current

**ADVANCED
SCIENCE NEWS**
www.advancedsciencenews.com

**ADVANCED
ENERGY
MATERIALS**
www.advenergymat.de

understanding of the SEI has been obtained from post-mortem studies at a selected dis-/charge state of batteries, for example, the SEI after a specific cycle number, with less attention given on the dynamic change of the SEI over cycling, especially the change of the SEI during a specific Li plating or stripping process.

It is also necessary to point out that the post-mortem SEI under investigation is extracted from cycled batteries, washed and dried before characterization in order to avoid the disturbance of residue electrolyte in data analysis. SEI is an interfacial film immersed in the liquid electrolyte in batteries, and may change its physical/chemical properties once leaving the liquid environment and dried. It has a porous outer layer (i.e., the electrolyte side) that may be similar to gel, which may be easily washed away, altering the components, structure, and properties of the SEI, when cleansing the adhered electrolytes from the Li metal anode. Besides, the inner part of the SEI (i.e., Li metal side), especially the one formed in carbonate ester electrolytes, may also dissolve in the solvent during rinsing.[102] Therefore, such investigations of SEI miss important information on the real and natural state of SEI and may lead to inaccurate conclusions. Cryo-FIB is capable of preserving many parts of the SEI structure, including amorphous regions, as demonstrated in previous reports.[17,103] It could be used to prepare cross-section specimen or lamella of Li-electrolyte interface containing (frozen) liquid electrolyte for cryo-STEM, without rinsing and drying processes. Very recently, Zhang et al.[104] has captured the swollen state of SEI with cryo-STEM by preserving the SEI in its native organic liquid electrolyte environment with the original thin film vitrification method. However, the presence of frozen liquid electrolyte would cause difficulty in distinguishing the SEI in TEM analysis, because the electrolyte, which contains Li salt(s) and solvent, has a similar contrast to the SEI under TEM.

Despite the formidable challenges for understanding the composition, structure, and properties of SEI, the regulation of SEI, mainly through a trial-and-error process, has achieved significant advances. In particular, tailoring the formulation of electrolytes has been proven to be an effective strategy to regulate the composition and structure of SEI.[105] Besides, in situ formation of a surface/interface film on Li metal through chemical or physical pretreatment has also been popular.[106]

3.1.2. Unestablished Property–Functional Relationship of SEI

The physicochemical properties of the SEI can affect the Li growth behaviors and the cycling performance of Li metal anode, thus attracting tremendous attention with extensive studies on the mechanical,[29,107] kinetic,[10,106b,108] and chemical properties.[100e,109] The modulus of the SEI is typically in the range of hundreds of megapascal and several gigapascal depending on the formulations of electrolytes. The kinetic properties of the SEI have been widely studied with electrochemical methods, such as electrochemical impedance spectroscopy (EIS),[108b] and cyclic voltammetry (CV),[10,110] which typically show the charge-transfer resistance in the range of tens to hundreds of Ohm (Ω). The chemical properties such as chemical stability and thermal stability of SEI have also been investigated

through theoretical calculations. It has been shown that Li_2O crystals in the SEI layer would act as the nucleophilic agent to initiate the decomposition of ester solvents in electrolytes, which may help explain the mosaic structure of the SEI.[109] Meanwhile, the alkyl carbonate Li salts would decompose into Li_2CO_3 affecting the chemical stability of SEI.[100e]

However, understandings of these properties remain very limited and the relationship between these properties of SEI and the behaviors of Li deposition underneath has not been established. Many controversial conclusions have been drawn based on a single property of the SEI. For instance, it has been found that high exchange current densities suppress the growth of Li dendrites,[106b,108a] while contrary conclusions have been drawn in literature.[10,110] This may result from different specific areas of Li deposition when the components of electrolytes are changed, which affects the SEI resistance and Li plating kinetics. Besides, the SEI with high modulus is believed to suppress the Li dendrites, but the flexible and organic-rich SEI with low modulus can also facilitate the planar Li growth.[94f,111] Moreover, probably multiple properties of the SEI contribute to the shaping of Li deposits. Those complicated factors are interwoven together, which aggravates the challenges for distinguishing the key factor dictating the Li deposition behaviors.

3.1.3. Criteria of an Ideal SEI

The criteria of an ideal SEI should be considered from both kinetic and thermodynamic points of view. On the kinetic aspect, an ideal SEI should possess a high Li-ion conductivity to facilitate fast Li-ion transport and redox reactions (deposition and dissolution). In particular, the conductivity of SEI should be homogeneous, which requires uniform chemical distribution and thickness of the SEI film. Uniform and high ionic conductivity result in spherical or columnar Li growth, imposing the lowest stress onto the SEI layer and minimizing the breakage of SEI and the evolution of "dead" Li. Thereby, the CE of Li plating and stripping processes would be maximized. From the perspective of thermodynamics, the SEI should be chemically and thermally stable during the storage and cycling of LMBs. For the chemical stability, it should exhibit high resistance against the corrosion of electrolytes over a long term, especially at an elevated temperature (e.g., 60 °C). It should also be thermodynamically stable against decomposition/degradation when the cells are placed at a high temperature. With high chemical and thermal stability, the SEI layer can well protect Li metal from contact with and oxidation by the electrolyte, which largely reduces the loss of active Li metal and maintains the cell capacity over long-term cycling.

3.1.4. Li-Electrolyte Interphases in SSBs

The interphase between solid electrolyte and Li metal anode in SSBs is also commonly termed as SEI. As mentioned above, there was initially hope that the interface between solid electrolytes with Li is chemically more stable compared to liquid electrolytes. For some materials, this is indeed the case. An

illustrative example, although for Na, is beta-alumina which is used as a solid electrolyte in high-temperature sodium-sulfur and ZEBRA batteries. The stability of beta-alumina against molten Na recently spurred interest in using this solid electrolyte also at lower temperatures.[112] The driving force for reactions between Li and solid electrolytes, however, is generally larger. Overall, it turned out that the chemical stability window of solid electrolytes is quite limited, and may decompose upon direct contact with lithium. Typical reactions between lithium and solid electrolytes involve the formation of stable binary compounds such as Li_2S, Li_3P or Li_2O along with the reduction of metal cations (when available). For example, Ti or Ge cations in NASICON-type solid electrolytes are being reduced by lithium.[113] The highly conductive solid electrolyte $Li_{10}GeP_2S_{12}$ (LGPS)[114] reacts with lithium to form Li_2S, Li_3P and Ge/Ge_4Li_{15}.[115] Li_2S is also experimentally found during the reduction of Li_3PS_4[116] and the argyrodite Li_6PS_5Cl (LPSC).[117] The stability of the recently explored group of halide solid electrolytes[118] is also limited, with Li_3InCl_6 (Li_3YCl_6) showing full reduction of the In and Y cations upon contact with lithium metal (likely along with formation $LiCl$).[119] Oxide solid electrolytes show a larger electrochemical stability window.[120] Reduction of solid electrolytes by lithium is not really surprising and the observed decomposition simply indicates that, just like for liquid electrolytes, some sort of SEI needs to form from the decomposition products. Conceptually, three different kinds of interfaces between lithium and solid electrolytes can be distinguished: 1) a thermodynamically stable interface. This is the preferred situation but only a few materials such as the binary compounds Li_2S, Li_3P and Li_3N satisfy this situation as most complex materials will readily react with lithium due to its strong reducing power; 2) unstable interfaces with mixed electronic and ionic conductivity (which is undesired as it leads to continuous degradation); and 3) unstable interfaces that are kinetically stabilized but conductive of Li ions. Case (3) represents the classical case of an SEI that could enable stable lithium plating/stripping. Satisfying the requirements for case (3) requires interphase with suitable "chemomechanical" properties, that is, the interphase needs to be chemically and mechanically compatible with lithium and the solid electrolyte. In favorable cases, this interphase may form directly between the solid electrolyte and the lithium metal. Such an almost ideal scenario is obtained in the case of cubic-$Li_{7-3x}Al_xLa_3Zr_2O_{12}$ (LLZO). In contact with lithium, c-LLZO only shows a very limited reaction involving the formation of a tetragonal-like LLZO interface which extends only over about 5 unit cells.[121] In other cases, an interface engineering by coatings may be applied which is also an important strategy to improve the compatibility of solid electrolytes with cathode materials.[122]
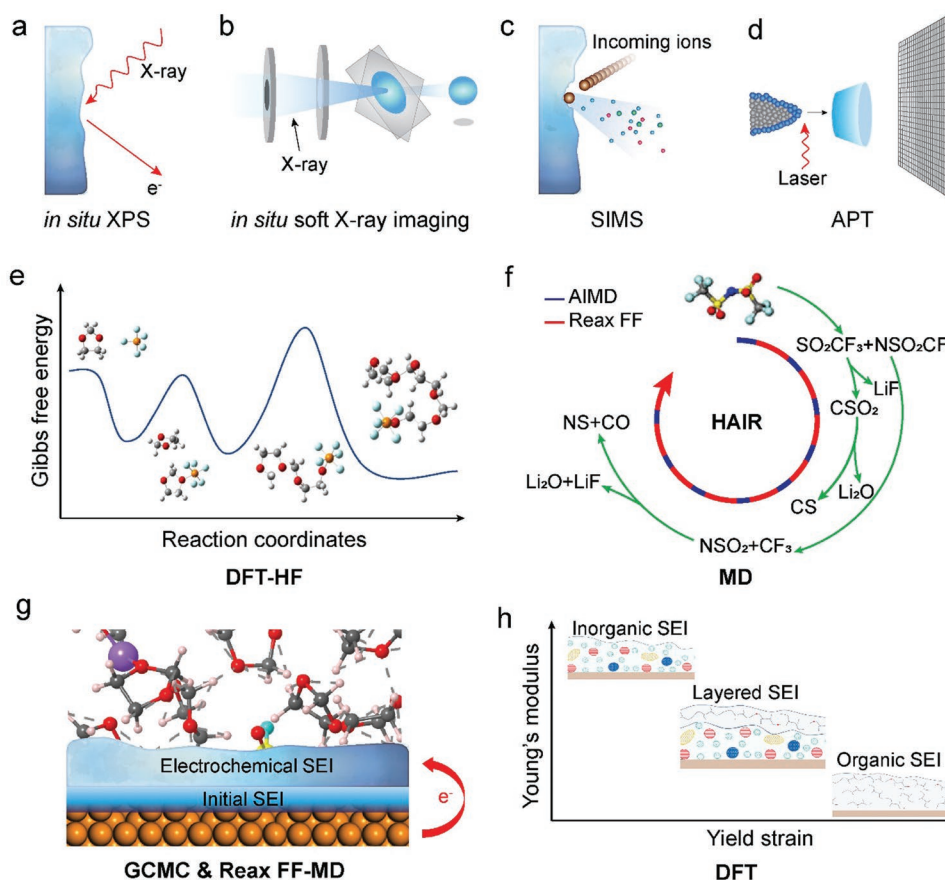
3.2. Limitations in Current Understandings of SEI and Perspectives on Future Studies

The SEI is poorly understood due to its extreme sensitivity to ambient air, moisture, and high-energy radiation. Up to now, characterization of the SEI has been limited to ex situ techniques such as XPS and Fourier-transformed infrared spectroscopy (FTIR). However, these spectra merely provide the average results of the SEI chemistries leaving the chemistry distribution of SEI unknown.

