Stabilizing metal battery anodes through the design of solid electrolyte interphases

Qing Zhao[1], Sanjuna Stalin[1], and Lynden A. Archer[1]*

[1]Robert Frederick Smith School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, New York 14853, USA

*email: laa25@cornell.edu

The solid electrolyte interphase (SEI) is a chemically distinct material phase formed by a combination of electrochemical reduction and chemical reactions at both the explicit and implicit interfaces in all electrochemical cells. The structure, chemistry, and thermodynamics of the materials that accumulate in such interfacial material phases have emerged over the last decade to play crucial roles in achieving high levels of anode reversibility in secondary batteries, especially in systems where electrochemically active metals are used as anodes for high-energy-density and cost-effective storage. Here we review the history, chemistry, formation characteristics and rational design of the SEI at metal anodes. Strategies that explicitly take advantage of redox chemistry of electrolyte components to build designed SEI inside electrochemical cells, as well as those that benefit from ex-situ chemistries performed outside the cell to create artificial SEI that enhance anode reversibility are highlighted. Taking advances based on these methods as a point of departure, the review also considers interphase design strategies that facilitate chemical, mechanical, and electrochemical stability and fast ion transport through the SEI. Finally, we discuss differences and similarities of SEI formed on monovalent (Li, Na, K), divalent (Mg, Ca, Zn) and trivalent (Al) metals of contemporary interest for developing cost-effective but high-performance anodes, and on that basis underscore the urgent need for intrusive experimental approaches able to analyze the SEI on metals at atomic levels.

Introduction

The commercialization of Li-ion batteries—a technological innovation that was recognized with the Noble Chemistry Prize in 2019 is expected to play a crucial role in all aspects of mobile technology for the foreseeable future.[1] The high level of electrochemical reversibility achieved at the anode (graphite) in Li-ion batteries is often taken for granted but is a key source of the Li-ion batteries success. It is known to depend crucially on the spontaneous construction of solid-state ion conducting interphases termed the solid electrolyte interphase (SEI), as a result of chemical and electrochemical reactions of components in the electrolyte.[2,3] For example, a SEI that restricts access of aprotic carbonate electrolyte solvent has completely resolved early issues of exfoliation and electrolyte solvent co-intercalation in graphite anodes, allowing the anodes to achieve high and long term reversibility.[4] At the simplest level, the SEI formed on graphite is an electronically insulating but ionically conductive material that regulates electrolyte and ionic access to the anode. A well-formed SEI on graphite must also facilitate de-solvation of ions in the electrolyte medium in order to achieve low overpotentials and long-term stability.

In pursuit of high-energy-density electrical energy storage/conversion devices, rechargeable batteries that employ metals (Li, Na, K, Mg, Ca, Zn, Al, *etc*) as anodes have recently gained increasing attention.[5] For example, replacing the low capacity graphite anode (372mAh/g) with a pure Li metal anode (3860 mAh g^{-1}), it is possible, at least in principle, to create rechargeable battery cells that break through the energy density ceiling (~300 Wh kg^{-1}) of conventional Li-ion batteries. With suitable optimization, batteries with energy densities exceeding 500 Wh/kg can be achieved.[6] Unlike the graphite anode, the SEI on a Li metal anode plays a different, more complicated role. Specifically, as an alkali metal with the most negative electrochemical potential (-3.04 V), Li readily reacts with nearly all electrolyte components inside a battery cell. The difference in electrochemical potentials between lithiated graphite (~0.2 V vs Li^+/Li) and Li metal also results in quite substantial differences in the ease with which electrolyte components are reduced at the battery anode, which again results in significant differences in the composition and spatial uniformity of the SEI formed on Li.[7] A large and growing body of work shows that the SEI formed on a Li metal anode is typically inhomogeneous. With additional deposition, Li metal accumulates in regions on the electrode where fast ion transport is supported by the SEI, ultimately producing non-planar electrodeposition of Li metal in the form of mossy or dendritic structures.[8,9] Such uncontrolled growth of Li electrodeposits generates at least two serious problems: (i) low anode reversibility either as a result of parasitic side reactions between the high-surface area mossy/dendritic deposits and electrolyte components, or physical loss/orphaning of active electrode material when the fragile deposits break away from the anode mass to become electronically isolated; (ii) the non-planar deposits may grow to fill the inter-electrode space causing battery cell failure when the metal deposits bridge the interelectrode space to internally short-circuit the cells.

Figure 1 summarizes the key developments over the past 70 years that support our current understanding of the functionality and composition of SEI formed on a metallic Li anode. Over fifty years ago, it was proposed that a film formed on the lithium metal anode results in its extended stability and reversibility.[10] This film was defined as a SEI in 1979 by Peled.[3] Different models including vacancies (Schottky lattice defects),[3] multilayer,[11] mosaic (polyhetero microphase),[12] double layer capacitor (fixed positive charges within the SEI counteract the negatively charged anode),[13] and monolithic SEI (amorphous and homogenous),[14] have been proposed to explain the physical and transport properties of the SEI. The SEI generated in traditional carbonate electrolytes was, for example, thought to be composed primarily of Li_2CO_3 and Li alky carbonate, which would not satisfy the demand of homogeneity, uniform ion transport and mechanical strength needed to achieve high anode reversibility.[15,16] In order to compensate for shortcomings of the spontaneously formed SEI, artificial SEI designed using organic/polymer coatings,[17] inorganic/ceramic electrolyte coatings,[18] or even carbon spheres,[19] that may challenge the traditional understanding of the electronically insulating SEI have been developed to regulate the stability of reduplicative metal stripping/plating. The recent development of advanced characterization methods such as cryogenic scanning transmission electron microscopy (cryo-STEM) as a tool for interrogating in-tact interphases on Li have advanced understanding of the native structures and compositions formed on a Li metal electrode.[20,21]

The functionality and composition of what is now known to be the SEI formed spontaneously on a metallic Li anode have received significant attention. The most complete of these studies reveal that it is dynamic, not necessarily thin, and must possess an impossible set of physico-chemical features (*e.g.,* electrochemical stability in the highly reducing environment at the electrode; facilitate ion desolvation; enable fast interfacial ion transport; high enough mechanical strength and toughness to flex and contract to accommodate volume change of the Li metal during cycles of charge and discharge; and enabling good wetting by electrolyte components) to enable the hundreds to thousands of trouble free cycles of charge and discharge demanded of a practical metal battery anode. Reliable strategies for manipulating SEI formed on metals such as Li have consequently emerged as a global research priority. Unfortunately, the rich literature resulting from such studies is quite fragmented and difficult to consolidate to present a unified scientific understanding of the SEI. Many reports advocate one desired material configuration over other, typically based on at best modest evidence and with no clear connections to root causes or general design rules. The simultaneous rapid rise in the number of publications and the technical richness of the field creates urgency for a review that unifies the disparate SEI concepts, not only on lithium metal, but also on other emerging metal anodes (*e.g.,* Na, K, Mg, Ca, Zn, Al) that hold the potential for lowering the cost of electrical energy storage in batteries. The review is organized as follows. We begin with a brief history of the SEI on the lithium anode, with an emphasis on fundamentals that govern formation processes, and which explain how and why SEI design has emerged as a fundamental barrier to progress towards Li anodes with high reversibility. We subsequently consider strategies for creating purpose-build SEIs, either in-built by components intentionally added to the electrolyte or externally formed using components that are not present in the electrolyte. SEIs on other emerging metal anodes (Na, K, Mg, Ca, Zn, Al) are discussed next both to underscore the generality of the interface chemistry principles and to illustrate differences between SEIs formed on different metals. We finally consider the role advanced techniques have and will play in enabling a comprehensive understanding of the properties of the SEI.

