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Li$^+$ Ion Transport at the Lithium Metal Anode: A Fundamental Picture and Future Perspectives

Benjamin P. Williams, Haochuan Zhang, Yu Mu, James R. Wilkes, Haden Wikar, and Dunwei Wang*

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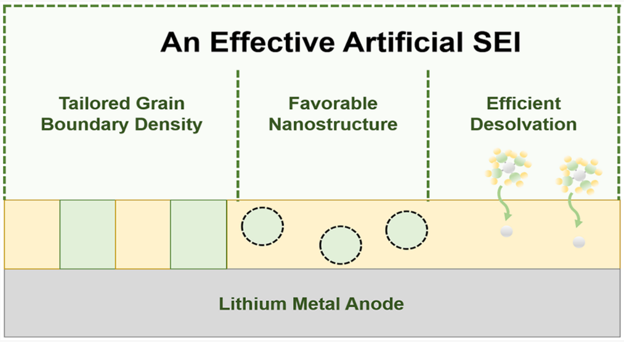

ABSTRACT: The unsurpassed energy density of lithium metal batteries (LMBs) offers a promising route to meet increasing clean energy demand. Nonetheless, their instability creates critical safety and performance concerns that prevent their effective implementation. Careful design of the solid-electrolyte interphase (SEI) that passivates the lithium metal anode could allow for stable, efficient cycling, unlocking the commercialization of LMBs. However, the complexity of the SEI, both formed *in situ* through electrolyte decomposition and fabricated *ex situ*, introduces significant ambiguity. Here, we present several mechanisms that define ionic transport through the SEI, grounded in studies that concretely relate structure to ionic conductivity. We build on these mechanisms with examples of their application in real battery systems. Overall, we seek to lay a foundation of structure−property relationships that will guide the rational design of stable SEIs that efficiently transport Li$^+$ ions.

1. INTRODUCTION

Since their commercialization in the late 20th century, lithium ion batteries (LIBs) have powered the portable devices that underpin modern society.[1] However, meeting increasing renewable energy demand and further decreasing global dependence on fossil fuels requires energy densities that LIBs cannot yet achieve.[2] With the highest predicted capacity of any battery system, lithium metal batteries (LMBs) offer a promising alternative, but their reliance on the lithium metal anode (LMA) creates safety and longevity concerns that have stalled their development.[3] Due to its low chemical potential, the LMA will react with any electrolyte to form a solid-electrolyte interphase (SEI) layer, as identified by Peled almost 50 years ago.[4] An ideal SEI layer can eliminate further degradation of the electrolyte by preventing charge transfer and can ensure uniform Li plating and stripping by regulating Li$^+$ ion flux to the anode surface.[5] Yet in practice, SEIs formed on bare LMAs have structural heterogeneities that lead to areas of high and low flux, causing uneven Li growth and battery failure.[6] Much attention has been given to designing artificial SEIs, but a robust structure that allows for long cycling at high currents remains elusive.[7]

Over the years, Peled's model has been refined, and it has been further reinforced by recent cryo-electron microscopy (cryo-EM).[8−11] Aurbach and co-workers notably pioneered the detailed study of SEI composition, identifying complex mixtures through a number of spectroscopic techniques.[12,13] The revealed complicated mosaic structure of the SEI introduces significant ambiguity into the fundamental mechanisms governing Li$^+$ ion transport. Myriad strategies have been developed to address this knowledge gap, including both computational and experimental efforts,[2,14] but a clear relationship between SEI structure and Li$^+$ ion transport remains unclear. The aim of this Perspective is to distill these past efforts into a coherent story, in the hope of moving closer to developing design rules for high-functioning SEIs. Though the topics of Li$^+$ ion transport and of artificial SEIs have been extensively reviewed elsewhere,[15,16] we will take a more focused approach, targeted specifically at the relationship between the SEI and ionic transport properties. Section 2 will outline the current understanding of Li$^+$ ion transport mechanisms, primarily in LMB systems with nonaqueous electrolytes, and their dependence on the SEI. Section 3 will build on this fundamental knowledge to demonstrate practical effects in experimental systems. To conclude, structure−performance relationships and the critical remaining questions will be outlined, with the ultimate goal of laying a foundation for the rational design of SEIs with fast, selective Li$^+$ ion transport that can enable high-performance LMBs.

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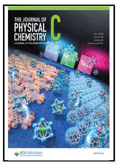