In recent years, the chemistry and structure of SEI have been partially elucidated by ex situ characterization techniques such as cryo-EM that alleviate the damage of the high-energy electron beams.[100a,e] It has been shown that most investigated SEIs have an amorphous matrix filling with randomly distributed inorganic crystalline domains especially Li_2O and Li_2CO_3, with minor LiF.[123] Also, some SEIs are completely amorphous in some studied regions.[105a,124] However, cryo-TEM can only identify grains of inorganic Li salts in the SEI that have good crystallinity. Meanwhile, SEI is still very sensitive to the electron beam even at cryogenic temperature, with most components decomposing into Li_2O.[17] Therefore, cryo-EM with controlled electron dosage and dose rate is imperative for studying SEI. Characterization of the amorphous content in the SEI is possible through cryo-STEM based EDX and EELS, but the electron dosage should be controlled more carefully, and a low accelerating voltage could be used to minimize the beam energy and hence the damage to the specimen. A recent study using cryo-STEM-EDX unraveled the 3D distribution of the SEI layer on Si nanowires and suggested that the progressive SEI inwards propagation induced by the electrolyte permeation leads to a capacity loss. This methodology can be incorporated into studies on SEI on Li whiskers and balls. Meanwhile, EELS is capable of identifying inorganic compounds like LiF in the amorphous part of the SEI, which might be a tool to investigate the distribution of amorphous LiF and understand its role in the SEI. The organic components in the SEI may be identified by ssNMR, and 2D NMR may help to reveal their molecular structures. 2D exchange NMR can unravel the Li-ion diffusion properties inside the SEI and between SEI and Li deposits. However, the high detection limit of ssNMR poses challenges for studying SEI. Moreover, time-of-flight secondary ion mass spectroscopy[30,125] (ToF-SIMS, **Figure 4**c) depth profiling could identify species of the SEI and their 3D distribution on micro- to nanometer scale, which could be combined with atom probe tomography[126] (APT, Figure 4d) to show the chemistry and distribution of SEI on atom scale. In addition, to probe the Li-solid electrolyte interface, in situ formation of Li-solid electrolyte interface inside a microscope chamber with an in situ electron microscope could be a solution.

However, ex situ techniques fail to elucidate the natural state of SEI in batteries. It makes the development of in situ probes vitally important for capturing the real-state of SEI in real-time during battery operation, due to the advantages in enabling the monitoring of the dynamic change of SEI. In situ spectroscopies like near-ambient-pressure (NAP) XPS (Figure 4a) which, being capable to identify the dynamic chemical evolution of SEI could be very powerful tools in the foreseeable future for studying changes in the element content of SEI. In situ soft X-ray spectromicroscopy (Figure 4b) may provide quantitative 2D distribution of chemical species of SEI with a spatial resolution as low as 30 nm. EC-AFM can capture the dynamic SEI formation and evolution process on copper substrates in liquid by controlling the potential of the Cu electrode. Combined with linear scanning voltammetry (LSV) which reflects the reduction potential and reactivity of electrolytes, the correlation between the reactivity of electrolytes and the growth behavior and

ADVANCED
SCIENCE NEWS
www.advancedsciencenews.com

ADVANCED
ENERGY
MATERIALS
www.advenergymat.de

Figure 4. Advanced characterization (a–d) and (e–h) theoretical methods to obtain more understandings related to SEI formation. a) In situ XPS, b) in situ soft X-ray imaging, c) SIMS, and d) APT. e) DFT and HF based QM calculations, f) HAIR for predicting the SEI formation reaction pathways (this figure is modified from Ref. [24j] (Reproduced with permission.[24j] Copyright 2021, American Chemical Society), g) GCMC and ReaxFF based MD for understanding the evolution of SEI chemistry, and h) DFT computation of the physicochemical properties of the SEI layer.

structure of the SEI on the Cu electrode can be understood. The growth of SEI on Li metal may also be investigated by AFM. The mechanical properties of the wet SEI in liquid electrolytes can be attained as well, which helps distinguish the distribution of the inorganic and organic compounds at the nanometer scale. Such characterization technique can provide invaluable knowledge on the wet SEI, approaching the real working state. However, it should be noted that AFM faces limitations on the characterization of wet SEI due to its incapability of obtaining its chemical information.

Apart from characterization tools, first-principles calculations are powerful for studying the SEI structure and its dynamic evolution.[24c,127] There are a large number of reports on initial reaction prediction and SEI model derivation using first-principles methods. For example, Camacho-Forero et al.[24c] applied DFT and ab initio molecular dynamics methods (AIMD) to Li−S systems, and found that DOL solvent and DME solvent are more stable than EC during the entire simulation length. These results have greatly filled the existing gap for the SEI microstructure. They have contributed significantly to the understanding of SEI. However, the first principles approach, which is computationally too expensive, has very limited time and space scales for its simulations. To solve the above prob-

lems, empirical potential function methods have also been used. Quantum mechanics, which derives potential energy functions from electron correlation properties, can only deal with small systems. Among them, DFT and Hartree–Fock (HF) method (Figure 4e) are commonly used in quantitative calculations, and are usually applied to the HOMO–LUMO level calculation and thermodynamic calculation of reactions related to electrolyte decomposition and SEI formation.

These methods can substantially improve the computational efficiency and extend the simulation scale from a few nanometers to up to several hundred nanometers. However, there are certain problems with such methods. First, since empirical potential function methods rely on force field parameters, a large number of standpoint parameters about battery simulations are still missing. Thus, many important battery systems are not yet available to be simulated by empirical potential function methods. Second, the accuracy of the empirical potential function method is generally lower than that of the first nature principle. So the results obtained by prediction have relatively large errors. The traditional molecular dynamics simulation is divided into the AIMD method and reactive force field molecular dynamics (ReaxFF MD) method based on empirical potential function. To solve

**ADVANCED
SCIENCE NEWS**

www.advancedsciencenews.com

**ADVANCED
ENERGY
MATERIALS**

www.advenergymat.de

the above problems, T. Cheng's team has developed a hybrid AIMD combined with reactive force fields (HAIR) (Figure 4f) method that utilizes both the first nature principle and the empirical potential function. It can be simulated at a higher accuracy. The simulation efficiency of the empirical potential function is achieved. We have used these methods to make theoretical predictions regarding massive SEI formation in different electrolyte systems.[24d,i,j]

The nucleation/growth and dynamic evolution of the SEI is also a matter of interest. Although there have been a few investigations on the nucleation/growth of the SEI on graphite electrode or Cu current collector,[128] the SEI nucleation on the Li metal electrode is rather poorly understood to date due to the vigorous and uncontrollable reactions between metallic Li and the electrolytes. In situ EC-AFM with a fast scanning mode and in situ TEM may have the capability of monitoring this process. The dynamic evolution of SEI, especially its regrowth and reconfiguration during charge and discharge, involves particularly complex electrochemical reactions. Theoretical simulation of electrochemical reactions in the battery system is difficult at present. Some specialized techniques are needed. For example, constant voltage simulation based on grand canonical Monte Carlo (GCMC) ensemble is a necessary simulation tech-

nique. In recent years, significant progress has been made in the development of electrochemical simulation methods. These methods in combination with existing simulation methods such as the high-precision ReaxFF method (Figure 4g), are possible solutions to achieve dynamic evolutionary simulation of SEI.

Finally, the physical and chemical properties of SEI are calculated by the first-principles method. For example, the DFT-VASPKIT program package (Figure 4h) is called to calculate Young's modulus of the SEI to determine the mechanical stability of the SEI. In addition, the AIMD method can help us obtain the Li-ion conductivity of SEI.

4. Outlook for Future Research

In the sections above, we have discussed the recent progress on understanding the mechanisms of Li deposition and SEI formation as well as the remaining mysteries in these processes. Meanwhile, characterization and theoretical methods that could solve these mysteries and obtain fundamental understandings of Li plating and stripping and SEI layer have also been proposed, and are herein summarized in **Figure 5** together with
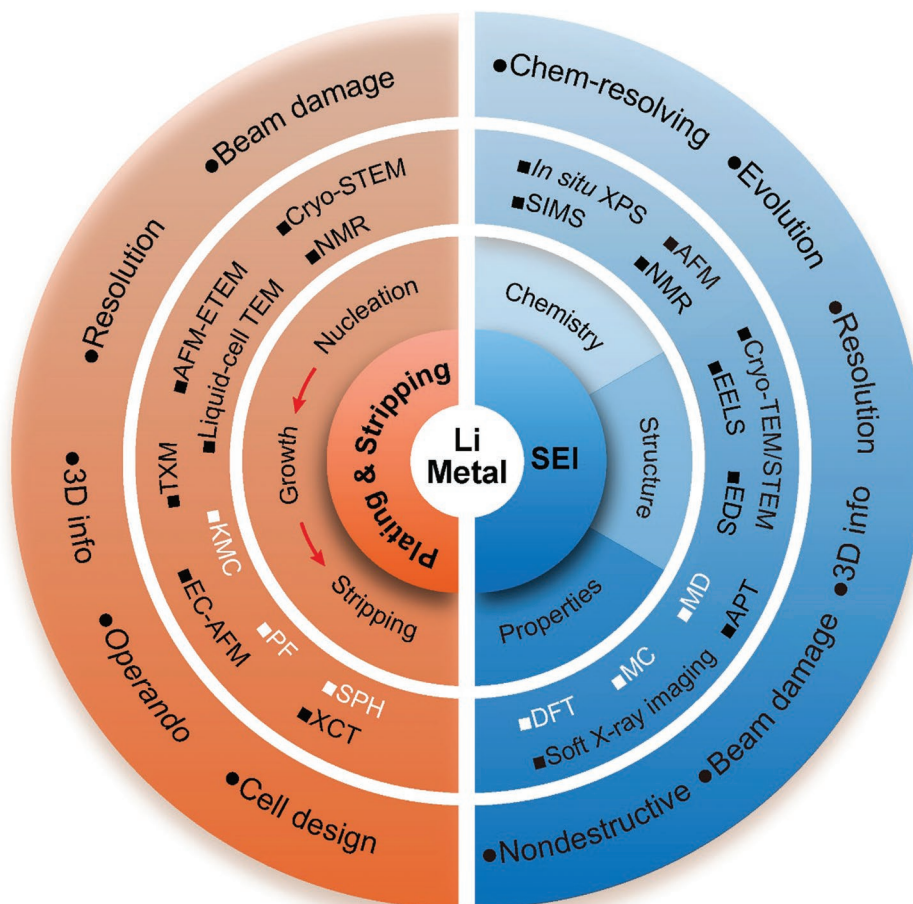
Figure 5. An overview of various characterization and theoretical techniques and their corresponding requirements for investigating the mechanisms of Li plating/stripping and SEI formation.
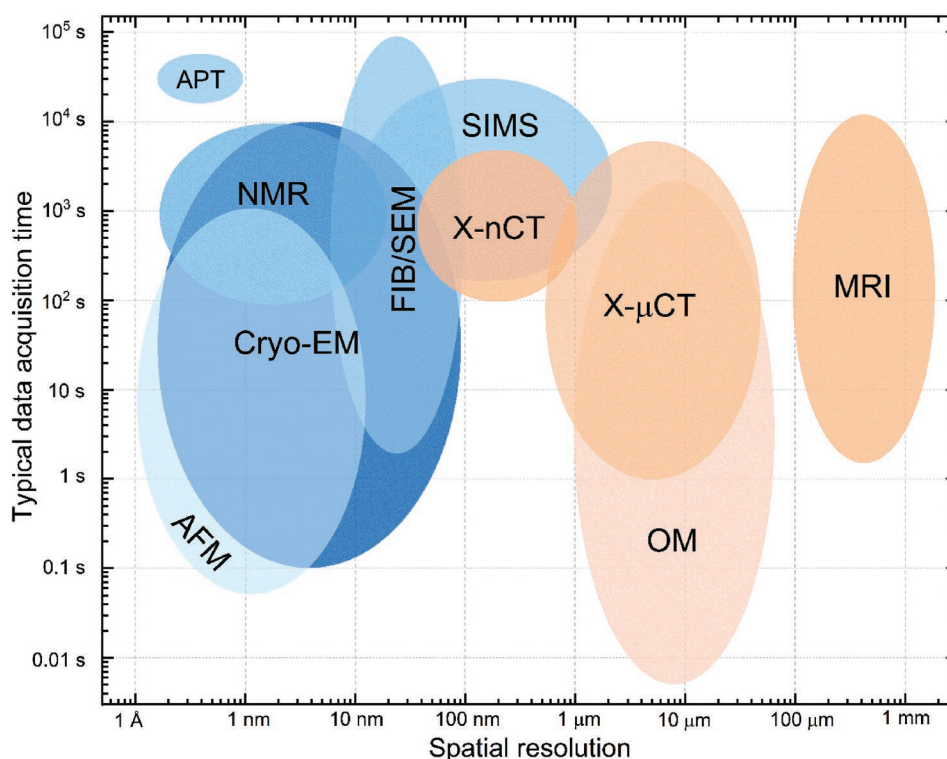
Figure 6. An overview of characterization methods for understanding Li deposition and SEI formation on various spatial and temporal scales. Characterization techniques that have chemical resolving ability are marked in blue, while others are highlighted in orange. X-nCT and X-μCT denote for X-ray computer tomography on nano- and micrometer-scale, respectively.