Composition and properties of the solid electrolyte interphase

All electrode reactions in a battery are normally assumed to occur within a voltage range termed the *electrochemical stability window* where the electrolyte is electrochemically stable. The stability window is controlled by the energy of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), according to the frontier molecular orbital theory.[22] Depending on the method of production and supplier, the surface of lithium foils used in batteries mainly consist of Li_2CO_3, as well as Li_2O, and may also include LiOH as a result of contamination by atmospheric moisture.[23] Due to the low standard electrode potential of lithium metal (Li^+/Li, -3.04 V), most components in the electrolyte (solvents, salts, additives) will be reduced at the lithium electrode to form a passivation film. The composition of the SEI is consequently quite complicated, typically containing a combination of inorganic species and organics/polymers/oligomers. Once formed, the SEI should be electronically insulating, thus retarding the further reactions between lithium and electrolytes (**Figure 2A**). In this regard, components with high voltage band-gap (E_g) are preferred. The results in **Figure 2B** suggest that among SEI components, LiF (E_g, 14.6 eV) would be a naturally favored choice due to its insulting behavior, compared with Li_2O (E_g, 8.1 eV).[24] Simultaneously, once the solvated Li^+ ion transports to the surface of SEI under an applied electric field, the SEI take another crucial function to de-solvate the Li^+ ion and transport the naked Li^+ to the negative electrode where it is reduced. Here, the activation energy for diffusion (diffusion barrier) can be measured to estimate the time scale of Li-ion transport. A general picture of diffusion barrier in common inorganic SEI components is summarized in Figure 2B, in which lithium halides especially LiCl and LiBr stand out.[25,26] It should be mentioned here that the transport can be largely influenced by the defects and vacancies within the SEI, particularly within the inorganic crystal components.[25,27]

The intercalation of Li-ion into graphite anode with the formation of LiC_6 only causes a volume expansion of ~13.2% (**Figure 2C**).[28] In comparison, lithium metal stripping transforms an ordered crystalline, solid metal into a disordered, solvated (liquid) ionic state; the reverse occurs during metal plating. The result is that during the strip/plate (discharge/charge) cycle the Li metal anode undergoes a very large volume change (Figure 2C).[29] The stresses generated in the SEI are therefore significant and may cause it to break and reform during repeated cycles. The tendancy of Li metal to deposit in non-planar even dendrite like morphologies, add other mechanical requirements that may or may not be easily met by inorganic salts like LiF. For example, Monroe and Newman's theory indicates that non-uniform Li deposition can be suppressed when the shear modulus of separator of the material in contact with the metal deposit is about twice higher than lithium metal (4.2 GPa),[30] which can be achieved by most inorganic crystals (For example, LiF, 48.6 GPa) (**Figure 2D**).[31] On the other hand, like most inorganic salts, LiF lacks the ability to flex and shrink to accommodate volume change, which would compromise reversibility of a Li electrode if it was the only interphase component. High surface tension, usually resulting from interfaces with high interfacial energy, can also force to stabilize deposition, and offer better dendrite resistance as the formation of non-planar morphologies will cause the increase of surface area.[8] The SEI that displays more distinguished surface energy with lithium metal will results in higher interfacial energy. Figure 2d demonstrates that LiF shows highest surface energy amongst the inorganic SEI components.[26]

Table 1 summarizes the most effective methods used to form a SEI on Li and the corresponding composition and properties of the formed SEI. In-built SEI formation methods with modifications of electrolytes, and fabrication of artificial SEI including chemical reactions that utilize the reactivity of lithium, thin film techniques such as chemical vapor deposition (CVD), atomic layer deposition (ALD) and sputtering methods *etc* have been applied to synthesize SEI. Beyond the compounds listed in Table 1, there are a large number of reports on the fabrication of polymer/hybrid SEI. The SEI is also dynamic and may change in thickness and composition over time as the anode undergoes multiple cycles of charge and discharge. Overall considering the band-gap, diffusion barrier, mechanical modulus, and surface energy, LiF seems to be one of the most powerful inorganic SEI components that protects the lithium metal from dendrite growth if it can cooperate with flexible organic/polymer SEI components to accommodate volume changes.

In-built solid electrolyte interphase on Li metal

SEI formed from components intentionally added to an electrolyte provides a particularly powerful tool for creating interphases on metal electrodes. Electrolytes carry active ions for transport between electrodes and slowly react with anode and cathode to form stable/unstable SEI on both anode and cathode side. Electrolytes can be a mixture of salts and liquid solvent/polymer matrix with or without the functional additives, or single solid inorganic compounds. An ideal electrolyte should own merits of high cation transport ability in wide temperature region, high stable voltage region, and formation of stable SEI towards anode and cathode. The SEI is affected by the coordination environments of ions and solvents, which can be affected by the types of ingredients as well as the concentrations distributions of these ingredients. When optimized SEI is designed by electrolytes, the kinetics and voltage window of electrolytes should be unaffected.

Conventional electrolytes. Ethers and organic carbonates are the two most important solvent chemistries used as electrolytes for lithium metal batteries. Ethers are of fundamental interest because their intrinsic high LUMO energy imparts excellent stability against reduction by the metal.[4] Solvents with even lower LUMO energies like amide and sulfolane based electrolytes, are also reported in literature, due to their tendency to selectively generate a beneficial SEI composition on the lithium metal.[32] The LUMO energy of solvents can also be altered using pendant groups. For example, electron donating groups such as -CH_3, -OH, -NO_2, *etc.* can increase the LUMO energy of the molecule, making it harder to be reduced at the Li plating potential. In contrast, electron withdrawing groups such as -F, -Cl, -Br, double bond, triple bonds, decrease the LUMO energy, facilitating reduction at the electrode and hence incorporation into the SEI. Additionally, depending on the salt concentration in the electrolyte, two additional effects can influence the relative ease with which electrolyte components are reduced and, consequently, the composition of the SEI. Specifically, at all salt concentrations substantial amount of solvent will be coordinated with Li-ions, which impact availability of solvent at the electrode; the relative solvating power, which is defined as the ratio of a test solvent to a reference solvent in terms of the coordination percentage, captures this effect well in a more quantitative manner than dielectric constant or donor numbers (**Figure 3A**).[33,34] In the first effect, solvents with high relative solvating power are able to solvate more Li^+, which will facilitate their transport to the surface of Li metal under the action of an electric field, making them more prone to be reduced. In the second effect, the LUMO energy of the solvent is changed by coordinating with a less than optimal amount of Li^+. As shown in **Figure 3B**, although ether molecules (Dioxolane-DOL and 1,2-Dimethoxyethane-DME) exhibits higher LUMO energy than carbonate solvents, the Li^+–ether complex undergo significant down-regulation of LUMO energy, making it much smaller and more prone to reduction than the complexes of Li^+-carbonate.[35]