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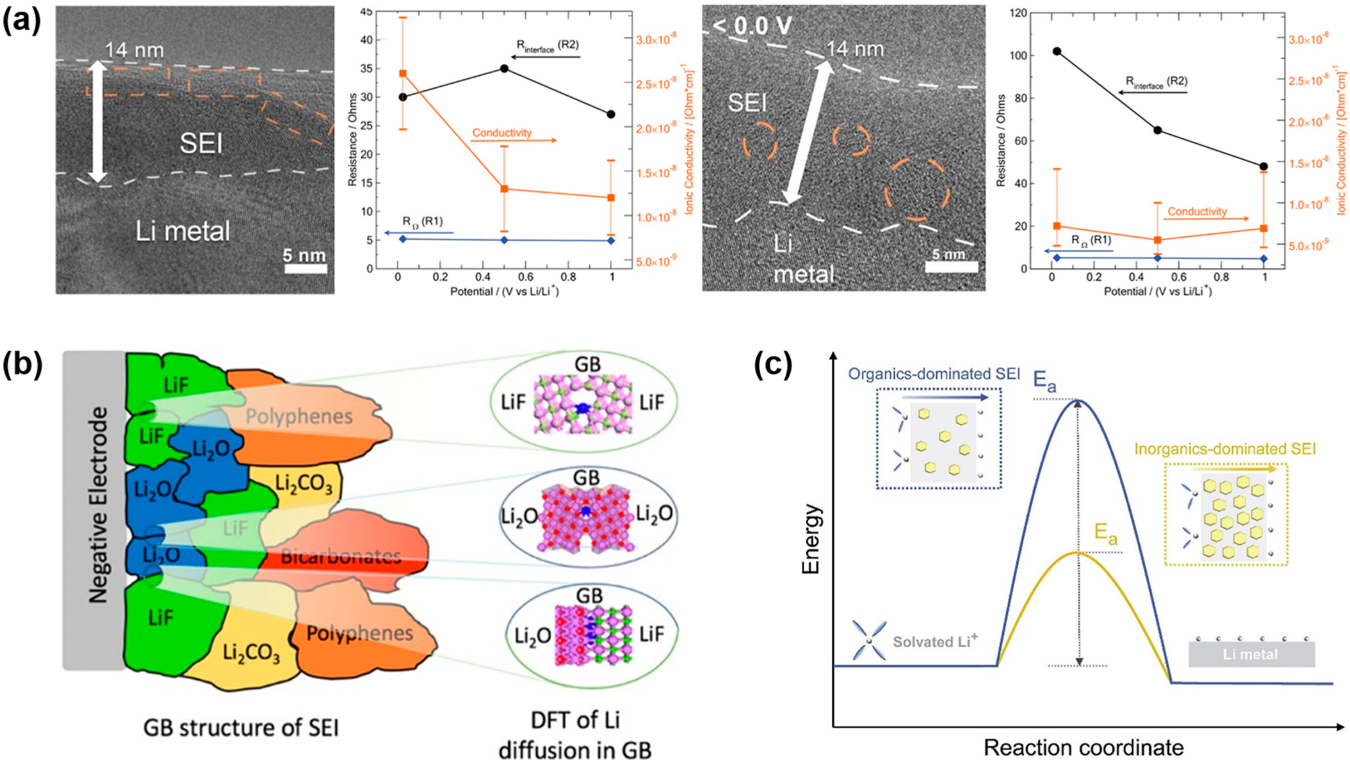

Figure 1. Three characteristic mechanisms by which the SEI can affect Li$^+$ ion transport. (a) Additive-induced inversion of the SEI structure (left) improves conductivity over the conventional SEI (right) formed in bare electrolyte. Orange boxes highlight inorganic regions. (b) Grain boundaries within the SEI serve as channels for Li$^+$ ion transport. (c) Inorganic species within the SEI can lower desolvation barriers and improve transport. Reproduced with permission from refs 25, 34, and 41, respectively. Copyright 2019 American Chemical Society and Copyright 2020 Elsevier.

2. LI$^+$ ION TRANSPORT MECHANISMS

The complex structure of the SEI gives rise to an equally complex array of properties that can affect Li$^+$ ion transport. The purpose of this section is to order the mechanisms into digestible categories, featuring examples that illustrate each. It should be noted, however, that each transport pathway does not happen in a vacuum. There is interplay between them, and papers demonstrating multiple mechanisms at work will also be mentioned.

To ground the interpretation of multicomponent SEIs, we present a brief discussion of foundational work on inorganic single SEI components. Ouyang, Sun, and co-workers calculated the electronic structures of Li_2CO_3, Li_2O, and LiF, finding all to be insulators but also that Li$^+$ ion conduction may be significant in Li_2O and Li_2CO_3 with available Li vacancies.[17] In LiF, conversely, they calculated a large barrier to Li$^+$ ion migration of 0.729 eV. Qi and co-workers refined this picture, constructing theoretical models to perform detailed studies of Li$^+$ ion conduction in Li_2CO_3[18] and LiF[19] through a variety of defect sites. Similarly, they found LiF to be highly ionically insulating, with a conductivity of ∼10^{-31} S/cm at 25 °C. They predicted excess interstitial Li$^+$ ions to serve as the main carriers in Li_2CO_3, with calculated energy barriers to Li$^+$ ion migration ranging from 0.227 to 0.491 eV. In each case, they found that electrode composition and applied voltage greatly affect diffusion pathways, with the ionic conductivity of Li_2CO_3 varying from 10^{-11} to 10^{-8} S/cm at room temperature. Maier and co-workers used electromotive force and impedance measurements to study ionic transport in Li_2O.[20] Their conductivity measurements on a Li_2O pellet were well-described by a defect chemical model, defining an upper bound for Li_2O ionic conductivity of ∼10^{-12} S/cm, well below typical SEI layers. The activation energy for Li$^+$ ion diffusion in Li_2O was determined to be 0.58 eV by their temperature-dependent measurements. However, first-principles calculations by Lowe and Siegel show facile Li$^+$ ion conduction by Li_2O on the surface of metallic Li, suggesting that the properties of bulk Li_2O may not be applicable within the SEI.[21] This idea will be expanded upon below.