the corresponding limitations and challenges. On this basis, this section focuses on the future perspectives regarding the fundamental research related to Li deposition and SEI.

4.1. Li Dendrite and SEI Formation Avoidable?

Intrinsically, Li dendrite formation is thermodynamically unavoidable and can only be slowed down kinetically. The utmost external factor determining the morphology of Li deposition is the SEI layer. The formation of SEI is derived from the electro-/chemical reactions between Li metal and electrolyte. Li metal has the lowest redox potential and can theoretically react chemically with almost all organic electrolytes. Also, Li metal is extremely sensitive to oxygen and moisture, and is highly susceptible to chemical reactions. It is difficult to eliminate the reaction between lithium metal and electrolyte fundamentally from thermodynamics. Especially during the charging and discharging process, the inflow and outflow of electrons will further intensify the reaction. An effective solution is to kinetically stop the reaction from taking place. This design idea is especially important for solid electrolytes. It is well known that the bottleneck of solid electrolytes is ionic conductivity. Although a high ionic conductivity facilitates the transport of Li-ions, fast solid conductors tend to be chemically reactive and have difficulty to form stable SEI interfaces. Stable solid electrolytes, however, tend to have too low ion conductivity, which affects their use. From the perspective of rational design, breaking the above linear relationship may be an effective solution.

4.2. Characterization Methods for Monitoring Li Deposition/Dissolution and Probing SEI

Every characterization method has its pros and cons and thus has some limitations. Therefore, complementary characterization involving both in and ex situ spectroscopic and microscopic probes are required in order to gain a comprehensive understanding of the electrochemical behavior of Li metal and the SEI layer thereon (**Figure 6**).

In terms of Li plating and stripping, operando studies have been proven to be the optimal means to explore the dynamic evolution of Li deposits. Multimodal characterization techniques especially methods with different spatial resolutions should be combined, in order to uncover the whole process of Li plating and stripping from the initial nucleation, growth, and dissolution. We emphasize that more attention should be drawn on Li stripping and the re-deposition, which play important roles during the long-term operation of LMBs but are relatively less explored than plating. In addition, since conventional characterization tools are generally infeasible to probe the buried interphases as well as the bulk electrodes/electrolytes in SSBs due to limited penetration depth, 3D characterization methods like XCT, FIB-SEM, and SIMS are anticipated to play important roles in uncovering the interfacial, structural, and mechanical degradation in the bulk and/or at the interphases from millimeter- to nanometer-scale.

Regarding the SEI layer, in situ analyses are essential to acquire reliable information, considering that the SEI layer is generally sensitive to air and moisture and its structure

and chemistry are prone to be altered during sample preparation and transfer. Moreover, an operando mode that is able to monitor the evolution of SEI would be invaluable to obtain in-depth insights into the formation of SEI. In addition, irradiation damages from various beams, for example, electrons, ions, and X-rays, are non-negligible and should be well controlled and suppressed. On this basis, analysis tools that offer nanometer-scale resolution and are operated under cryogenic conditions like cryo-EM[129] are ideal analytical tools for investigating the SEI layer and thus will continue to play an important role. Moreover, spectroscopic techniques like EDX and EELS[130] will be indispensable to help determine the local elemental distribution and chemistry correlated to the local nanostructures.

4.3. Multiscale Simulation of Li Deposition and SEI Formation

Theoretical computation and simulation methods are rather undeveloped for interpreting the processes related to Li deposition and SEI formation, given the fundamental physical- and chemical principles of these processes are not well established. Just a few theoretical methods have been developed based on certain mathematic and physical models, and each can only reveal very partial information on a limited spatial and temporal scale.

Among the theoretical methods, DFT- and MD-based computations are commonly used for revealing the thermodynamics and physicochemical properties of the SEI layer, while KMC, SPH, and PF are suitable to simulate the Li deposition behaviors. Multiscale simulation (**Figure 7**) is required to ensure complementariness and obtain a more comprehensive understanding of the chemical and structural evolution of both Li deposition and SEI formation. The reliability of the results shall be further validated with experiments.

- Quantum mechanical (QM) calculation based on the DFT method obtains potential energy function. It can be used to calculate the reaction potential energy surface and the physical and chemical properties of materials in the SEI.
- AIMD generates finite-temperature dynamical trajectories and thus allows chemical bond breaking and forming events to occur and accounts for electronic polarization effects.
- HAIR enables simulations of the initial chemical reactions related to SEI formation, which may take up to 1 ns, far too long for AIMD. The AIMD part of HAIR can describe the localized electrochemical reactions accurately, while ReaxFF MD could accelerate chemical reactions and mass transfer with a much more affordable cost while keeping the QM accuracy when the force field parameter is well trained.
- MC methods, as a widespread class of computational algorithms that depend on repeated random sampling to obtain numerical value, are often applied to solve unsolvable physical and mathematical problems. The side reactions and ion diffusion in the charge and discharge process may be simulated by the constant voltage simulation method based on GCMC to observe the gradual formation process of SEI film with the increase of cycles.
- PF substitutes boundary conditions at the interface of Li dendrite growth by a partial differential equation for the evolution of an auxiliary field (the phase-field) that takes the role of an order parameter. This model equation is extremely complex. Now PF has been developed into open-source software such as MOOSE, FiPy, and PRISMS.
- SPH is a computational method used for simulating the mechanics of continuum media and has been used in lithium dendrite growth, based on building mass continuity and mass transport governing equations and solutions. A Lagrangian particle-based SPH model also simulates the cycling lithium dendrite growth in multiscale including time and space.
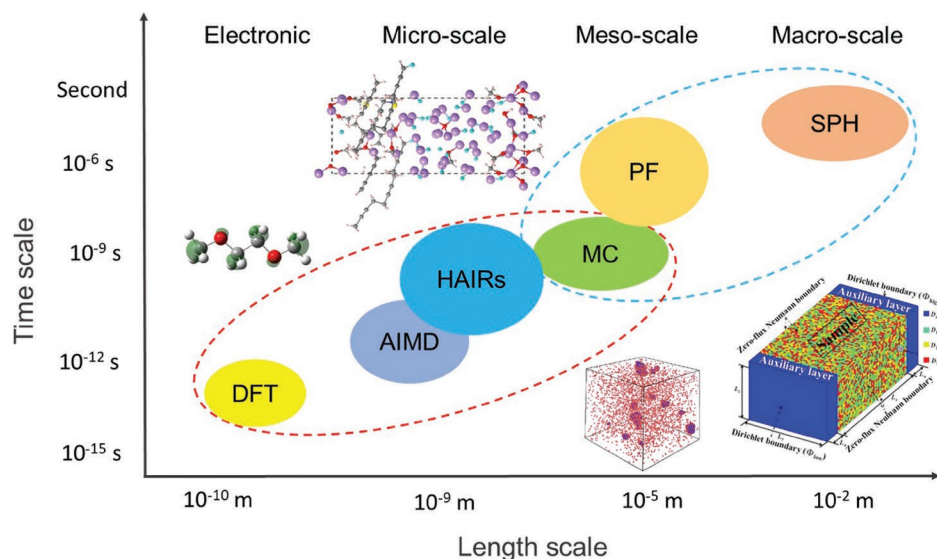
Figure 7. An overview of simulation methods for understanding Li deposition and SEI formation on various spatial and temporal scales. Computation methods for SEI formation are cycled in red, while those for simulation of Li deposition are cycled in blue. Figures of KMC and SPH methods are adopted from Ref. [131] (Reproduced with permission.[131] Copyright 2017, American Physical Society) and Ref. [132] (Reproduced with permission.[132] Copyright 2014, Elsevier), respectively.

4.4. Machine Learning for a Fundamental Understanding of Li Deposition/Dissolution and SEI Evolution, Material Discovery, and Data Analysis

The intersection of multiple disciplines will generate new knowledge. In recent years, machine learning and artificial intelligence have grown increasingly mature. As an effective tool, machine learning is increasingly applied to battery simulation. In the foreseeable future, machine learning methods will also play an active role in understanding dendrite growth and SEI evolution, such as the comprehension of initial reactions and structure of SEI with the help of such technique as graph neural network (GNN) and data-driven automated methodology.[133] Among them, significant progress has been made in spectrum resolution, complex reaction prediction, and material property prediction. These methods will be continuously refined and used for complex, structure resolution and growth mechanism studies, thus, providing a clearer physical picture, which, however, still requires sufficient experimental data to train the algorithm and simulation model. With the increasing understanding of electrolyte structure, reaction interfaces, the ultimate goal is to develop an end-to-end property prediction model that connects atomic structure and device performance, enabling the prediction of important experimental properties, such as CE, directly from microstructure.