In addition to the solvent molecule, the salt may also be reduced at the Li electrode, meaning that it too will participate in the SEI formation chemistry. **Figure 3C** illustrates this effect, by comparing the stability of electrolytes composed of the same solvent but differing salts.[36] The electrochemical reduction potential clearly varies with different salts. The salts mainly contribute the inorganic composition of SEI.[37] The kinetics of the salt decomposition can also be influenced by formation of other reactive species near the surface of the Li metal electrode.[38] Taking the decomposition of Lithium bis(fluorosulfonyl)imide (LiFSI) salt as an example (**Figure 3D**), the decomposition becomes thermodynamically spontaneous under the Li radical attack .[38]

In summary, the SEI generated by the decomposition of electrolytes on metallic lithium is particularly complex because of the low reduction potential of the metal. At the Li reduction potential, nearly all components in an electrolyte are unstable to reductive degradation, meaning that the SEI formation chemistry involves multiple simultaneous reactions of essentially all components in the electrolyte. Moreover, the SEI generated by products formed at higher potentials will hamper mass transfer and electroreduction of more stable solvent molecules/complexes/salts due to its insulating character. As a first step to understanding which components in an electrolyte may dominate the SEI chemistry, Density-functional theory (DFT) calculations can be used to predict the order of decomposition. To illustrate the power of such calculations, we first consider the example of an electrolytes composed of $LiPF_6$-ethylene carbonate (EC)/dimethyl carbonate (DMC). In this electrolyte, the decomposition of the salt and solvent are predicted to take place simultaneously, implying that the SEI will be a thick, organic-inorganic hybrid material.[39] In contrast, in the electrolyte $LiPF_6$/tetrahydrofuran (THF) the decomposition of salt is predicted to occur well before the solvent, with the consequence that the SEI is composed of a thin LiF-dominant inorganic layer. The high bandgap of the LiF also makes the chemistry self-limiting; retarding reduction of the organic component at lower potentials.[39] We note that these simple-sounding principles are quite powerful and can be used to understand the SEI in a broad range of electrolyte systems, including those formed in solid-state Li metal batteries where the electrolyte is a solid state polymer or inorganic material.[40] In these systems, the already high mass transport barrier in the electrolyte bulk plays an additional role in limiting SEI growth to a thinner layer, compared to liquid electrolytes.[41] For inorganic solid electrolytes such as sulfides and NASCION, new interphases will also be generated even at open-circuit by chemical reactions between the electrolyte and lithium metal.

Sacrificial additives. The foregoing suggests that intentionally chosen additives with relatively high reduction potentials would be excellent candidates as sacrificial agents designed to form SEI of a desired chemistry. Indeed, in order to compensate for the shortcomings of conventional electrolytes, different solvents or salts have been added as so-called film forming additives designed to create SEI with desired features, such as high modulus/surface energy, high Li^+ conductivity, high elasticity *etc.* (**Figure 4A**). As discussed earlier, lithium halide, especially LiF, has been for long regarded as an ideal component of SEI for lithium metal. A direct evidence is that the cycle stability of lithium metal can be improved from 75 hours to over 2000 hours by adding LiF into the electrolytes.[42] Fluorinated solvents (Fluoroethylene Carbonate-FEC) and salts ($LiPF_6$ and LiFSI) are generally used as additives to generate LiF rich SEI.[43] In the battery systems where the cathode reaction products are soluble in electrolytes (sulphur, iodine, organic compounds), the SEI must be designed to prevent the Li anode from the attack by the soluble species at the same time. $LiNO_3$, sometimes combined with polysulfides (Li_2S_6 or Li_2S_8) are common additives used for this purpose. They are thought to readily form a passivation layer on the lithium metal that can suppress the shuttle reaction between soluble species and lithium.[44-46] In addition, the SEI (LiN_xO_y and Li_3N) generated by NO_3^- has been argued to possess a high ionic conductivity, which can regulate the lithium morphology to be more spherical and compact rather than needle-like with high surface area.[47]

The large volume change after lithium deposition can cause great stress for the integrity of electrochemical cells. In addition to building a rigid SEI with high enough modulus to prevent the structural change by the imposed stress, an elastic polymer SEI is also good choice to accommodate the volume change. Monomer such as DOL which contain a cyclic structure and unsaturated monomers like VC are known to undergo polymerization on the surface of lithium metal.[48,49] Meanwhile, adding a cross-linker additive, for example, $SiCl_4$, can transform the original SEI to a hybrid SEI consisting of elastic Si-cross-linked polymer and inorganic LiCl with low Li-ion diffusion barrier.[50] In some case, the design of the interphase can also deviate from the traditional solid phase. For example, additives such as Cs^+ have been reported to provide an electrostatic shield around the initially deposited lithium tips with a positive charge. This dynamic interphase will repulse the Li^+ and push its reduction to the neighboring flat substrate, thus suppressing the dendrite growth of lithium metal.[51]

Highly concentrated electrolytes. Electrolytes with high salt concentrations (usually >3~5 M) have gained intensive research in recent years due to their remarkable and unique properties, including the different formation mechanisms of the SEI caused by the coordination environment. In highly concentrated electrolytes (HCEs), the LUMO energy of total electrolytes will shift from the solvent dominant to the salt dominant, therefore the salts can be reduced before solvent at electrode surface.[52] As illustrated in **Figure 4B**, in HCEs, the crowded Li^+ has to be coordinated with both anion and solvent. Therefore, when Li^+ transports to the surface of electrode and undergoes reductive reactions, both anions and solvent will take part in the formation of SEI. The salts that can be dissolved in highly concentrated are typical ionic liquid based such as lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and LiFSI, thus the SEI will be usually in rich of the LiF.[53]

Although the HCEs possess advantages of long-term interfacial stability, the high cost and high viscosity are problematic at the scales required for commercial applications. As the SEI formation chemistry is largely affected by the surrounding environment of Li^+, other strategies have also been designed to prepare conventional electrolytes with similar cation structures. Diluting the HCEs with "inert" diluent to prepare localized HCEs is an emerging approach, in which the coordination structures of Li^+ won't be affected, therefore forming similar SEI with HCE (Figure 4b).[54] The appropriate diluent should exhibit negligible solvating power as well as stability against lithium metal. Highly fluorinated organic solvents such as bis(2,2,2-trifluoroethyl) ether and 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether are considered eligible choices.[54,55] The reactivity of solvents can also be affected with salt additives. Recent study demonstrates that

$LiNO_3$ can reinforces the bulk performance of electrolyte through electrostatically cross-links and strong interaction with solvent molecules, which also results in stable lithium stripping/plating behaviors exceeding 1000 cycles with high coulombic efficiencies over 99%.[56]

Artificial SEI for Li metal

Artificial SEI (ASEI) is a second attractive solution for overcoming shortcomings of intrinsically formed interphases. Because the SEI is created outside an electrochemical cell, the properties and composition of the interphase can be precisely tuned, due to many degrees of freedom, to control the morphology of the electrodeposited metal. Most of the instabilities associated with the SEI can be traced back to its heterogenous phase composition. A stable, homogeneous ASEI with known composition on the current collector or the electrode can overcome these problems and allow structure-property relationships to be well-defined and characterized. Several design features have emerged as important and must be carefully considered when fabricating an ASEI (**Figure 5**).