It should also be mentioned that diffusion through the SEI can generally be divided into two major steps, which are induced by the layered structure adopted by the organic and inorganic SEI components.[22] In a representative study, Lu and Harris outlined transport through a $LiClO_4$ artificial SEI immersed in $^6LiBF_4$ electrolyte, finding facile transport through a porous outer layer followed by interstitial- or vacancy-mediated diffusion through a dense, inorganic layer near the electrode surface.[23] With Qi and co-workers, they refined this picture with theoretical modeling, identifying a knock-off model within the dense Li_2CO_3 layer.[24] This two-layered SEI structure will frame the following discussion.

2.1. SEI Structure.

Cui and co-workers studied SEI formation through cryo-EM by cycling CuO nanowire TEM grids in ethylene carbonate/diethyl carbonate (EC/DEC) electrolyte, with and without fluoroethylene carbonate (FEC) additive.[25] They demonstrated that the addition of FEC altered the layering of the SEI, which became inverted relative to the SEI in EC/DEC (Figure 1a). As the applied potential moved from 1.0 to 0.025 V, this inverted structure led to increasing ionic conductivity despite increasing SEI thickness. In contrast, a typical mosaic SEI formed in EC/DEC and resistance increased with thickness. Their result suggests that the nanostructure of the SEI plays a critical role in ionic conductivity. Importantly,

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the authors also note that the counter electrode must be chosen carefully to allow for accurate interpretation of electrochemical impedance spectroscopy (EIS) results.

Another paper from the Cui group highlighted the difficulty of effectively characterizing the nanostructure of the SEI, positing that even the μm-sized beam of X-ray photoelectron spectroscopy (XPS) cannot probe the SEI structure directly on the LMA.[26] Cryo-EM suggests that LiF identified by XPS consists of large particles atop a compact SEI rich in Li_2O. It is the compact SEI layer that controls Li^+ ion conductivity to the LMA. Gallant and co-workers introduced further ambiguity to the role of LiF, demonstrating that, despite its touted mechanical strength, an *ex situ*-deposited LiF layer impedes Li^+ ion flux with higher ionic resistance and breaks down under cycling.[27] They instead attribute the performance enhancement associated with LiF to features of concentrated fluorinated electrolytes, such as the quick passivation of Li and self-repairing of SEI. Clearly, care must be taken when associating SEI structure with better battery performance, and simple properties like mechanical strength cannot capture the full picture.

As mentioned above, an additional major challenge associated with the nanostructured nature of SEIs is that the transport properties of Li-containing compounds on the nanoscale may be significantly different from that measured in the bulk. Guo and Gallant synthesized Li_2O and LiF with nanoscale thickness through exposure of Li to gaseous O_2 or NF_3, respectively.[28] Their EIS results showed that ionic conductivity of the nanoscale Li_2O was several orders of magnitude higher than bulk measurements, in good agreement with measurements on native SEIs. The difference was assigned to the richer interstitial sites in nanoscale Li_2O than in the bulk Li_2O pellet. In addition, synthesized Li_2O showed higher conductivity than LiF, suggesting that a Li_2O-rich SEI may be suitable for an effective battery system.

The crystallographic structure of SEI components also plays an important role in guiding Li^+ ion diffusion. For example, Balbuena and co-workers found that Li^+ ions prefer to transport through an interstitial mechanism in Na-based SEI structures due to the smaller size of the Li^+ ion relative to the Na^+ ion.[29] In contrast, larger Na^+ ions tend to adopt a concerted-exchange mechanism in Li-based SEI structures. Their results suggest that ionic diffusion coefficients within the SEI layer are highly dependent on the dimensions of the ionic diffusion channel.

Similar to the mentioned liquid electrolyte systems, a multilayered SEI structure was also observed at the interface of Li metal and a solid electrolyte by Meng and co-workers.[11] By combining cryo-FIB and cryo-TEM techniques, they directly accessed the interphase between the LMA and LiPON, revealing a unique concentration gradient of N- and P-containing species along the interphase. The observed structure consisted of an inner layer rich in Li_2O and an outer layer rich in Li_3N and Li_3PO_4. The high ionic conductivity of the SEI is attributed to the outer layer, while the inner layer guarantees electronic insulation. The dynamic nature of SEI structure thus plays a significant role in Li^+ ion transport behavior.