Apart from its potential application in first-principles, atomistic and physics-based electrochemical modeling and simulations, machine learning also has great potential in predicting new materials.[134] Compared with the conventional trial-and-error methods for materials research, data-driven machine learning models could remarkably accelerate the discovery of battery materials with targeted properties, such as novel electrolytes and Li electrodes that could enable the formation of a robust and stable SEI and dendrite-free Li plating.[135]

In addition, imaging techniques (e.g., FIB/SEM, XCT, and MRI) often require identifying and extracting complex features/structures from the obtained images during data processing and analysis, namely image segmentation. Classical segmentation methods are often unsuccessful in effectively and accurately distinguishing the boundaries, where there are predominant changes of features/textures but no apparent variations of intensities.[136] Machine learning and deep learning have demonstrated their capability of tackling the challenges related to image segmentation in research on LIBs,[137] and are anticipated to be widely employed to address the Li anode associated issues in the near future.

4.5. Gap and Collaboration between Experimentalist and Theorist

The improvement of the theoretical basis of batteries requires a close combination of experimental and theoretical simulations. Happily, the importance of this combination has now been recognized and some preliminary results are available. However, if further improvement is desired, a closer combination of experiment and theory is needed. It is worth noting that there is still a clear divide between the combination of experimental and theoretical calculations. The device performance can be obtained through experiments which is difficult to do with theoretical simulations. At the same time, theoretical simulations can naturally obtain the atomic structure, which is difficult to do experimentally. The complementariness between the two is also what makes their combination challenging. A combination needs to be found where the two can be combined and iterated on each other. We think that the universal scientific prediction of the theory could be such a combination. Experiments can produce spectroscopic evolution of the SEI and dendrite growth processes. Theoretical simulations can also make predictions of spectroscopy based on the predicted structure and processes. In this way, theory and experiment can be cross-validated at the spectroscopic level. On the one hand, the theoretical model can be optimized iteratively. On the other hand, accurate theoretical models can be reversed to give atomic information for experimental reference. The close cooperation between theory and experiment will be an important driving force for the development of new theories.

5. Conclusion

In this perspective article, we highlight the recent understandings and observations on Li deposition/dissolution and SEI formation, identify the major limitations and open questions during these processes, and provide our perspectives on advanced characterization and theoretical simulation methods to promote more in-depth and comprehensive understanding of these processes. We also give an outlook into the cutting-edge interdisciplinary research topics on Li metal anodes. This article will push beyond the current understanding of Li deposition/dissolution and SEI formation to accelerate the development of Li metal anodes toward their application in practice.

Conflict of Interest

The authors declare no conflict of interest.

[1] a) R. Van Noorden, *Nature* **2014**, *507*, 26; b) M. Armand, J.-M. Tarascon, *Nature* **2008**, *451*, 652.

[2] a) J. Janek, W. Zeier, *Nat. Energy* **2016**, *1*, 16141; b) J. Liu, Z. Bao, Y. Cui, E. J. Dufek, J. B. Goodenough, P. Khalifah, Q. Li, B. Y. Liaw, P. Liu, A. Manthiram, Y. S. Meng, V. R. Subramanian, M. F. Toney, V. V. Viswanathan, M. S. Whittingham, J. Xiao, W. Xu, J. Yang, X.-Q. Yang, J.-G. Zhang, *Nat. Energy* **2019**, *4*, 180.

[3] a) P. G. Bruce, S. A. Freunberger, L. J. Hardwick, J. M. Tarascon, *Nat. Mater.* **2011**, *11*, 19; b) T. Krauskopf, F. H. Richter, W. G. Zeier, J. Janek, *Chem. Rev.* **2020**, *120*, 7745.

[4] X. B. Cheng, R. Zhang, C. Z. Zhao, Q. Zhang, *Chem. Rev.* **2017**, *117*, 10403.

[5] M. S. Whittingham, *Science* **1976**, *192*, 1126.

[6] a) H. Liu, X.-B. Cheng, Z. Jin, R. Zhang, G. Wang, L.-Q. Chen, Q.-B. Liu, J.-Q. Huang, Q. Zhang, *EnergyChem* **2019**, *1*, 100003; b) E. Winter, T. J. Schmidt, S. Trabesinger, *Batteries Supercaps* **2022**, *5*, 202100145.

[7] a) S. Yan, C.-H. Yim, V. Pankov, M. Bauer, E. Baranova, A. Weck, A. Merati, Y. Abu-Lebdeh, *Batteries* **2021**, *7*, 75; b) C. Brissot, M. Rosso, J. N. Chazalviel, P. Baudry, S. Lascaud, *Electrochim. Acta* **1998**, *43*, 1569; c) K. Dong, M. Osenberg, F. Sun, H. Markötter, C. J. Jafta, A. Hilger, T. Arlt, J. Banhart, I. Manke, *Nano Energy* **2019**, *62*, 11.

[8] a) E. Peled, *J. Electrochem. Soc.* **1979**, *126*, 2047; b) D. Aurbach, E. Zinigrad, Y. Cohen, H. Teller, *Solid State Ionics* **2002**, *148*, 405; c) D. Aurbach, B. Markovsky, G. Salitra, E. Markevich, Y. Talyossef, M. Koltypin, L. Nazar, B. Ellis, D. Kovacheva, *J. Power Sources* **2007**, *165*, 491; d) E. Peled, S. Menkin, *J. Electrochem. Soc.* **2017**, *164*, A1703.

[9] F. Liu, R. Xu, Y. Wu, D. T. Boyle, A. Yang, J. Xu, Y. Zhu, Y. Ye, Z. Yu, Z. Zhang, X. Xiao, W. Huang, H. Wang, H. Chen, Y. Cui, *Nature* **2021**, *600*, 659.

[10] G. M. Hobold, J. Lopez, R. Guo, N. Minafra, A. Banerjee, Y. Shirley Meng, Y. Shao-Horn, B. M. Gallant, *Nat. Energy* **2021**, *6*, 951.

[11] J. H. Um, S.-H. Yu, *Adv. Energy Mater.* **2021**, *11*, 2003004.

[12] T. Foroozan, S. Sharifi-Asl, R. Shahbazian-Yassar, *J. Power Sources* **2020**, *461*, 228135.

[13] T. Krauskopf, R. Dippel, H. Hartmann, K. Peppler, B. Mogwitz, F. H. Richter, W. G. Zeier, J. Janek, *Joule* **2019**, *3*, 2030.

[14] A. Kushima, K. P. So, C. Su, P. Bai, N. Kuriyama, T. Maebashi, Y. Fujiwara, M. Z. Bazant, J. Li, *Nano Energy* **2017**, *32*, 271.

[15] a) P. Bai, J. Li, F. R. Brushett, M. Z. Bazant, *Energy Environ. Sci.* **2016**, *9*, 3221; b) K. N. Wood, E. Kazyak, A. F. Chadwick, K. H. Chen, J. G. Zhang, K. Thornton, N. P. Dasgupta, *ACS Cent. Sci.* **2016**, *2*, 790.

[16] Y. Li, Y. Li, A. Pei, K. Yan, Y. Sun, C.-L. Wu, L.-M. Joubert, R. Chin, L. Koh Ai, Y. Yu, J. Perrino, B. Butz, S. Chu, Y. Cui, *Science* **2017**, *358*, 506.

[17] M. J. Zachman, Z. Tu, S. Choudhury, L. A. Archer, L. F. Kourkoutis, *Nature* **2018**, *560*, 345.

[18] X. Li, B. Han, X. Yang, Z. Deng, Y. Zou, X. Shi, L. Wang, Y. Zhao, S. Wu, M. Gu, *iScience* **2021**, *24*, 103418.

[19] B. Han, X. Li, S. Bai, Y. Zou, B. Lu, M. Zhang, X. Ma, Z. Chang, Y. S. Meng, M. Gu, *Matter* **2021**, *4*, 3741.

[20] a) F. Sun, R. Moroni, K. Dong, H. Markötter, D. Zhou, A. Hilger, L. Zielke, R. Zengerle, S. Thiele, J. Banhart, I. Manke, *ACS Energy Lett.* **2017**, *2*, 94; b) D. S. Eastwood, P. M. Bayley, H. J. Chang, O. O. Taiwo, J. Vila-Comamala, D. J. L. Brett, C. Rau, P. J. Withers, P. R. Shearing, C. P. Grey, P. D. Lee, *Chem. Commun.* **2015**, *51*, 266.

[21] C. Fang, J. Li, M. Zhang, Y. Zhang, F. Yang, J. Z. Lee, M.-H. Lee, J. Alvarado, M. A. Schroeder, Y. Yang, B. Lu, N. Williams, M. Ceja, L. Yang, M. Cai, J. Gu, K. Xu, X. Wang, Y. S. Meng, *Nature* **2019**, *572*, 511.

[22] A. Aryanfar, D. Brooks, B. V. Merinov, W. A. Goddard, A. J. Colussi, M. R. Hoffmann, *J. Phys. Chem. Lett.* **2014**, *5*, 1721.

[23] J. Tan, A. Cannon, E. Ryan, *J. Power Sources* **2020**, *463*, 228187.

[24] a) Y. Li, Y. Qi, *Energy Environ. Sci.* **2019**, *12*, 1286; b) Y. Liu, Q. Sun, P. Yu, B. Ma, H. Yang, J. Zhang, X. Mie, T. Cheng, *J. Mater. Chem. A* **2022**, *10*, 632; c) L. E. Camacho-Forero, T. W. Smith, S. Bertolini, P. B. Balbuena, *J. Phys. Chem. C* **2015**, *119*, 26828; d) M. Xie, Y. Wu, Y. Liu, P. P. Yu, R. Jia, W. A. Goddard, T. Cheng, *Mater. Today Energy* **2021**, *21*, 100730; e) D. E. Galvez-Aranda, J. M. Seminario, *J. Phys. Chem. C* **2020**, *124*, 21919; f) C. Yan, L.-L. Jiang, Y.-X. Yao, Y. Lu, J.-Q. Huang, Q. Zhang, *Angew. Chem., Int. Ed.* **2021**, *60*, 8521; g) S. A. Delp, O. Borodin, M. Olguin, C. G. Eisner, J. L. Allen, T. R. Jow, *Electrochim. Acta* **2016**, *209*, 498; h) M. J. Hossain, G. Pawar, B. Liaw, K. L. Gering, E. J. Dufek, A. C. T. van Duin, *J. Chem. Phys.* **2020**, *152*, 184301; i) Y. Liu, Q. Sun, P. Yu, Y. Wu, L. Xu, H. Yang, M. Xie, T. Cheng, W. A. Goddard, *J. Phys. Chem. Lett.* **2021**, *12*, 2922; j) Y. Liu, P. Yu, Y. Wu, H. Yang, M. Xie, L. Huai, W. A. Goddard, T. Cheng, *J. Phys. Chem. Lett.* **2021**, *12*, 1300.