Mechanical stability. The mechanical modulus of the interphase is a tunable parameter that can be controlled through the structure and chemistry of the SEI. During electrodeposition, the SEI faces large amounts of stress and strain, including the transitions from compressive to tensile stresses due to dendrite growth as well as tensile to compressive stresses due to cavity formations.[57] Mechanically unstable SEI can easily be ruptured under these extreme conditions and allow for penetration of dendrites. These create hotspots, whereby large local flux of Li ions leads to unabated dendrite growth. Even without dendrite formation, the mechanical degradation of the SEI will expose fresh lithium to the electrolytes, leading to the consumption of both lithium and electrolyte. The degradation from mechanic and chemical instabilities accelerate the failure of batteries.

Monroe and Newman's theory predicted that an electrolyte/interphase modulus that is at least twice as high as the metal is required for effective suppression of lithium dendrites.[30] High Young's modulus values in the range of 1-10 Gpa can be achieved with crystalline and semi-crystalline polymers like poly(methyl methacrylate) (PMMA), polystrene and other polymers containing aromatic rings that increase strength via pi-pi stacking. Inorganics like ceramics on the other hand in general consistently offer high Young's modulus, in the range of 10-100 Gpa, which is orders of magnitude higher than that of the metallic Li anode (4.2Gpa), being able to counter the stresses imposed by growing dendrites. Lithium ion conducting inorganics like LiF,[58] Li_3PO_4[59] as well as passive inorganics that solely impart mechanical stiffness at the interface like Al_2O_3[60] and nano-diamond coatings[61] are attractive candidates as high mechanical modulus coatings. Carbon based coatings including graphene oxide,[19, 62] metal coatings such as Sn, Zn, In, Bi,[63,64] are often not considered ASEI as most of them are electronic conductors. However, the electronic resistance will increase with Li-ion insertion and formation of alloy phases, as well as insulating compounds that generate at the same time with alloy, which provides for the sole migration of ions and enable deposition under the ASEI. Moreover, the alloy phase not only exhibits enough stiffness to stop the dendrite growth, but also exhibits strong lithiophilicity and can accommodate the volume change of lithium metal.

Recent works indicate that suppression of dendrites can be also achieved by interphase/electrolytes with lower modulus values than that predicted by Monroe and Newman, through fine-tuning other properties like electrolyte/interphase micro and nanostructure, cation diffusivity and transference number and surface tension forces that synergistically stabilize electrodeposition of the metal.[8] Linear stability analysis has shown that confinement of deposition using nanostructured materials like polymer networks can also effectively suppress dendritic deposition at relatively moderate Young's modulus values.[8] Organic materials like polymers offer advantageous properties like viscoelasticity that can handle high levels of strains and act conformally to accommodate the volume changes of the anode. Ultra-high molecular weight polymers that adsorb on the metal electrode to form a polymeric SEI and self-healing polymers have been demonstrated to stabilize deposition through this mechanism.[65-67] Amorphous polymers with low glass transition temperatures like polyethylene oxide (PEO) based elastomers,[68] polydimethylsiloxane (PDMS)[69] and hydrogen bonded networks,[66,67] have shear modulus within 10 MPa while being able to accommodate a large amount of strain (>100%). These artificial interphases can reduce SEI ruptures due to volume changes and related electrolyte consumption that directly impacts capacity fade over time. The freedom to incorporate different functionalities and tune the network architecture prove attractive for fabrication of a task specific ASEI.[70] Recent coarse-grained model and simulation study reported that the relaxation time of the polymeric ASEI is another key factor in determining stability of the deposition underneath.[71]

However, designing a SEI solely based on these parameters is more complicated than apparent. Recent chemomechanical analyses show that high modulus inorganics with minimally reconfigurable ion-conducting domains in fact lead to unstable electroplating due to density-driven rather than pressure-driven instabilities.[72] This feature points towards design of hybrid systems that can combine the advantageous properties of both inorganics and organic materials while overcoming their shortcomings. Several successful efforts in creating a hybrid ASEI include Si-PEO,[73] Li_3PS_4-PDMS,[74] and Al_2O_3-Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP).[75] Layered organic-inorganic ASEI have also been reported taking inspiration from native SEI formed in fluorinated electrolytes that enable stable electrodepsition.[20, 76-78] These hybrid materials often have multiple interfaces where there can be bottlenecks for efficient transport of ions. Therefore, careful and systematic understanding and design of these materials is vital to enable suppression of dendritic growth in metal anodes via mechanical forces.

Apart from consideration of the above-mentioned physical properties, interfacial strength between the metal electrode and the artificial interphase is also very important as it determines the physical stability of these interphases on the electrode over continuous stripping/plating cycles. A recent DFT study of a polymer/metal interface reports the importance of interfacial adhesion and its effect on the delamination of the polymeric coating from the metal electrode surface.[79] In general, Li_2O and the polymer-metal interface showed higher work of separation values, especially in the presence of reactive chain ends in the polymer (ex. -OH), due to high Li-bonded O density. Polymers with reactive functional ends thus can be a route to creating high adhesion between the artificial interphase and the lithium metal anode.