It should be noted that real SEIs may exhibit extended 3-dimensional (3D) structure rather than the simplified 2-dimensional (2D) film often pictured at the LMA surface. Meng, Gu, and co-workers recently reported the formation of a 3D SEI framework in FEC-containing electrolyte solution, imaged with cryo-STEM tomography.[30] They determined the SEI layer was predominantly composed of a LiF-containing inner layer and an organic/polymeric outer layer. Importantly, the porous SEI husk crumpled but did not collapse during Li stripping. Such flexibility assists fast Li^+ ion transport and prevents additional SEI formation during the nucleation of newly plated Li. This work emphasizes the importance of proper SEI structure design on improving the reversibility of LMAs.

Taken together, recent works suggests that the SEI structure controls the transport mechanisms operative on the LMA surface. Future work is needed to produce a higher resolution picture of this structure, which exists on a length scale below the resolution of common characterization techniques such as XPS.

2.2. Grain Boundaries and Defects.

For decades, it has been recognized that boundaries between nanocrystalline domains can positively affect ionic transport.[31] Similar mechanisms have been identified within the mosaic SEI. For example, notable work from Qi and co-workers identified space-charge regions between Li-containing inorganic SEI components as potential channels for ion transport, reinforcing their model in an experimental system.[32,33] While synthetic limitations prevented an exact match between their computational model and synthesized artificial SEI, more approaches like this are needed, where computational and experimental efforts work in concert. The boundary transport mechanism was further elucidated by the Mashayek group, who modeled grain boundaries (GBs) between Li-containing inorganic components commonly found in LMB SEIs (Figure 1b).[34] By comparing diffusion barriers through three stable interfacial structures (LiF/LiF, Li_2O/Li_2O, and LiF/Li_2O), their work reinforced the conclusion that diffusion occurs preferentially at GBs. Further, their work suggests that heterogeneous GBs present a lower energy barrier to Li^+ ion transport than homogeneous GBs, indicating that the different compositions formed through electrolyte decomposition may promote transport and that artificial SEIs may show better performance when incorporating multiple compounds.

It is worth mentioning that the effect of GBs on SEI performance is not always positive. While enhancing ionic transport is beneficial, DFT calculations by Smeu and Leung show that highly heterogeneous SEIs enhance electron tunneling, which can allow electron leakage that leads to further electrolyte degradation and battery breakdown.[35] Further calculations by Qi and co-workers revealed that the fine structure of the GBs determines the ability of LiF to retain its insulating electronic structure.[36] Amorphous LiF GBs, notably, generate unoccupied states below the Li^+/Li^0 potential that can induce dendrite growth. These studies suggest that simply increasing GB density, though it may improve ionic conduction, is not sufficient for designing an effective SEI.

Aside from GBs between materials, Li^+ ions may also be preferentially conducted through defect sites within the crystalline domains. Modeling by Li and Qi studied this effect in Li_2CO_3, positing that Li^+ ions are transported through interstitial sites.[37] The formation of interstitial Li^+ ions is aided by negative charge buildup on the electrode surface, with induced defects further reducing the diffusion barrier. Modeling by Liu and co-workers combined the two mechanisms to study La-doped LiF.[38] Incorporation of La into the LiF reduces tensile strain and stabilizes vacancy defects along the La-LiF GB, which provide a stable path for Li^+ ion transport. This work highlights the importance of the fine structure of GBs on transport and suggests that doping may be a pathway toward increased ionic transport.

In summation, it is relatively clear that heterogeneous GBs introduced into the SEI can promote Li^+ ion conduction;