[25] a) J.-N. Chazalviel, *Phys. Rev. A* **1990**, *42*, 7355; b) V. Fleury, J.-N. Chazalviel, M. Rosso, B. Sapoval, *J. Electroanal. Chem. Interfacial Electrochem.* **1990**, *290*, 249.

[26] A. J. Ilott, M. Mohammadi, H. J. Chang, C. P. Grey, A. Jerschow, *Proc. Natl. Acad. Sci. U. S. A.* **2016**, *113*, 10779.

[27] Y. Li, Y. Li, A. Pei, K. Yan, Y. Sun, C. L. Wu, L. M. Joubert, R. Chin, A. L. Koh, Y. Yu, J. Perrino, B. Butz, S. Chu, Y. Cui, *Science* **2017**, *358*, 506.

[28] L. Zhang, T. Yang, C. Du, Q. Liu, Y. Tang, J. Zhao, B. Wang, T. Chen, Y. Sun, P. Jia, H. Li, L. Geng, J. Chen, H. Ye, Z. Wang, Y. Li, H. Sun, X. Li, Q. Dai, Y. Tang, Q. Peng, T. Shen, S. Zhang, T. Zhu, J. Huang, *Nat. Nanotechnol.* **2020**, *15*, 94.

[29] Y. Han, Y. Jie, F. Huang, Y. Chen, Z. Lei, G. Zhang, X. Ren, L. Qin, R. Cao, S. Jiao, *Adv. Funct. Mater.* **2019**, *29*, 1904629.

[30] Y. Zhou, M. Su, X. Yu, Y. Zhang, J. G. Wang, X. Ren, R. Cao, W. Xu, D. R. Baer, Y. Du, O. Borodin, Y. Wang, X. L. Wang, K. Xu, Z. Xu, C. Wang, Z. Zhu, *Nat. Nanotechnol.* **2020**, *15*, 224.

[31] M. A. Hope, B. L. D. Rinkel, A. B. Gunnarsdóttir, K. Märker, S. Menkin, S. Paul, I. V. Sergeyev, C. P. Grey, *Nat. Commun.* **2020**, *11*, 2224.

[32] N. Takenaka, Y. Suzuki, H. Sakai, M. Nagaoka, *J. Phys. Chem. C* **2014**, *118*, 10874.

[33] G. Yoon, S. Moon, G. Ceder, K. Kang, *Chem. Mater.* **2018**, *30*, 6769.

[34] A. Aryanfar, D. M. Saad, W. A. GoddardIii, *Comput. Mater. Sci.* **2021**, *187*, 110059.

[35] a) J. Zheng, M. S. Kim, Z. Tu, S. Choudhury, T. Tang, L. A. Archer, *Chem. Soc. Rev.* **2020**, *49*, 2701; b) X. Zhang, A. Wang, X. Liu, J. Luo, *Acc. Chem. Res.* **2019**, *52*, 3223.

[36] D. Wang, W. Zhang, W. Zheng, X. Cui, T. Rojo, Q. Zhang, *Adv. Sci.* **2017**, *4*, 1600168.

[37] E. Cha, J. H. Yun, R. Ponraj, D. K. Kim, *Mater. Chem. Front.* **2021**, *5*, 6294.

[38] G. Jiang, F. Li, H. Wang, M. Wu, S. Qi, X. Liu, S. Yang, J. Ma, *Small Struct.* **2021**, *2*, 2000122.

[39] a) C. Wang, A. Wang, L. Ren, X. Guan, D. Wang, A. Dong, C. Zhang, G. Li, J. Luo, *Adv. Funct. Mater.* **2019**, *29*, 1905940; b) S. Park, H.-J. Jin, Y. S. Yun, *Adv. Mater.* **2020**, *32*, 2002193.

[40] Q. Lu, Y. Jie, X. Meng, A. Omar, D. Mikhailova, R. Cao, S. Jiao, Y. Lu, Y. Xu, *Carbon Energy* **2021**, *3*, 957.

[41] W. Liu, D. Lin, A. Pei, Y. Cui, *J. Am. Chem. Soc.* **2016**, *138*, 15443.

[42] F. Ding, W. Xu, G. L. Graff, J. Zhang, M. L. Sushko, X. Chen, Y. Shao, M. H. Engelhard, Z. Nie, J. Xiao, X. Liu, P. V. Sushko, J. Liu, J.-G. Zhang, *J. Am. Chem. Soc.* **2013**, *135*, 4450.

[43] X.-B. Cheng, M.-Q. Zhao, C. Chen, A. Pentecost, K. Maleski, T. Mathis, X.-Q. Zhang, Q. Zhang, J. Jiang, Y. Gogotsi, *Nat. Commun.* **2017**, *8*, 336.

[44] P. Zhai, L. Liu, X. Gu, T. Wang, Y. Gong, *Adv. Energy Mater.* **2020**, *10*, 2001257.

ADVANCED
SCIENCE NEWS

www.advancedsciencenews.com

ADVANCED
ENERGY
MATERIALS

www.advenergymat.de

[45] R. Xu, X.-B. Cheng, C. Yan, X.-Q. Zhang, Y. Xiao, C.-Z. Zhao, J.-Q. Huang, Q. Zhang, *Matter* **2019**, *1*, 317.

[46] J.-F. Ding, R. Xu, C. Yan, B.-Q. Li, H. Yuan, J.-Q. Huang, *J. Energy Chem.* **2021**, *59*, 306.

[47] M. Winter, *Z. Phys. Chem.* **2009**, *223*, 1395.

[48] a) B. Li, Y. Wang, S. Yang, *Adv. Energy Mater.* **2018**, *8*, 1702296; b) B. Liu, J.-G. Zhang, W. Xu, *Joule* **2018**, *2*, 833; c) W. Xu, J. Wang, F. Ding, X. Chen, E. Nasybulin, Y. Zhang, J.-G. Zhang, *Energy Environ. Sci.* **2014**, *7*, 513; d) H. Kim, G. Jeong, Y. U. Kim, J. H. Kim, C. M. Park, H. J. Sohn, *Chem. Soc. Rev.* **2013**, *42*, 9011; e) D. Lin, Y. Liu, Y. Cui, *Nat. Nanotechnol.* **2017**, *12*, 194; f) B. Horstmann, J. Shi, R. Amine, M. Werres, X. He, H. Jia, F. Hausen, I. Cekic-Laskovic, S. Wiemers-Meyer, J. Lopez, D. Galvez-Aranda, F. Baakes, D. Bresser, C.-C. Su, Y. Xu, W. Xu, P. Jakes, R.-A. Eichel, E. Figgemeier, U. Krewer, J. M. Seminario, P. B. Balbuena, C. Wang, S. Passerini, Y. Shao-Horn, M. Winter, K. Amine, R. Kostecki, A. Latz, *Energy Environ. Sci.* **2021**, *14*, 5289; g) D.-H. Liu, Z. Bai, M. Li, A. Yu, D. Luo, W. Liu, L. Yang, J. Lu, K. Amine, Z. Chen, *Chem. Soc. Rev.* **2020**, *49*, 5407; h) P. Albertus, V. Anandan, C. Ban, N. Balsara, I. Belharouak, J. Buettner-Garrett, Z. Chen, C. Daniel, M. Doeff, N. J. Dudney, B. Dunn, S. J. Harris, S. Herle, E. Herbert, S. Kalnaus, J. A. Libera, D. Lu, S. Martin, B. D. McCloskey, M. T. McDowell, Y. S. Meng, J. Nanda, J. Sakamoto, E. C. Self, S. Tepavcevic, E. Wachsman, C. Wang, A. S. Westover, J. Xiao, T. Yersak, *ACS Energy Lett.* **2021**, *6*, 1399; i) Y. Zhang, T.-T. Zuo, J. Popovic, K. Lim, Y.-X. Yin, J. Maier, Y.-G. Guo, *Mater. Today* **2020**, *33*, 56.

[49] a) X. Gao, Y.-N. Zhou, D. Han, J. Zhou, D. Zhou, W. Tang, J. B. Goodenough, *Joule* **2020**, *4*, 1864; b) H. Wu, H. Jia, C. Wang, J.-G. Zhang, W. Xu, *Adv. Energy Mater.* **2021**, *11*, 2003092; c) K. N. Wood, M. Noked, N. P. Dasgupta, *ACS Energy Lett.* **2017**, *2*, 664.

[50] C.-C. Su, M. He, J. Shi, R. Amine, J. Zhang, K. Amine, *Angew. Chem., Int. Ed.* **2020**, *59*, 18229.

[51] a) J. Ming, Z. Cao, W. Wahyudi, M. Li, P. Kumar, Y. Wu, J.-Y. Hwang, M. N. Hedhili, L. Cavallo, Y.-K. Sun, L.-J. Li, *ACS Energy Lett.* **2018**, *3*, 335; b) W. Wahyudi, V. Ladelta, L. Tsetseris, M. M. Alsabban, X. Guo, E. Yengel, H. Faber, B. Adilbekova, A. Seitkhan, A.-H. Emwas, M. N. Hedhili, L.-J. Li, V. Tung, N. Hadjichristidis, T. D. Anthopoulos, J. Ming, *Adv. Funct. Mater.* **2021**, *31*, 2101593; c) J. Holoubek, H. Liu, Z. Wu, Y. Yin, X. Xing, G. Cai, S. Yu, H. Zhou, T. A. Pascal, Z. Chen, P. Liu, *Nat. Energy* **2021**, *6*, 303; d) S. H. Lee, J.-Y. Hwang, J. Ming, Z. Cao, H. A. Nguyen, H.-G. Jung, J. Kim, Y.-K. Sun, *Adv. Energy Mater.* **2020**, *10*, 2000567.

[52] H. Cheng, Q. Sun, L. Li, Y. Zou, Y. Wang, T. Cai, F. Zhao, G. Liu, Z. Ma, W. Wahyudi, Q. Li, J. Ming, *ACS Energy Lett.* **2022**, *7*, 490.

[53] J. Zhang, Z. Cao, L. Zhou, G. Liu, G.-T. Park, L. Cavallo, L. Wang, H. N. Alshareef, Y.-K. Sun, J. Ming, *ACS Energy Lett.* **2020**, *5*, 2651.

[54] A. Khaleghi, S. M. Sadrameli, M. Manteghian, *Rev. Inorg. Chem.* **2020**, *40*, 167.

[55] X. Chen, X.-R. Chen, T.-Z. Hou, B.-Q. Li, X.-B. Cheng, R. Zhang, Q. Zhang, *Sci. Adv.* **2019**, *5*, eaau7728.