Chemical stability. An artificial SEI ideally has to be both chemically and electrochemically stable against the lithium metal anode, preventing both faradaic and non-faradaic reactions from the electrolyte components apart from lithium ion reduction. This is an essential characteristic of a stable SEI for preventing the corrosion of the anode over time, according to the SEI model first proposed by Peled.[3] In order to prevent these reactions from the electrolyte components, the ASEI should be electrolyte blocking, ideally allowing only the diffusion of Li^+ ions, while also maintaining electronic insulation. The ASEI should itself possess chemical stability against redox reactions with the lithium metal anode, which demands relatively inert chemistries while electrochemical stability requires the LUMO of the ASEI to be higher than the fermi energy of the metal anode.[22] Polymer networks have been successfully reported to block electrolyte penetration to certain degree. They are attractive candidates for this purpose because in theory, polymer networks have a maximum limit in swelling due to a balance between the entropy of mixing and the entropy of polymer chain configuration. Polyethylene glycol diacrylate (PEGDA)/polyacrylonitrile (PAN),[80] poly(ethylene glycol) dimethacrylate (PEGDMA),[70] and per-fluorinated networks[81,82] are some examples that have been reported to successfully limit electrolyte penetration and side reactions at the anode. Instances where the ASEI reacts conformally to result in favorable decomposition products at the interphase have also been reported. A polymer composite composed of poly(vinylsulfonylfluoride-ran-2-vinyl-1,3-dioxolane) and graphene oxide whereby both the components contained reactive groups towards lithium, was found to stabilize the anode through the formation of compounds like LiF and –COOLi.[83] A copolymer coating that had hydrogen bonding ureido-pyrimidinone (UPy) moieties which were also reactive towards lithium metal was reported to form a self-stabilized tightly adhered interphase that stabilized the anode from corrosion by the bulk electrolyte.[67] A deeper understanding of these interfacial reactions is necessary to lay out design principles in terms of desired chemical composition of the ASEI and demands further in-depth characterizations and mechanistic studies.

Stable and uniform Li^+ ion transport. Heterogenous Li^+ ion transport due to variances in diffusivity at different locations in the native SEI is one of the main triggers of dendritic electrodeposition. For example, first principle calculations have shown that the Li^+ ion diffuses faster along the heterogenous grain boundaries like compared to individual domains.[84] Maintaining uniform and fast Li^+ ion diffusivity is the key to designing a stable ASEI capable of suppressing dendritic growth. Simulations and theoretical analyses on metal electrodeposition have also shown that reaction limited conditions are most favorable for stable deposition, whereby the ratio of reaction to mass transfer flux is low.[85] Anionic polymers and fast ion conducting inorganic solids offer these advantages and are attractive candidates for this purpose. Lithion or lithiated Nafion™ was the first reported single ion conducting polymer as an ASEI.[86,87] The high Li^+ ion transference numbered ensures selective transport of the cations which is favors uniform deposition. Crosslinked ionic networks on the other hand offer both single ion conduction and electrolyte blocking multifunctionality. [81] Recent reports show that the Li^+ ion diffusivity within the interphase should be similar to or greater than that in the bulk for stable deposition.[82] This emphasizes the need to create materials with high Li^+ ion conductivity, and inorganic materials like LLZTO[88] and Li_3PS_4[89] fit well within this category. Apart from diffusivity within the interphase, the surface diffusivity of ions has been widely reported to have a big impact on the morphology of electrodeposited lithium. High surface diffusivity is in general enabled by halogenated compounds like LiF, LiBr and LiI as well as lithiophillic materials like rGO[90] and MOS_2.[91] In general it has also been reported that high surface tension at the ASEI/Metal interface leads to uniform electroplating and this can be used as a guide to fabricating materials.[82,92]

While maintaining high diffusivity within the artificial SEI is crucial, functionality can also be tuned to impact redox reaction kinetics at the electrode surface. In general, Li deposition kinetics at the electrode surface is characterized by exchange current density (J_0) that describes the rate of reaction at zero overpotential. It is generally considered that low exchange current density values are preferred to enable planar electrodeposition.[93] Li deposition at the electrode surface with ideal SEI can be thought to happen over three steps- (i) cation desolvation (ii) diffusion through the SEI, (iii) Charge transfer. While there has been no evidence of direct impact of diffusion through SEI on the exchange current density, cation desolvation and charge transfer impact the exchange current density, depending on the rate limiting step. A growing body of work suggests that tuning the solvation energy of the cation at the interface through ionic polymers or artificial interphases containing functional groups that have high affinity towards the cation is an elegant way to lower exchange current density and enable planar deposition of lithium.[81]

SEI design rules and applications to other metals

Recently, the development of batteries with other metals such as Na, K, Mg, Ca, Zn and Al has also been gaining increasing interests. The variations in physical-chemical performance and surface information point out the different strategies to design the SEI in these metals. In general, Na and K share similar physical-chemical properties with lithium but exhibit more electronegative properties,[94] which results in the different solubility and modulus in the recipes of SEI. Meanwhile, K and Na are softer than metallic Li when comparing the shear modulus, bulk modulus and Mohs hardness, indicating that the dendrite growth is more easily suppressed by physical means. As a comparison, the interphases of multivalent metals (Mg, Ca, Zn and Al) are less understood in the past few decades. The dendrite growths of them are even more dangerous due to the high modulus, especially Zn and Al (**Figure 6A**). To make matters worse, the higher charge density of multivalent ions usually results in the low ion mobility in SEI, increasing the difficulties of designing SEI. In principle, the calculation shows that Mg exhibits lower diffusion barriers than both lithium and sodium, thus Mg has tendency to grow in smooth structures (**Figure 6B**).[85] The hexagonal closest packed (HCP) structure of metal Mg also favors higher-coordinated configurations than face-centered cubic (BCC) metals (Li and Na).

Comparison of SEI formed on alkali metals. Although Na shares a lot of similarities with Li, the SEI forming on sodium is somewhat different. A comparison of ionic diffusion through first-principles calculation shows that both LiF and NaF, vacancy defects are more favorable for ion transport, in which the Li-ion transports faster through LiF with higher diffusion coefficient than the diffusion of Na-ion through NaF (**Figure 6C**).[96] In carbonate SEI, the Na-ion in general diffuses a little faster through Na_2CO_3 than that Li-ion diffuses in Li_2CO_3 (**Figure 6C**).[97,98] It is also simulated that Na^+ can also be transported through Li-SEI (LiF and Li_2CO_3) with preferred knock-off and vacancy mechanisms. In comparison, Li^+ prefers to migrate through Na-based SEI (NaF and Na_2CO_3) involving interstitial ion by direct hopping or knock off mechanism (**Figure 6D**).[99] In principle, due to lower polarity of Na^+, most Na-SEI is soluble than Li-SEI,[100] which leads to much lower stripping/plating efficiencies of Na than Li in electrolytes especially in carbonate electrolytes and results in the higher capacity loss of Na-metal after pausing in the electrolytes (**Figure 6E**).[100,101] However, in certain electrolytes (For example, $NaPF_6$ in diglyme), the average coulombic efficiency of Na plating/stripping can reach 99.9%,[102] a value that has never been achieved by Li metal, which is contributed by the generation of inorganically rigid Na_2O and NaF SEI. Inspired by the less soluble Li-based SEI, recent works also demonstrate that building a stable Li-SEI on sodium metal have been proved as an effective method to protect sodium metal, even in challenging carbonate based electrolytes,[103] providing a new approach of heterosexual-design of SEI.