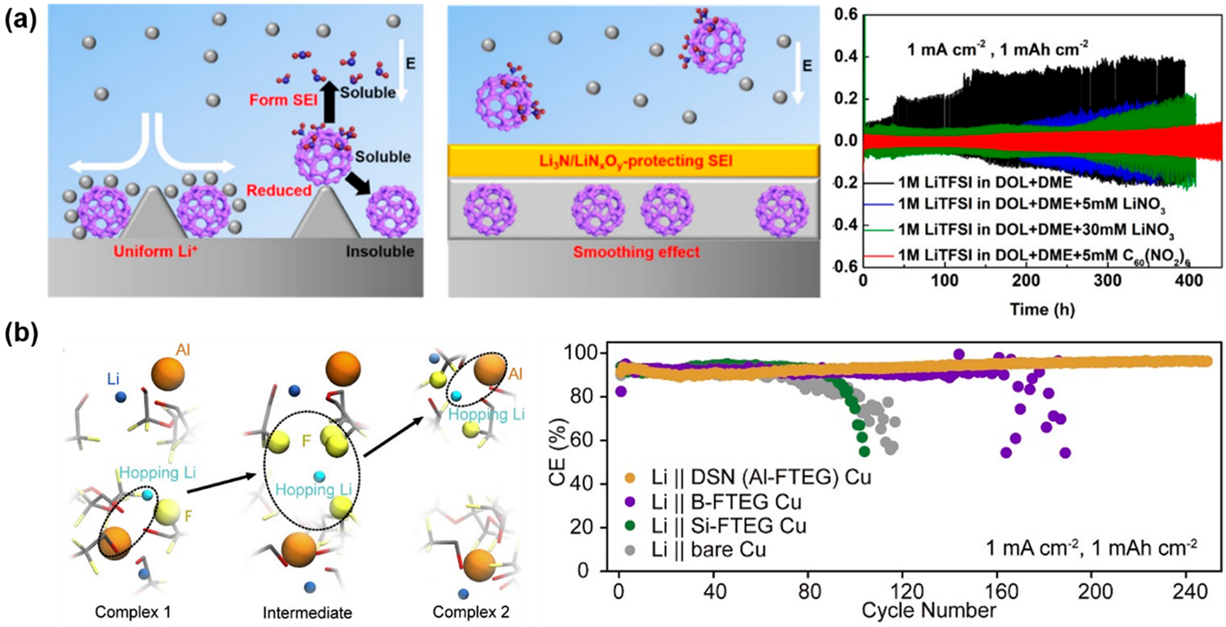

Figure 2. Two examples of the effective application of SEI transport mechanisms to solid-state battery systems. (a) Insoluble C_{60} and soluble NO^{2-} combine to induce uniform, conductive SEI formation leading to improved cycling performance. (b) Al centers in the Al-FTEG DSN allow facile Li transport, outperforming analogous nondynamic networks. Reproduced with permission from refs 47 and 60, respectively. Copyright 2019 American Chemical Society and Copyright 2019 Elsevier.

however, if the density is too high, they may undermine the ability of the SEI to effective passivate the LMA. Further study is needed to identify the ideal density of GBs and to identify compositional heterogeneities that may be particularly effective at promoting ionic transport.

2.3. Desolvation. Another aspect of battery cycling in which the SEI plays a key role is through the desolvation of Li^+ ions, which are coordinated by the electrolyte in solution.[39] Before being transported through the SEI, there is a barrier to reorganization of the Li^+ ion solvation shell that must be accounted for in overall transport properties.[40] Huang and co-workers studied the interfacial transfer kinetics of solvated Li^+ ions in SEIs with various ratios of inorganic to organic Li-containing species (Figure 1c).[41] Model SEIs were generated by cycling in different electrolytes and were characterized by XPS. Through further electrochemical characterization, inorganic-rich SEIs were identified to have faster transfer kinetics and lower overpotentials, attributed to lesser interfacial transfer energy barriers.

Modification of the Li ion solvation sheath can further guide the formation of SEIs with desirable Li^+ ion transport properties. It was demonstrated by Li and co-workers that introducing lithium trifluoroacetate (LiTFA) into a dimethyl ether (DME)/FEC electrolyte yielded an SEI with a favorable dense morphology and abundant LiF and Li_2O. This SEI structure lowered the energy barrier to both desolvation and Li^+ ion transport. Zhang and co-workers used $LiNO_3$ as an additive to generate NO_3^- anions that disrupted the solvation structure of bis(fluorosulfonyl)imide (FSI^-) around Li^+ ions in a DME electrolyte.[42] With NO_3^-, FSI^- could be completely decomposed to form $LiSO_x$, LiF, and LiN_xO_y. The resulting SEI showed an exchange current density for Li plating/stripping four times larger than with LiFSI alone. The solvation sheath could also be effectively modulated by other anions ($LiClO_4$) and an anion acceptor (tris(pentafluorophenyl)borane (TPFPB)),[43] indicating that this strategy made be widely applicable.

Taken together, these works imply that altering the Li^+ ion solvation sheath may form a virtuous cycle where facile desolvation forms favorable SEIs that further decrease solvation barriers. The diversity of known electrolytes and additives creates a broad parameter space to try new combinations of Li salts, electrolytes, and additives to control both Li^+ ion solvation and *in situ* SEI formation. Beyond the SEI, the Li^+ ion solvation structure may play other roles in battery performance, which are beyond the scope of this Perspective and have been reviewed in detail elsewhere.[44]

Taken together, the groups outlined in Section 2 have demonstrated that several factors work in concert to allow efficient ionic transport through the SEI. Although framed by a two-layered overall structure, the SEI nanostructure is critical to Li^+ ion diffusion, and it is not captured by bulk conductivities and mechanical strengths. GBs between components can offer facile diffusion pathways, but there is an upper limit beyond which dense GBs promote electron leakage. A favorable structure at the SEI-electrolyte interface can also enhance conductivity by easing desolvation. Researchers should pay careful attention to area specific resistance (ASR) as a figure of merit to capture the interplay between the outlined complex mechanisms of transport within the SEI. Discrepancies between predicted and actual ASR values could be due to the microstructure of SEIs in real battery systems, which may have confounding factors, like captured liquid electrolyte, that cloud interpretation.

3. DESIGNING HIGHLY CONDUCTIVE SEIS

This section aims to build on the fundamental understanding outlined in Section 2 through its application in the rational design of concrete battery systems. The first subsection will focus on creating effective SEIs, both by synthesizing artificial SEIs *ex situ* and by guiding SEI formation *in situ*. The second will center on solid-state battery systems, which offer extended networks for Li^+ ion conduction.

3.1. Modifying the Electrode Surface.

As mentioned, both *in situ* and *ex situ* approaches can lead to SEIs that efficiently transport Li^+ ions. Recent work has even demonstrated that modifying other parts of the battery, such as the separator, can regulate SEI formation on the LMA.[45] Here, we present several representative papers of both *in situ* and *ex situ* methods that are paired with definitive conductivity measurements to illustrate the effective implementation of highly conductive SEIs in real battery systems.