[56] L. Sun, G. Yuan, L. Gao, J. Yang, M. Chhowalla, M. H. Gharahcheshmeh, K. K. Gleason, Y. S. Choi, B. H. Hong, Z. Liu, *Nat. Rev. Methods Primers* **2021**, *1*, 5.

[57] S. M. George, *Chem. Rev.* **2010**, *110*, 111.

[58] S. A. Vasudevan, Y. Xu, S. Karwal, H. G. M. E. van Ostaay, G. M. H. Meesters, M. Talebi, E. J. R. Sudhölter, J. Ruud van Ommen, *Chem. Commun.* **2015**, *51*, 12540.

[59] B. Jin, Z. Liu, R. Tang, *CrystEngComm* **2020**, *22*, 4057.

[60] K. Cao, J. Biskupek, C. T. Stoppiello, R. L. McSweeney, T. W. Chamberlain, Z. Liu, K. Suenaga, S. T. Skowron, E. Besley, A. N. Khlobystov, U. Kaiser, *Nat. Chem.* **2020**, *12*, 921.

[61] a) X.-R. Chen, B.-C. Zhao, C. Yan, Q. Zhang, *Adv. Mater.* **2021**, *33*, 2004128; b) X. Guan, A. Wang, S. Liu, G. Li, F. Liang, Y.-W. Yang, X. Liu, J. Luo, *Small* **2018**, *14*, 1801423.

[62] a) Y. Xu, A. S. Menon, P. P. R. M. L. Harks, D. C. Hermes, L. A. Haverkate, S. Unnikrishnan, F. M. Mulder, *Energy Storage Mater.* **2018**, *12*, 69; b) K. Dong, Y. Xu, J. Tan, M. Osenberg, F. Sun, Z. Kochovski, D. T. Pham, S. Mei, A. Hilger, E. Ryan, Y. Lu, J. Banhart, I. Manke, *ACS Energy Lett.* **2021**, *6*, 1719; c) W. Liu, P. Liu, D. Mitlin, *Chem. Soc. Rev.* **2020**, *49*, 7284.

[63] a) F. Shi, A. Pei, A. Vailionis, J. Xie, B. Liu, J. Zhao, Y. Gong, Y. Cui, *Proc. Natl. Acad. Sci. USA* **2017**, *114*, 12138; b) A. Pei, G. Zheng, F. Shi, Y. Li, Y. Cui, *Nano Lett.* **2017**, *17*, 1132.

[64] X.-B. Cheng, R. Zhang, C.-Z. Zhao, F. Wei, J.-G. Zhang, Q. Zhang, *Adv. Sci.* **2016**, *3*, 1500213.

[65] J. Wang, W. Huang, A. Pei, Y. Li, F. Shi, X. Yu, Y. Cui, *Nat. Energy* **2019**, *4*, 664.

[66] a) J.-M. Doux, H. Nguyen, D. H. S. Tan, A. Banerjee, X. Wang, E. A. Wu, C. Jo, H. Yang, Y. S. Meng, *Adv. Energy Mater.* **2020**, *10*, 1903253; b) C. Fang, B. Lu, G. Pawar, M. Zhang, D. Cheng, S. Chen, M. Ceja, J.-M. Doux, H. Musrock, M. Cai, B. Liaw, Y. S. Meng, *Nat. Energy* **2021**, *6*, 987; c) J. Kasemchainan, S. Zekoll, D. S. Jolly, Z. Ning, G. O. Hartley, J. Marrow, P. G. Bruce, *Nat. Mater.* **2019**, *18*, 1105.

[67] W. Li, H. Zheng, G. Chu, F. Luo, J. Zheng, D. Xiao, X. Li, L. Gu, H. Li, X. Wei, Q. Chen, L. Chen, *Faraday Discuss.* **2014**, *176*, 109.

[68] Q. Zhao, S. Stalin, C.-Z. Zhao, L. A. Archer, *Nat. Rev. Mater.* **2020**, *5*, 229.

[69] J. C. Bachman, S. Muy, A. Grimaud, H.-H. Chang, N. Pour, S. F. Lux, O. Paschos, F. Maglia, S. Lupart, P. Lamp, L. Giordano, Y. Shao-Horn, *Chem. Rev.* **2016**, *116*, 140.

[70] Y. Chen, Y. Jiang, S.-S. Chi, H. J. Woo, K. Yu, J. Ma, J. Wang, C. Wang, Y. Deng, *J. Power Sources* **2022**, *521*, 230921.

[71] M. Hou, F. Liang, K. Chen, Y. Dai, D. Xue, *Nanotechnology* **2020**, *31*, 132003.

[72] C. Wang, K. Adair, X. Sun, *Acc. Mater. Res.* **2022**, *3*, 21.

[73] L. Zhou, N. Minafra, W. G. Zeier, L. F. Nazar, *Acc. Chem. Res.* **2021**, *54*, 2717.

[74] X. Li, J. Liang, X. Yang, K. R. Adair, C. Wang, F. Zhao, X. Sun, *Energy Environ. Sci.* **2020**, *13*, 1429.

[75] R. Mohtadi, *Molecules* **2020**, *25*, 1791.

[76] S. Xia, X. Wu, Z. Zhang, Y. Cui, W. Liu, *Chem* **2019**, *5*, 753.

[77] F. Sun, K. Dong, M. Osenberg, A. Hilger, S. Risse, Y. Lu, P. H. Kamm, M. Klaus, H. Markötter, F. García-Moreno, T. Arlt, I. Manke, *J. Mater. Chem. A* **2018**, *6*, 22489.

[78] Q. Tu, L. Barroso-Luque, T. Shi, G. Ceder, *Cell Rep. Phys. Sci.* **2020**, *1*, 100106.

[79] Z. Yu, X. Zhang, C. Fu, H. Wang, M. Chen, G. Yin, H. Huo, J. Wang, *Adv. Energy Mater.* **2021**, *11*, 2003250.

[80] D. Cao, X. Sun, Q. Li, A. Natan, P. Xiang, H. Zhu, *Matter* **2020**, *3*, 57.

[81] T. Swamy, R. Park, B. W. Sheldon, D. Rettenwander, L. Porz, S. Berendts, R. Uecker, W. C. Carter, Y.-M. Chiang, *J. Electrochem. Soc.* **2018**, *165*, A3648.

[82] J. A. Lewis, J. Tippens, F. J. Q. Cortes, M. T. McDowell, *Trend. Chem.* **2019**, *1*, 845.

[83] Y.-G. Lee, S. Fujiki, C. Jung, N. Suzuki, N. Yashiro, R. Omoda, D.-S. Ko, T. Shiratsuchi, T. Sugimoto, S. Ryu, J. H. Ku, T. Watanabe, Y. Park, Y. Aihara, D. Im, I. T. Han, *Nat. Energy* **2020**, *5*, 299.

[84] a) M. B. Dixit, N. Singh, J. P. Horwath, P. D. Shevchenko, M. Jones, E. A. Stach, T. S. Arthur, K. B. Hatzell, *Matter* **2020**, *3*, 2138; b) K. Borzutzki, K. Dong, J. R. Nair, B. Wolff, F. Hausen, R.-A. Eichel, M. Winter, I. Manke, G. Brunklaus, *Cell Rep. Phys. Sci.* **2021**, *2*, 100496.

[85] M. Nagao, A. Hayashi, M. Tatsumisago, T. Kanetsuku, T. Tsuda, S. Kuwabata, *Phys. Chem. Chem. Phys.* **2013**, *15*, 18600.

[86] J.-H. Cheng, A. A. Assegie, C.-J. Huang, M.-H. Lin, A. M. Tripathi, C.-C. Wang, M.-T. Tang, Y.-F. Song, W.-N. Su, B. J. Hwang, *J. Phys. Chem. C* **2017**, *121*, 7761.

2200398 (18 of 22)

[87] a) L. Zhang, T. Yang, C. Du, Q. Liu, Y. Tang, J. Zhao, B. Wang, T. Chen, Y. Sun, P. Jia, H. Li, L. Geng, J. Chen, H. Ye, Z. Wang, Y. Li, H. Sun, X. Li, Q. Dai, Y. Tang, Q. Peng, T. Shen, S. Zhang, T. Zhu, J. Huang, *Nat. Nanotechnol.* **2020**, *15*, 94; b) Y. He, X. Ren, Y. Xu, M. H. Engelhard, X. Li, J. Xiao, J. Liu, J.-G. Zhang, W. Xu, C. Wang, *Nat. Nanotechnol.* **2019**, *14*, 1042.

[88] a) V. M. Fokin, E. D. Zanotto, J. W. P. Schmelzer, *J. Non-Cryst. Solids* **2010**, *356*, 2185; b) L. Bosetti, B. Ahn, M. Mazzotti, *Cryst. Growth Des.* **2022**, *22*, 87.

[89] P. Biswal, A. Kludze, J. Rodrigues, Y. Deng, T. Moon, S. Stalin, Q. Zhao, J. Yin, L. F. Kourkoutis, L. A. Archer, *Proc. Natl. Acad. Sci. USA* **2021**, *118*, e2012071118.

[90] Z. Kochovski, G. Chen, J. Yuan, Y. Lu, *Colloid Polym. Sci.* **2020**, *298*, 707.

[91] B. Meng, W. H. Weinberg, *Surf. Sci.* **1996**, *364*, 151.

[92] a) Z. Hong, V. Viswanathan, *ACS Energy Lett.* **2018**, *3*, 1737; b) Z. Hong, V. Viswanathan, *ACS Energy Lett.* **2020**, *5*, 3254.

[93] a) J. Tan, E. M. Ryan, *Int. J. Energy Res.* **2016**, *40*, 1800; b) J. Tan, A. M. Tartakovsky, K. Ferris, E. M. Ryan, *J. Electrochem. Soc.* **2015**, *163*, A318; c) J. Tan, E. M. Ryan, *J. Power Sources* **2016**, *323*, 67; d) E. M. Ryan, K. Ferris, A. Tartakovsky, M. Khaleel, *ECS Trans.* **2013**, *45*, 123.

[94] a) F. Ding, W. Xu, X. Chen, J. Zhang, M. H. Engelhard, Y. Zhang, B. R. Johnson, J. V. Crum, T. A. Blake, X. Liu, *J. Electrochem. Soc.* **2013**, *160*, A1894; b) Y. Jie, X. Ren, R. Cao, W. Cai, S. Jiao, *Adv. Funct. Mater.* **2020**, *30*, 1910777; c) X. Ren, P. Gao, L. Zou, S. Jiao, X. Cao, X. Zhang, H. Jia, M. H. Engelhard, B. E. Matthews, H. Wu, H. Lee, C. Niu, C. Wang, B. W. Arey, J. Xiao, J. Liu, J.-G. Zhang, W. Xu, *Proc. Natl. Acad. Sci. USA* **2020**, *117*, 28603; d) Q. Wang, Z. Yao, C. Zhao, T. Verhallen, D. P. Tabor, M. Liu, F. Ooms, F. Kang, A. Aspuru-Guzik, Y.-S. Hu, M. Wagemaker, B. Li, *Nat. Commun.* **2020**, *11*, 4188; e) G. G. Eshetu, X. Judez, C. Li, M. Martinez-Ibañez, I. Gracia, O. Bondarchuk, J. Carrasco, L. M. Rodriguez-Martinez, H. Zhang, M. Armand, *J. Am. Chem. Soc.* **2018**, *140*, 9921; f) S. Jiao, X. Ren, R. Cao, M. H. Engelhard, Y. Liu, D. Hu, D. Mei, J. Zheng, W. Zhao, Q. Li, N. Liu, B. D. Adams, C. Ma, J. Liu, J.-G. Zhang, W. Xu, *Nat. Energy* **2018**, *3*, 739.