In most case, due to similar chemical properties, most additives such as DOL that is used to form polymer SEI on Li surface, and FEC that forms inorganic/organic F compounds also works for Na metal.[104] However, in some case, the additives that can generate ideal SEI for lithium metal ($LiNO_3$), their analogues ($NaNO_3$) have negative effects on sodium metal.[105] The SEI formed by $NaNO_3$ is thought to fail to prevent the further decomposition of electrolytes. Due to the more negative electrochemical potential of Li^+/Li, Li^+ can provide a shielding effect for Na^+, forming a dynamic interphase to regulate the deposition of Na metal. This theory results in the flat deposition of Na metal when using Li/Na alloy as anode[104] or Li/Na hybrid electrolytes[106].

Potassium metal is the softest metal among all the anodes and shares a lot of similarities with Li and Na. The over reactivity of K, especially towards solvent, results in the SEI is even more unstable than the alkali analogues. Forest dendrite like morphologies of K is observed at a small plating current density of 0.2 mA/cm^2.[107] HCEs are one of the most effective approaches to stabilize the interphase of K metal.[107]

SEI on multivalent metals. For a cation, the higher charge number and lower ionic radius result in the higher ability of polarization. In this case, Li and Mg share a lot of similarities in chemical properties. Although Mg surface exhibits low diffusion barrier, fractal Mg dendrites are still observed in recent studies.[108] The high shear modulus of Mg raised more challenges to design SEI to regulate its growth. Mg usually undergoes reversible stripping/plating only in highly corrosive and low oxidative stable electrolytes (for example, Grignard reagents). The traditional carbonate electrolytes (for example, Propylene carbonate-PC) are regarded to be reduced on the surface of Mg, forming less conductive SEI and suppressing the reversible stripping/plating of Mg. An artificial Mg SEI built by the thermal cyclization of PAN units with the presence of Mg salts shows a high ionic conductivity (1.19×10^{-6} S cm^{-1}). Combining with the thin thickness of ~100nm, this artificial SEI enable the reversible stripping/plating in carbonate electrolytes ($Mg(TFSI)_2$ in PC).[109] As an element in same group, Ca metal is regarded to face similar problem. The surface of Ca seem immediately covered by the ionically insulating SEI due to decomposition of electrolytes.[110] Cross-linked borate polymers are suggested as conducting components for Ca-ion migration.[110] Forming alloy interphases (for example, Ca-Sn alloys) can also protect the Ca anode from the passivation by the electrolytes.[111] Trivalent metal Al anode with highest volume specific capacity (8040 mAh cm^{-3}) also faces sluggish kinetics in traditional electrolytes, which usually undergoes reversible electrochemistry under highly corrosive ionic liquid (IL) based electrolytes such as the mixture of $AlCl_3$ and – 1-ethyl-3-methylimidazolium chloride (EMImCl). Recent studies reveal that the IL electrolytes in facts work by forming an artificial SEI on Al surface, through removing the original highly resistant oxidation layer. This ASEI on Al metal can even enable the operation of Al anode under aqueous media, demonstrating the importance of designing SEI on multivalent metals.[112]

Zn metal has a long history as anode of battery. The compatibility with water enables intrinsic safety of Zinc chemistry in aspects of noninflammability. However, shape change and even dendrite formation at high Zn utilizations traps the large scale application of rechargeable Zn batteries.[113] In alkaline electrolytes, the formation of soluble ZnO_2^{2-} at anode side will shuttle to the cathode side and cause its structure distortion. New interfacial layers including cation selective membrane and $Ca(OH)_2$ have been applied to stabilized the Zinc anode side.[113,114] Additives of polymer such polyethlenime are regarded to be adsorbed on the surface of Zinc, suppressing the dendrites growth by slowing down the kinetics of deposition.[115] To solve the dendrite growth of zinc metal, a strategy of epitaxial eletrodeposition is applied, in which a graphene interfacial layer with low lattice mismatch with Zn is designed as new interphase to deposit Zinc. The growth of Zn on graphene is planar, with a locked orientation relation, and exhibits high reversibility with coulombic efficiency of 99.9 % over 10000 cycles.[116]

Due to the low ionic conductivity, designing traditional SEI on multivalent metal which allows the transport of zinc ion and deposit of Zn underneath the SEI is rather difficult.[117] Zinc metal originally forms a dense layer composed of $Zn_5(CO_3)_2(OH)_6$ in the atmosphere of air and moisture, which can be corroded in mild acid electrolytes (for example, $ZnSO_4$) and transferred to a loose interphase of $Zn_4SO_4(OH)_6 \cdot xH_2O$. This uneven SEI can't stop the continuously corrosion of Zn, resulting in the dendrite growth and low coulombic efficiencies of Zn stripping/plating.[118] ASEI of ZnS with ionic conductivity of ~1.3×10^{-5} S/cm have been fabricated as ASEI on Zinc metal with extended cycle life.[118]

Characterizing structure, properties, and geometrical features of the SEI

Understanding the composition, morphologies, and mechanical properties of SEI is important to direct further design of interphases on metal anode.[94] Due to the elusory and highly dynamic properties, various approaches need to join hands together to thoroughly recognize SEI at the atomic level. Previous studies mainly focus on spectroscopic techniques, such as FTIR, Raman XPS, which is sensitive enough to study the functional groups on the surface of electrode. These traditional techniques continuously upgrade as recent work shows that Tip-enhanced Raman spectroscopy can be used to unveil the SEI at nanoscale.[119] As the SEI is usually covered by the electrolyte, the strong absorption of beam by electrolyte traps the characterization by X-ray reflectometry in the native state. In comparison, Neutron reflection endowed with high penetration power is possible to probe the interphase even with the electrolyte on it. The intrinsically interface-sensitive nature of neutron refection can also enable the detection of SEI with nanoscale thickness.[120]

In order to trace the SEI in their native states, and meanwhile, observe the different morphologies that lacked understanding since its definition in 1970s, Cryo-electron beam based techniques have provided the possibility to observe the lightweight metal without damage by the electron beam.[20] At cryogenic temperatures, Li metal and the SEI does not react with the liquid nitrogen.[20,21] Both Mosaic-type and multilayer-type SEI have been observed in various electrolytes. Combining with mill trenching and lifting out tools, the lithium metal as well as frozen electrolyte on the top of lithium metal can be transferred for TEM test in their native state.[21] According to the results of electron-energy-loss spectroscopy (EELS), lithium hydride

(LiH) is found as one of the main interphase components on dendrite lithium. This result confirms the high reactivity of lithium metal, and also indicates the differences in SEI on lithium metal and graphite in lithium ion batteries. Comparing with XPS technique that generally investigates the SEI in micro-scale, Cryo-TEM can detect the SEI in nano-scale. One distinguished result from Cryo-TEM is that LiF, which is regarded as an important SEI to stabilize the Li metal, is not located in the compact SEI, but distribute across the electrode surface as particles.[78] The non-compact LiF rich SEI promotes a slightly higher coulombic efficiency by reducing porosity of the deposited lithium, it doesn't prevent dead lithium dissolution through the SEI. Organic fluorine containing flexible polymeric components of the SEI formed through polymerization of solvents/additives like FEC are more effective in preventing dead lithium dissolution by formation of a more compact SEI. This result demonstrates that the LiF may be quite dynamic and the cooperation of LiF with flexible SEI components such as polymer and oligomers synergistically stabilize lithium anode.