Electrolyte additives are one of the most promising routes to directing *in situ* formation of robust, highly conductive SEIs.[46] Xie and co-workers, for example, introduced nitro-functionalized C_{60} (nitrofullerene) to induce compact SEI formation.[47] Upon addition, the binding of insoluble C_{60} smooths the Li surface while NO_2^- reacts with the Li metal to form an SEI (Figure 2a). The resulting SEI is rich in N- and O-containing inorganic Li compounds that lead to fast transport, as evidenced by high exchange current densities. Archer and co-workers added the cross-linking agent $SiCl_4$ to $LiPF_6$ in propylene carbonate (PC) to form an SEI of Si-linked organic carbonate oligomers doped with LiCl. The addition of $SiCl_4$ greatly lowered the charge transfer resistance (R_{CT}) of the SEI and increased exchange current densities, allowing for even and fast Li metal deposition.[48] Światowska, Sun, Chen, Li, and co-workers added 50 vol % EC to $LiNO_3$ in tetraethylene glycol dimethyl ether (TEGDME) to suppress consumption of the $LiNO_3$ additive and form a multilayered SEI with an outer C-rich region and an inner N-rich region.[49] The N-rich region allowed the hybrid system to maintain a low barrier to ionic diffusion while the C-rich region prevented deleterious electrolyte consumption. $LiClO_4$ is also an effective additive, as showcased by Zhang, Ding, Li, and co-workers, who attributed its improved cycling performance in ether and carbonate electrolytes to its ability to optimize the decomposition of LiTFSI to form an effective SEI.[50] P_2S_5-saturated CS_2 served as an excellent additive to an ester-based electrolyte for Sun and co-workers, who used EIS to show that the interfacial resistance in the presence of the additive was stable over 200 cycles.[51] Their work suggests that compounds with P−S bonds may stabilize the SEI layer and prevent the accumulation of dead Li and consumption of the electrolyte that leads to battery failure. These examples demonstrate that carefully chosen additives can drive SEI composition to favor efficient ionic transport.

In the realm of *ex situ* artificial SEIs, the groups of Li, Wang, and Xiong combined the superionic conductor Li_3Sb with insulating LiF to generate a stable yet highly conductive SEI.[52] To synthesize the film, Li metal was immersed in DME containing SbF_3. The resulting high ionic conductivity and electronic resistivity clearly demonstrated the synergistic effect of combining the two materials into an effective battery system. Gong and co-workers employed a Li_2S layer to govern ion and electron transport on 3D porous Cu.[53] Li^+ ions were introduced into Cu_2S nanowires through galvanostatic electroplating to form the Li_2S. Rapid Li^+ ion transport led to homogeneous Li metal deposition and stable cycling. By extracting Al from ternary Ti_3AlC_2, the Niu group synthesized $Ti_3C_2T_x$ (T = O, F, OH) MXene stacks that were pressed onto thin Li metal.[54] With the stacks, the thickness of the inorganic-rich layer of the SEI was significantly reduced, lowering charge transfer resistance and allowing Li metal to reversibly plate and strip from the lithiophilic layers of the MXene. Shi, Ke, Guo and co-workers took advantage of the "self-adaptive" nature of Li alginate to generate a stable artificial SEI by reacting alginic acid and LiOH.[55] Although initially large, the charge transfer resistance of the artificial SEI decreased over 100 cycles and remained stable to 1000 cycles, which was attributed to its ability to repair its structure and to reduce parasitic reactions. Wu and co-workers introduced a superstructured single-ion conductive polymer brush (CNF-*g*-PSSLi) rich in $-SO_3^-$ groups that can serve as fast Li^+ ion transport channels.[56] With the polymer, the LMA cycled stably for 270 h at a current density of 20 mA/cm^2, and the authors suggest that the anionic $-$ SO_3^- groups also electrostatically suppress Li dendrite formation. The groups of Zhang, Guan, and Huang similarly used a 3D structural network to regulate Li^+ ion flux, employing gelatin-based fibers as a coating for the LMA in a Li−S battery system.[57] Polar moieties in the fibers controlled Li^+ ion transport, and the fibers were also able to reduce the shuttling of polysulfides to enable long-term cycling. All told, these examples highlight the diversity of successful *in situ* and artificial SEI approaches in the literature, which is a testament to the ingenuity of battery researchers, but more work is needed to unequivocally identify the most effective approach.