[95] a) R. Weber, M. Genovese, A. J. Louli, S. Hames, C. Martin, I. G. Hill, J. R. Dahn, *Nat. Energy* **2019**, *4*, 683; b) D. Lin, Y. Liu, Y. Li, Y. Li, A. Pei, J. Xie, W. Huang, Y. Cui, *Nat. Chem.* **2019**, *11*, 382; c) K. N. Wood, K. X. Steirer, S. E. Hafner, C. Ban, S. Santhanagopalan, S.-H. Lee, G. Teeter, *Nat. Commun.* **2018**, *9*, 2490; d) J. E. Morales-Ugarte, A. Benayad, C. C. Santini, R. Bouchet, *ACS Appl. Mater. Interfaces* **2019**, *11*, 21955; e) A. Etxebarria, D.-J. Yun, M. Blum, Y. Ye, M. Sun, K.-J. Lee, H. Su, M. Á. Muñoz-Márquez, P. N. Ross, E. J. Crumlin, *ACS Appl. Mater. Interfaces* **2020**, *12*, 26607.

[96] a) E. Markevich, G. Salitra, F. Chesneau, M. Schmidt, D. Aurbach, *ACS Energy Lett.* **2017**, *2*, 1321; b) D. Aurbach, M. Daroux, P. Faguy, E. Yeager, *J. Electrochem. Soc.* **1987**, *134*, 1611; c) D. Aurbach, O. Chusid, *J. Electrochem. Soc.* **1993**, *140*, L1; d) D. Aurbach, E. Granot, *Electrochim. Acta* **1997**, *42*, 697; e) Y. Gofer, M. Ben-Zion, D. Aurbach, *J. Power Sources* **1992**, *39*, 163.

[97] S. Menkin, C. A. O'Keefe, A. B. Gunnarsdóttir, S. Dey, F. M. Pesci, Z. Shen, A. Aguadero, C. P. Grey, *J. Phys. Chem. C* **2021**, *125*, 16719.

[98] a) C. Fiedler, B. Luerssen, M. Rohnke, J. Sann, J. Janek, *J. Electrochem. Soc.* **2017**, *164*, A3742; b) W. Li, U.-H. Kim, A. Dolocan, Y.-K. Sun, A. Manthiram, *ACS Nano* **2017**, *11*, 5853.

[99] a) X. Fan, L. Chen, X. Ji, T. Deng, S. Hou, J. Chen, J. Zheng, F. Wang, J. Jiang, K. Xu, C. Wang, *Chem* **2018**, *4*, 174; b) L. Suo, W. Xue, M. Gobet, S. G. Greenbaum, C. Wang, Y. Chen, W. Yang, Y. Li, J. Li, *Proc. Natl. Acad. Sci. USA* **2018**, *115*, 1156; c) Z. Shadike, H. Lee, O. Borodin, X. Cao, X. Fan, X. Wang, R. Lin, S.-M. Bak, S. Ghose, K. Xu, C. Wang, J. Liu, J. Xiao, X.-Q. Yang, E. Hu, *Nat. Nanotechnol.* **2021**, *16*, 549; d) M. He, R. Guo, G. M. Hobold, H. Gao, B. M. Gallant, *Proc. Natl. Acad. Sci. USA* **2020**, *117*, 73.

[100] a) Y. Li, Y. Li, A. Pei, K. Yan, Y. Sun, C.-L. Wu, L.-M. Joubert, R. Chin, A. L. Koh, Y. Yu, J. Perrino, B. Butz, S. Chu, Y. Cui, *Science* **2017**, *358*, 506; b) D. T. Boyle, W. Huang, H. Wang, Y. Li, H. Chen, Z. Yu, W. Zhang, Z. Bao, Y. Cui, *Nat. Energy* **2021**, *6*, 487; c) X. Wang, M. Zhang, J. Alvarado, S. Wang, M. Sina, B. Lu, J. Bouwer, W. Xu, J. Xiao, J.-G. Zhang, J. Liu, Y. S. Meng, *Nano Lett.* **2017**, *17*, 7606; d) Y. Li, W. Huang, Y. Li, A. Pei, D. T. Boyle, Y. Cui, *Joule* **2018**, *2*, 2167; e) B. Han, Z. Zhang, Y. Zou, K. Xu, G. Xu, H. Wang, H. Meng, Y. Deng, J. Li, M. Gu, *Adv. Mater.* **2021**, *33*, 2100404.

[101] N. Brodusch, R. Gauvin, *Microsc. Microanal.* **2021**, *27*, 1318.

[102] C. Fang, J. Lau, D. Hubble, P. Khomein, E. A. Dailing, Y. Liu, G. Liu, *Joule* **2021**, *5*, 415.

[103] D. Cheng, T. A. Wynn, X. Wang, S. Wang, M. Zhang, R. Shimizu, S. Bai, H. Nguyen, C. Fang, M.-c. Kim, W. Li, B. Lu, S. J. Kim, Y. S. Meng, *Joule* **2020**, *4*, 2484.

[104] Z. Zhang, Y. Li, R. Xu, W. Zhou, Y. Li, T. Oyakhire Solomon, Y. Wu, J. Xu, H. Wang, Z. Yu, T. Boyle David, W. Huang, Y. Ye, H. Chen, J. Wan, Z. Bao, W. Chiu, Y. Cui, *Science* **2022**, *375*, 66.

[105] a) Z. Yu, H. Wang, X. Kong, W. Huang, Y. Tsao, D. G. Mackanic, K. Wang, X. Wang, W. Huang, S. Choudhury, Y. Zheng, C. V. Amanchukwu, S. T. Hung, Y. Ma, E. G. Lomeli, J. Qin, Y. Cui, Z. Bao, *Nat. Energy* **2020**, *5*, 526; b) Z. Yu, P. E. Rudnicki, Z. Zhang, Z. Huang, H. Celik, S. T. Oyakhire, Y. Chen, X. Kong, S. C. Kim, X. Xiao, H. Wang, Y. Zheng, G. A. Kamat, M. S. Kim, S. F. Bent, J. Qin, Y. Cui, Z. Bao, *Nat. Energy* **2022**, *7*, 94; c) A. J. Louli, A. Eldesoky, R. Weber, M. Genovese, M. Coon, J. deGooyer, Z. Deng, R. T. White, J. Lee, T. Rodgers, R. Petibon, S. Hy, S. J. H. Cheng, J. R. Dahn, *Nat. Energy* **2020**, *5*, 693; d) X. Fan, L. Chen, O. Borodin, X. Ji, J. Chen, S. Hou, T. Deng, J. Zheng, C. Yang, S.-C. Liou, K. Amine, K. Xu, C. Wang, *Nat. Nanotechnol.* **2018**, *13*, 715; e) X. Wang, G. Pawar, Y. Li, X. Ren, M. Zhang, B. Lu, A. Banerjee, P. Liu, E. J. Dufek, J.-G. Zhang, J. Xiao, J. Liu, Y. S. Meng, B. Liaw, *Nat. Mater.* **2020**, *19*, 1339.

[106] a) J. Xie, L. Liao, Y. Gong, Y. Li, F. Shi, A. Pei, J. Sun, R. Zhang, B. Kong, R. Subbaraman, J. Christensen, Y. Cui, *Sci. Adv.* **2017**, *3*, eaao3170; b) Y. Liu, D. Lin, Y. Li, G. Chen, A. Pei, O. Nix, Y. Li, Y. Cui, *Nat. Commun.* **2018**, *9*, 3656; c) Y. Gao, Z. Yan, J. L. Gray, X. He, D. Wang, T. Chen, Q. Huang, Y. C. Li, H. Wang, S. H. Kim, T. E. Mallouk, D. Wang, *Nat. Mater.* **2019**, *18*, 384.

[107] a) I. Yoon, S. Jurng, D. P. Abraham, B. L. Lucht, P. R. Guduru, *Nano Lett.* **2018**, *18*, 5752; b) K.-i. Morigaki, A. Ohta, *J. Power Sources* **1998**, *76*, 159; c) 揭. 李. 陈. 曹. 章. 焦. 黄凡洋, 物理化学学报 **2021**, *37*, 2008081.

[108] a) Y. Jie, X. Liu, Z. Lei, S. Wang, Y. Chen, F. Huang, R. Cao, G. Zhang, S. Jiao, *Angew. Chem.* **2020**, *132*, 3533; b) G. Zardalidis, D. Chatzogiannakis, E. Glynos, F. Farmakis, *ACS Appl. Energy Mater.* **2021**, *4*, 6815.

[109] R. Guo, B. M. Gallant, *Chem. Mater.* **2020**, *32*, 5525.

[110] Y. Liu, X. Xu, M. Sadd, O. O. Kapitanova, V. A. Krivchenko, J. Ban, J. Wang, X. Jiao, Z. Song, J. Song, S. Xiong, A. Matic, *Adv. Sci.* **2021**, *8*, 2003301.

[111] N. W. Li, Y. Shi, Y. X. Yin, X. X. Zeng, J. Y. Li, C. J. Li, L. J. Wan, R. Wen, Y. G. Guo, *Angew. Chem., Int. Ed.* **2018**, *57*, 1505.

[112] M. P. Fertig, K. Skadell, M. Schulz, C. Dirksen, P. Adelhelm, M. Stelter, *Batteries Supercaps* **2022**, *5*, 202100131.

[113] P. Hartmann, T. Leichtweiss, M. R. Busche, M. Schneider, M. Reich, J. Sann, P. Adelhelm, J. Janek, *J. Phys. Chem. C* **2013**, *117*, 21064.

[114] N. Kamaya, K. Homma, Y. Yamakawa, M. Hirayama, R. Kanno, M. Yonemura, T. Kamiyama, Y. Kato, S. Hama, K. Kawamoto, A. Mitsui, *Nat. Mater.* **2011**, *10*, 682.

[115] S. Wenzel, S. Randau, T. Leichtweiß, D. A. Weber, J. Sann, W. G. Zeier, J. Janek, *Chem. Mater.* **2016**, *28*, 2400.

[116] L. Sang, R. T. Haasch, A. A. Gewirth, R. G. Nuzzo, *Chem. Mater.* **2017**, *29*, 3029.