Nuclear magnetic resonance (NMR) techniques, especially ^{7}Li,[121] ^{19}F,[121] and ^{23}Na[122] spectra can be applied to quantify the structures of SEI due to their different chemical shifts. Combining with Magnetic resonance imaging (MRI), the microstructures including dendrite/mossy metal deposition can also be characterized.[122] In addition, sodium hydride NaH was also discovered as one of SEI components on the surface of sodium metal with NMR.[122] In operando real-time mass spectrometric technique has also been used to reveal the dynamic double layer SEI, where the inner SEI is a thin and denser inorganic rich layer that functions as Li-ion conductor and electron insulation, and outer layer is organic rich compound.[123] Both the formation of SEI and orphaning lithium will cause the lithium metal loss reversibility. The titration gas chromatography can be used to quantify the contribution.[124] The amount of orphaning lithium (dead lithium) is still chemically reactive, of which the content can be calculated through the reaction with water and measure the amount of generated H_2.

The transport properties of SEI are usually characterized by electrochemical impedance spectroscopy (EIS), where an equivalent circuit can be drawn to fit the resistance contributed by the SEI layer. For example, with an artificial SEI on electrode, the Nyquist plots can be fitted by an equivalent circuit composed of a bulk resistance, in series with a SEI component represented by a SEI capacitance in parallel with SEI resistance and in series with a charge transfer component represented by a double layer capacitance in parallel with charge transfer resistance.[82] Combining with the operando electrochemical quartz crystal microbalance (E-QCM),[125] the relationship between ion transport and composition of SEI can be understand synchronously. E-QCM is able to confirm the components by measuring the mass changes of electrodes with an accuracy of nanograms and is able to identify the molecular level composition by estimating the charge that accumulates on the electrode.

The mechanical strength of SEI is significant to suppress the dendrite growth, and electron probe technologies can quantitatively measure properties such as Young's modulus. The results of in-situ studies, combining with atomic force microscopy (AFM) and environmental transmission electron microscopy (TEM), prove that the dendritic Li deposition is caused by sluggish Li transport on the surface of deposited Li.[126] Meanwhile, the growth stress of lithium measured by this technology is up to 130 MPa, a value higher than the bulk, pointing out more challenges to design interphase for suppressing dendrite.[127]

Considering the difficulties to characterize the SEI using various techniques, theoretical simulation and calculation have also been used to predict the properties of the SEI. Brownian dynamics simulation shows that through thinning the SEI layer into a sub-nanometer scale, the radial diffusion of Li^+ results in an isotropic growth and suppresses the dendritic electrodeposition.[128] Linear analysis indicates that morphological instabilities of metal deposition can be suppressed by increased the surface tension through controlling the SEI. Meanwhile, ASEI with high elastic stresses as well as fixed anions can also enhance the interfacial stability.[129]

Conclusions, Perspectives, and Outlook

A large and growing body of work has identified the key roles played by the solid electrolyte interphase (SEI) in regulating ion transport, modulating interfacial energy and mechanics, and in passivating electrodes in contact with electrolytes outside their stability limits. Armed with results from more or less continuous explorations over the last 40 years, it is now understood that while it is generally not possible to spontaneously form SEI able to perform all of these functions, simultaneously, artificial SEI that approach these ideals are possible. Progress has been noticeably faster over the last few years as development of new, more powerful methods, including focused ion beams, cyro-TEM, in-situ electron spectroscopies, and efficient computational chemistry methods that need not ignore solvation effects have enabled the SEI formed at interphases to be interrogated in essentially any native electrolyte environment. These advances are for the first time allowing contributors in the field to move beyond simply playing the role of advocates for one presumed configuration of the SEI over others, typically with limited evidence, to the role of practitioners able to isolate and characterize the SEI. While there remains much room for progress, results from the most careful of these studies suggest that the SEI is generally not the idealized nanometer thin film depicted in older reviews and in texts, but that it is truly a dynamic material phase that grows, breaks, and reforms according to known rules associated with transport, mechanics, and electrochemical reaction kinetics, that can be reduced to analytical expressions in bulk systems. The fundamental challenge is that because electrochemical cells of contemporary interest are closed systems, these dynamics must be rigorously controlled to facilitate long-term cell reversibility over the hundreds or thousands of plating and stripping cycles demanded for practical battery operations.

The challenges associated with rational design of stable, functional SEI at metal electrodes are compounded when multivalent metals (*e.g.* Mg, Zn, Al) are involved. Multivalent metal anodes have been gaining intensive attention in the literature due to their promise of lower cost and compatibility with intrinsically safer liquid electrolytes, because the SEI must also promote fast desolvation kinetics of the *sticky* metal ions. This is an area where surprisingly little has been published, but where the opportunities for rapid advances can be made using methods under development for better studied metals such as Li. For example, the common assumption that the SEI is unimportant in chemically inert metal electrodes when used in tandem with aqueous electrolyte systems, is easily falsified by a simple assessment of the plethora of electrodeposit morphologies that can be induced in aqueous Zn batteries by simply changing the electrolyte salt. Indeed, we predict that the ability to simulate morphological features considered unique to metals such as Li and Na which form heterogenous SEI in aprotic liquid electrolytes in less reactive metals such as Zn, will provide the first concrete step towards electrolyte designs able to achieve the nearly immortal anode lifetimes required for Li and Na electrodes to enable their potential for high-energy storage in practical battery cells.

A handful of solvents and salts including ethers, $LiNO_3$, LiFSI *etc*, have emerged as particularly promising for their ability to form stable SEI on the most active metal anodes. A serious drawback is that these components typically exhibit poor oxidative stability and as such are not good candidates for the current metal battery paradigm in which a metal anode is paired with a high-voltage cathode. The most careful studies show that these compounds for SEI formation at the anode side of the battery cell, will generally either decompose at high voltage or corrode the current collector. Preparing highly concentrated electrolytes (aprotic or non-aprotic) has been demonstrated as an effective method to enlarge the stable window of liquid electrolytes, but this introduces new challenges associated with cost. Although not the focus of this review, we see the challenge of building a stable cathode electrolytes interphase (CEI) for such systems as a complementary challenge in need of focused efforts. The design rules for such a CEI are not remarkable – it must be mechanically and electrochemically stable at oxidizing cathode potentials; it must selectively regulate electrolyte access to prevent electrolyte decomposition at a cathode surface that may possess sites (*e.g.*, Ni-rich) that catalyze degradation of the electrolyte; and finally it must prevent co-intercalation of solvent in the cathode and its formation must not produce structural distortion of cathode. They are difficult to realize in practice, however, because few electrolytes can meet the first of these criteria particularly in intercalating transition metal oxide cathodes where high voltage operation are a requirement to compensate for the intrinsically low specific capacity.