3.2. Extending to Solid-State Electrolytes.

Though not a rigorous comparison, solid-state electrolytes (SSEs) can be conceptualized as extended SEI structures, where many of the mechanisms outlined in Section 2 are operative. Solid-state battery systems have been reviewed in great detail elsewhere,[16] so this section will emphasize papers that take advantage of the Li^+ ion conduction mechanisms commonly found in SEIs. First, we note that electrical conduction also looms as a key challenge to the commercialization of solid-state LMBs, given the large interfacial resistance between the LMA and the SSE. Introducing a small amount of liquid electrolyte can overcome this issue by generating a low-resistance interphase layer.[58] For example, Wang and co-workers demonstrated that a LiF-rich SEI could be formed *in situ* by infiltrating a drop (~20 μL) of highly concentrated 6 M LiFSI dimethoxyethane between the LMA and a Li_3PS_4 SSE.[59] Supported by DFT calculations, they claim the low electronic conductivity and electrochemical stability of LiF help effectively suppress Li dendrite formation and side reactions between the LMA and SSE.

Similar to the aforementioned combination of Li_3Sb and LiF,[52] several groups have shown that polymer and hybrid SSEs can provide ion channels that allow for the fast transport of Li^+ ions. Cui, Bao, and co-workers incorporated $Al(OR)_4^-$ centers into a dynamic single-ion-conductive network (DSN, Al-FTEG) that efficiently shuttled ions through a cross-linked polymer network.[60] Using ^{7}Li- and ^{19}F-NMR, they identified that high ionic conductivity is achieved through polymer-mediated hopping between Al centers (Figure 2b), with the DSN showing higher ionic conductivities than analogous nondynamic (B-FTEG) and non-single-ion-conductive (Si-FTEG) networks. The Archer group showed that polymerization of 1,3-dioxolane (DOL) by AlF_3 or $Al(OTf)_3$ could generate an SSE that retained a small fraction of incompletely polymerized, liquid-like DOL that aided ionic transport.[61,62]

Work by Fan and co-workers linked a $Li_{6.75}La_3Zr_{1.75}Ta_{0.25}O_{12}$ (LLZTO) framework with polytetrafluoroethylene (PTFE), then filled it with a succinonitrile SSE.[63] High ionic conductivities, attributed to transport through channels between LLZTO particles and succinonitrile, enabled efficient cycling. Guo, Sun, and co-workers reported that the size of inorganic SSE particles significantly affects the properties of hybrid SSEs.[64] Embedding small LLZTO particles in polymers yielded higher ionic conductivities while embedding large LLZTO particles resulted in better mechanical strength. Similarly, various synthesis methods have been developed to prepare composite SSEs comprised of 3D ion-conducting networks and polymer electrolytes.[65−68] Collectively, these examples demonstrate that incorporating efficient ion conducting channels into SSEs can maximize performance by pairing their natural high stability with effective Li^+ ion transport. Analogous to improved desolvation kinetics induced by the SEI in liquid electrolytes, interactions between Li^+ ions and ions within the SSE framework can destabilize bonds and promote transport.

Goodenough and co-workers demonstrated both mechanisms in one system by combining poly(ethylene oxide) (PEO) and perovskite $Li_{3/8}Sr_{7/16}Ta_{3/4}Zr_{1/4}O_3$ to generate a highly conductive composite electrolyte.[69] ^{7}Li NMR results identified transport along the PEO/LiTFSI (TFSI ≡ bis(trifluoromethylsulfonyl)imide) matrix between perovskite particles, while DFT suggested further enhancement from strong chemical coupling between the $TFSI^-$ anions and the perovskite through $Ta^{5+}-F^-$ bonding. Similar work by Shahbazian-Yassar and co-workers combined black phosphorus (BP) with PEO to increase ionic mobility.[70] Detailed computational analysis revealed that the addition of BP promotes ion-pair dissociation, as evidenced by an increased Li−N bond length. Shrewd future approaches may similarly combine multiple mechanisms to maximize transport efficiency.

4. CONCLUSION AND OUTLOOK

An idealized SEI, which offers efficient ionic conduction and reversible Li plating/stripping while preventing electrolyte breakdown, still offers the potential to unlock LMB systems. Advanced techniques like cryo-EM are beginning to reveal the detailed nanostructures that define Li^+ ion transport. Preferential pathways along GBs show promise for enhancing conductivity, although care must be taken that their introduction does not undermine the structural stability or insulating nature of the overall SEI. Careful design of the SEI-electrolyte interfacial structure lowers barriers to desolvation, functioning as an on-ramp for Li^+ ions to reach facile conduction pathways. Each of these mechanisms has been highlighted in effective batteries, with particular impact in SSB systems.

Despite these advances, effective SEI development still faces several major challenges. Though all electrode materials undergo volume change during charge and discharge, the relative volume change of the lithium anode is essentially infinite due to its host-free nature.[71] From a practical perspective, the areal capacity of a single-sided commercial electrode needs to reach at least 3 mAh/cm^2, equivalent to a relative change in thickness of ∼14.6 μm for LMAs. The change could be even higher for batteries with cathode chemistries featuring high specific capacity, such as sulfur and oxygen, which could induce interface movement of several tens of micrometers. Such volume change is a formidable challenge to SEI stability, even for materials with high Young's moduli, such as LiF. In order to understand Li^+ ion transport in real battery systems, targeted studies are needed to determine the effect of such changes on SEI transport mechanisms.