2200398 (19 of 22)

[117] T. K. Schwietert, V. A. Arszelewska, C. Wang, C. Yu, A. Vasileiadis, N. J. J. de Klerk, J. Hageman, T. Hupfer, I. Kerkamm, Y. Xu, E. van der Maas, E. M. Kelder, S. Ganapathy, M. Wagemaker, *Nat. Mater.* **2020**, *19*, 428.

[118] T. Asano, A. Sakai, S. Ouchi, M. Sakaida, A. Miyazaki, S. Hasegawa, *Adv. Mater.* **2018**, *30*, 1803075.

[119] L. M. Riegger, R. Schlem, J. Sann, W. G. Zeier, J. Janek, *Angew. Chem., Int. Ed.* **2021**, *60*, 6718.

[120] a) C. Zheng, L. Li, K. Wang, C. Wang, J. Zhang, Y. Xia, H. Huang, C. Liang, Y. Gan, X. He, X. Tao, W. Zhang, *Batteries Supercaps* **2021**, *4*, 8; b) W. D. Richards, L. J. Miara, Y. Wang, J. C. Kim, G. Ceder, *Chem. Mater.* **2016**, *28*, 266.

[121] C. Ma, Y. Cheng, K. Yin, J. Luo, A. Sharafi, J. Sakamoto, J. Li, K. L. More, N. J. Dudney, M. Chi, *Nano Lett.* **2016**, *16*, 7030.

[122] A. Banerjee, X. Wang, C. Fang, E. A. Wu, Y. S. Meng, *Chem. Rev.* **2020**, *120*, 6878.

[123] W. Huang, H. Wang, D. T. Boyle, Y. Li, Y. Cui, *ACS Energy Lett.* **2020**, *5*, 1128.

[124] X. Cao, X. Ren, L. Zou, M. H. Engelhard, W. Huang, H. Wang, B. E. Matthews, H. Lee, C. Niu, B. W. Arey, Y. Cui, C. Wang, J. Xiao, J. Liu, W. Xu, J.-G. Zhang, *Nat. Energy* **2019**, *4*, 796.

[125] C. Stetson, Y. Yin, A. Norman, S. P. Harvey, M. Schnabel, C. Ban, C.-S. Jiang, S. C. DeCaluwe, M. Al-Jassim, *J. Power Sources* **2021**, *482*, 228946.

[126] a) S. Stegmaier, R. Schierholz, I. Povstugar, J. Barthel, S. P. Rittmeyer, S. Yu, S. Wengert, S. Rostami, H. Kungl, K. Reuter, R. A. Eichel, C. Scheurer, *Adv. Energy Mater.* **2021**, *11*, 2100707; b) S.-H. Kim, S. Antonov, X. Zhou, L. T. Stephenson, C. Jung, A. A. El-Zoka, D. K. Schreiber, M. Conroy, B. Gault, *arXiv* **2021**, 2110.03716; c) B. Gault, J. D. Poplawsky, *Nat. Commun.* **2021**, *12*, 3740.

[127] a) E. P. Kamphaus, S. Angarita-Gomez, X. Qin, M. Shao, M. Engelhard, K. T. Mueller, V. Murugesan, P. B. Balbuena, *ACS Appl. Mater. Interfaces* **2019**, *11*, 31467; b) A. Wang, S. Kadam, H. Li, S. Shi, Y. Qi, *npj Comput. Mater.* **2018**, *4*, 15.

[128] a) Y. Shi, H.-J. Yan, R. Wen, L.-J. Wan, *ACS Appl. Mater. Interfaces* **2017**, *9*, 22063; b) S. Y. Luchkin, S. A. Lipovskikh, N. S. Katorova, A. A. Savina, A. M. Abakumov, K. J. Stevenson, *Sci. Rep.* **2020**, *10*, 8550; c) W.-W. Wang, Y. Gu, H. Yan, K.-X. Li, Z.-B. Chen, Q.-H. Wu, C. Kranz, J.-W. Yan, B.-W. Mao, *Faraday Discuss.* **2022**, https://doi.org/10.1039/D1FD00043H; d) T. Liu, L. Lin, X. Bi, L. Tian, K. Yang, J. Liu, M. Li, Z. Chen, J. Lu, K. Amine, K. Xu, F. Pan, *Nat. Nanotechnol.* **2019**, *14*, 50.

[129] D. Cheng, B. Lu, G. Raghavendran, M. Zhang, Y. S. Meng, *Matter* **2022**, *5*, 26.

[130] Y. He, L. Jiang, T. Chen, Y. Xu, H. Jia, R. Yi, D. Xue, M. Song, A. Genc, C. Bouchet-Marquis, L. Pullan, T. Tessner, J. Yoo, X. Li, J.-G. Zhang, S. Zhang, C. Wang, *Nat. Nanotechnol.* **2021**, *16*, 1113.

[131] C.-H. Huang, L. Gharaee, Y. Zhao, P. Erhart, J. Marian, *Phys. Rev. B* **2017**, *96*, 094108.

[132] J. Zeng, W. Wu, F. Jiang, *Solid State Ionics* **2014**, *260*, 76.

[133] M. Wen, S. M. Blau, E. W. C. Spotte-Smith, S. Dwaraknath, K. A. Persson, *Chem. Sci.* **2021**, *12*, 1858.

[134] C. Suh, C. Fare, J. A. Warren, E. O. Pyzer-Knapp, *Annu. Rev. Mater. Res.* **2020**, *50*, 1.

[135] M. Aykol, P. Herring, A. Anapolsky, *Nat. Rev. Mater.* **2020**, *5*, 725.

[136] A. M. Lucas, P. V. Ryder, B. Li, B. A. Cimini, K. W. Eliceiri, A. E. Carpenter, *Mol. Biol. Cell* **2021**, *32*, 823.

[137] a) Z. Jiang, J. Li, Y. Yang, L. Mu, C. Wei, X. Yu, P. Pianetta, K. Zhao, P. Cloetens, F. Lin, Y. Liu, *Nat. Commun.* **2020**, *11*, 2310; b) H. Xu, J. Zhu, D. P. Finegan, H. Zhao, X. Lu, W. Li, N. Hoffman, A. Bertei, P. Shearing, M. Z. Bazant, *Adv. Energy Mater.* **2021**, *11*, 2003908.
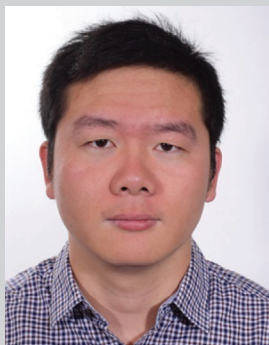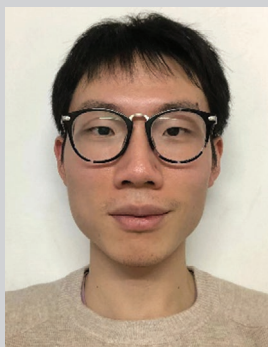
Yaolin Xu is currently working as a Postdoctoral Research Fellow on rechargeable batteries. He obtained his PhD in Li- and Na-ion batteries at Delft University of Technology (TU Delft, the Netherlands) in 2018. Later he received a Humboldt Research Fellowship and a DAAD-PRIME Fellowship for his Postdoctoral research. His research focuses on fundamental understanding of novel materials and interfaces in rechargeable batteries.
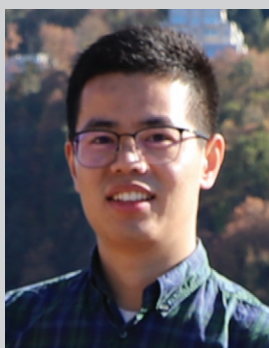

Kang Dong is a Post-Doc at Helmoltz-Zentrum Berlin (HZB). He got his PhD in Material Science at Technical University Berlin (TUB) under the supervision of Ingo Manke and John Banhart. His work is focused on in situ and operando characterization of lithium, sodium, and zinc batteries using X-ray and electron based imaging techniques.

2200398 (20 of 22)

**ADVANCED
SCIENCE NEWS**

www.advancedsciencenews.com

**ADVANCED
ENERGY
MATERIALS**

www.advenergymat.de

Yulin Jie is currently a PhD candidate at the School of Chemistry and Materials Science, University of Science and Technology of China (USTC). He received his Bachelor's degree from Shandong University in 2017. His research interests include organic liquid electrolytes and advanced characterization techniques for high-energy rechargeable batteries.
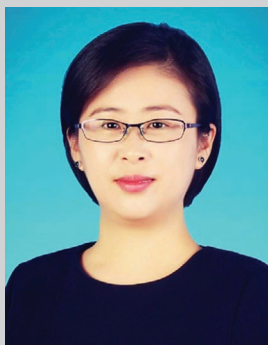
Shuhong Jiao is an Associate Professor at University of Science and Technology of China (USTC). She received her Ph.D. degree in Physical Chemistry from Peking University in 2011. She joined University of Science and Technology of China in 2017, after finishing her Postdoctoral training at Peking University and Pacific Northwest National Laboratory (PNNL) from 2011–2017, respectively. Her research interests mainly focus on electrolyte design and mechanism understanding for advanced energy storage devices.
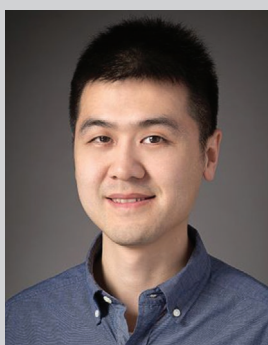
Tao Cheng received his Ph.D. degrees from Shanghai Jiao Tong University from 2007 to 2012, under the collaborative supervision of Huai Sun. In recent years, he is mainly engaged in theoretical research at the intersection of theoretical chemistry and energy catalysis, that is, developing theoretical simulation computational methods and applying them to energy-related important electrochemical reactions including reaction mechanism studies, material property prediction, and design of advanced functional materials. His main research interests are: multi-scale theoretical simulations of CO_2 electroreduction and high energy density batteries.

Ingo Manke is Head of the "Imaging Group" at the Helmholtz-Zentrum Berlin for Materials and Energy (HZB) and Reader at the Technical University Berlin (TUB). He studied Physics at the Freie Universität Berlin and received a PhD in Solid State Physics from TUB in 2002. His research area focuses on the development of imaging techniques based on X-rays, neutrons and electrons, and on their application on energy-related materials.

Yan Lu received her PhD with Summa Cum Laude in Macromolecular Chemistry at Dresden University of Technology, Germany. Afterwards, she worked as Post-Doc and Research Scientist at University of Bayreuth. Since 2009, she joined Helmholtz-Zentrum Berlin für Materialien und Energie (HZB) as a Group Leader in Colloid Chemistry. She received "Dr. Hermann-Schnell-Stipendium" by the German Chemical Society in 2011 and was selected as one of the top female researchers (W2/W3-Programme) in Helmholtz Association in 2015. Since 2017, she has been a Professor at Institute of Chemistry, University of Potsdam and the head of Department for Electrochemical Energy Storage at HZB.

2200398 (22 of 22)