Current density is another crucial factor that dictates LMA/electrolyte interfacial stability. Recent studies illustrate that the applied current density of both Li plating and stripping seriously affects the structure and composition of the SEI. For example, Xu and co-workers investigated the degradation of the LMA when raising charge current density and lithium capacity utilization to practical levels (2.0 mA/cm^2 and 4 mAh/cm^2, respectively).[72] They found that the increase in capacity utilization induces a thick degradation layer with large cracks on the LMA, and the increase in current density causes significant changes in SEI morphology and composition, greatly accelerating capacity fading. Cui and co-workers likewise showed that lithium stripping at high current densities caused the vigorous growth of voids (derived from accumulated leftover lithium vacancies) leading to a local collapse of the SEI layer.[73] High performance SEIs are needed that can remain effective under these harsh, practical conditions.

Several key questions about Li^+ ion transport also remain unanswered

1. What is the detailed nanostructure of the SEI and how may it be effectively designed to promote ionic transport? The recent development of advanced characterization techniques has improved our understanding of the nanostructure of the SEI. For example, recent efforts have shown that the *in situ* formation of highly uniform amorphous SEIs from novel electrolytes can guide homogeneous Li plating and stripping to guarantee high Coulombic efficiency.[74−76] However, a clearer picture of the detailed SEI composition and structure, and its association with Li^+ ion transport properties, is needed to direct further improvements.

2. What is the ideal density/composition of GBs to promote transport but prevent electron leakage? That is, what is the ideal level of heterogeneity within the SEI structure? As discussed above, heterogeneous GBs within the SEI can not only promote Li^+ ion transport but also enhance electron tunneling. More direct experimental evidence will be helpful to understand this trade-off under practical conditions.

3. How can we couple SEI structure/composition with electrolyte design for efficient Li^+ desolvation? Direct experimental evidence is limited regarding the Li^+ ion desolvation properties of SEI components and how they are affected by SEI structure. A better understanding of the desolvation process could not only benefit Li^+ ion transport but also assist Li plating and stripping overall.

4. Though they clearly improve performance, what is the direct relationship between electrolyte additives and SEI structure? *Ex situ* preparation of artificial SEIs is an effective approach to understand their intrinsic properties. However, *in situ* SEI formation in the presence of electrolyte additives is likely more feasible from a practical perspective. The complexity introduced into the *in situ* SEI formation process is a formidable barrier to understanding, but it is important to develop experimental methods to deconvolute the fundamental properties of electrolyte additives.

5. How can all of these mechanisms be effectively combined into one system? Researchers should bear in mind that a single strategy will not be sufficient to solve all of the problems outlined here. A comprehensive understanding of Li^+ ion transport across the SEI, grounded in many different experimental approaches, is indispensable to the ultimate application of the LMA. Concerted computational and experimental efforts will also be required.

These questions provide a roadmap for battery researchers to design and realize SEIs that can underpin the next generation of stable, high energy density LMBs.

■ AUTHOR INFORMATION

Corresponding Author

Dunwei Wang – *Department of Chemistry, Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts 02467, United States;* orcid.org/0000-0001-5581-8799; Email: dwang@bc.edu

Authors

Benjamin P. Williams – *Department of Chemistry, Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts 02467, United States;* orcid.org/0000-0002-5921-7998

Haochuan Zhang – *Department of Chemistry, Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts 02467, United States*

Yu Mu – *Department of Chemistry, Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts 02467, United States*

James R. Wilkes – *Department of Chemistry, Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts 02467, United States;* orcid.org/0000-0002-7429-9362

Haden Wikar – *Department of Chemistry, Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts 02467, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpcc.2c03215

Notes

The authors declare no competing financial interest.

Biographies

Benjamin P. Williams received his Ph.D. from Boston College, under the supervision of Prof. Chia-Kuang (Frank) Tsung. Since 2020, he has worked as a Postdoctoral Research Fellow at Boston College in the group of Prof. Dunwei Wang. His research interests include the chemistry of the lithium metal anode and the application of nanoparticles and porous materials to heterogeneous catalysis.

Haochuan Zhang received his Ph.D. from Boston College, under the supervision of Prof. Dunwei Wang. His research interests include the fundamental study and application of the solid electrolyte interphase of the lithium metal anode and the development of integrated catalysis approaches to sustainable synthesis.

Yu Mu received his B.S. in chemistry from Nanjing University in 2020. He is currently a doctoral candidate under supervision of Prof. Dunwei Wang at Boston College. His research interests include rechargeable batteries and electrochemistry-triggered integrated catalysis.

James Wilkes received his B.S. degree in chemistry from the University of New Hampshire in 2021. He is pursuing a doctoral degree at Boston College under the supervision of Prof. Dunwei Wang. He is interested in rechargeable batteries and integrated catalysis.

Haden Wikar is an undergraduate student at Boston College (Class of 2023). He has been working in the Wang group since 2021.

Dunwei Wang is the Vanderslice Professor of Chemistry at Boston College. He has a B.S. degree from the University of Science and Technology of China (2000) and a Ph.D. from Stanford University (2005). His research group studies energy conversion and storage, with a focus on solar water splitting, photocatalysis, and batteries and, more recently, on sustainable polymers.

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