Highly fluorinated solvents and salts provide what presently seems the most intellectually robust platform for spontaneously creating interphases with the required thermodynamic stability at both the reducing and oxidizing potentials at the anode and cathode, respectively. The most serious impediment is again generally considered to be related to cost, however when one considers the scale at which such components will be needed for practical, commercial impacts the environmental costs may ultimately prove more important. These considerations lead us to conjecture that two-compartment batteries will emerge as a viable option for managing the conflicting needs in cells where a metal anode must be paired with a high-voltage cathode. Building ASEI on the metal provides perhaps the simplest way of creating a localized anode-side environment (*e.g.*, composed of a polymerized ether and salts such as LiFSI or $LiNO_3$) that is physically separate from the cathode. If such a system can be designed in which the chosen anode salt is miscible in the ASEI but essentially immiscible with the electrolyte bulk, it may be possible to create batteries in a two-compartment design at a practical scale. We note however that fabricating the ASEI on a reactive metal electrode, maintaining the homogeneity of the ASEI on metal foil at large scales, and development of ASEI-bulk electrolyte systems that facilitate good interfacial ion transport between the electrolyte bulk and anode are all unsolved problems at present. We have shown previously that a strategy in which the ASEI is first fabricated on a mechanically hard, but chemically inert substrate (*e.g.* Cu, Al, etc.), and then transferred to a more reactive metal electrode of interest (*e.g.* Li, Na) in a roll-to-roll process provides a simple method of overcoming the first two of these challenges. Direct deployment of the ASEI-passivated Cu in an anode-free cell is another approach that has potential for solving all three challenges, but the electrode reversibility requirements for long-term cycling are higher than those reported in all but a small number of literature studies.

Finally, we note that metal electroplating is a traditional field with widespread applications outside the energy storage area. The systems are typically open and the role played by thin material layers on electrodeposit quality and uniformity largely ignored. Thus while numerous additives, including *leveling agents*, *suppressors, grain refining agents, and wetting agents* and so on, are widely used to improve electrodeposit uniformity and to control morphology, fundamental understanding of how these additives work is lacking. We foresee good opportunities for leveraging advances made in understanding the SEI in the more rigorous, closed-system context of a secondary/rechargeable metal anode battery, to develop more precise strategies for achieving finer control of catalytic or anticorrosion properties of electrodeposited metal films. As an interdisciplinary science arguably at its early stages, we see good opportunities for both newcomers and established alike who are willing to leverage advanced experimental, computer simulation, and theoretical tools push forward fundamental understanding of the SEI.

Author contributions

Q.Z., S.S., and L.A.A. researched data for the article. All authors contributed to the discussion of content, and writing and editing of the article prior to submission

Competing interests statement

The authors declare no competing interests.

Acknowledgements

The research was supported by the National Science Foundation, Partnerships for Innovation Program under award # IIP-1919013 and by the Beijing Institute of Collaborative Innovation.

References

1 Castelvecchi, D., and Stoye, E. (2019). Chemistry Nobel honours world-changing batteries. Nature *574*, 308.

2 Peled, E., and Menkin, S. (2017). Review—SEI: Past, present and future. J.Electrochem. Soc. *164*, A1703-A1719.

3 Peled, E. (1979). The electrochemical behavior of alkali and alkaline earth metals in nonaqueous battery systems—the solid electrolyte interphase model. J. Electrochem. Soc. *126*, 2047.

4 Xu, K. (2004). Nonaqueous liquid electrolytes for lithium-based rechargeable batteries. Chem. Rev. *104*, 4303-4417.

5 Cheng, X. B., Zhang, R., Zhao, C. Z. and Zhang, Q. (2017). Toward safe lithium metal anode in rechargeable batteries: a review. Chem. Rev. *117*, 10403-10473.

6 Liu, J., Bao, Z. N., Cui, Y., Dufek, E. J., Goodenough, J. B., Khalifah, P., Li, Q. Y., Liaw, B. Y., Liu, P., Manthiram, A. et al. (2019). Pathways for practical high-energy long-cycling lithium metal batteries. Nat. Energy *4*, 180-186.

7 Schmitz, R., Ansgar Müller, R., Wilhelm Schmitz, R., Schreiner, C., Kunze, M., Lex-Balducci, A., Passerini, S., and Winter, M. (2013). SEI investigations on copper electrodes after lithium plating with Raman spectroscopy and mass spectrometry. J. Power Sources *233*, 110-114.

8 Tikekar, M. D., Choudhury, S., Tu, Z., and Archer, L. A. (2016). Design principles for electrolytes and interfaces for stable lithium-metal batteries. Nat. Energy *1*, 16114.

9 Liu, W., Liu, P., and Mitlin, D. (2020). Tutorial review on structure-dendrite growth relations in metal battery anode supports. Chem. Soc. Rev. *49*, 7284-7300.

10 Scarr, R. F. (1970). Kinetics of the solid lithium electrode in propylene carbonate. J. Electrochem. Soc. *117*, 295.

11 Aurbach, D., Ein-Ely, Y., and Zaban, A. (1995). The study of electrolyte solutions based on ethylene and diethyl carbonates for rechargeable li batteries. J. Electrochem. Soc. *142*, 2873-2882.

12 Peled, E. (1997). Advanced model for solid electrolyte interphase electrodes in liquid and polymer electrolytes. J.Electrochem. Soc. *144*, L208.

13 Ein-Eli, Y. (1999). A new perspective on the formation and structure of the solid electrolyte interface at the graphite anode of Li-Ion cells. Electrochem. Solid-State Lett. *2*, 212.

14 Cao, X., Ren, X., Zou, L., Engelhard, M. H., Huang, W., Wang, H., Matthews, B. E., Lee, H., Niu, C., Arey, B. W., et al. (2019). Monolithic solid–electrolyte interphases formed in fluorinated orthoformate-based electrolytes minimize Li depletion and pulverization. Nat. Energy *4*, 796-805.

15 Dey, A. N. (1977). Lithium anode film and organic and inorganic electrolyte batteries. Thin Solid Films *43*, 131-171.

16 D. Aurbach, M. L. Daroux, Faguy, P. W., and Yeager, E. (1987). Identification of surface films formed on lithium in propylene carbonate solutions. J. Electrochem. Soc. *134*, 1611.

17 Liebenow, C., and Luhder, K. (1996). Electrochemical characterization of polymer precoated lithium electrodes. J. Appl. Electrochem. *26*, 689-692.

18 Chung, K.-i., Kim, W.-S., and Choi, Y.-K. (2004). Lithium phosphorous oxynitride as a passive layer for anodes in lithium secondary batteries. J. Electroanalytical Chem. *566*, 263-267.

19 Zheng, G., Lee, S. W., Liang, Z., Lee, H. W., Yan, K., Yao, H., Wang, H., Li, W., Chu, S., and Cui, Y. (2014). Interconnected hollow carbon nanospheres for stable lithium metal anodes. Nat. Nanotech. *9*, 618-623.

20 Li, Y., Li, Y., Pei, A., Yan, K., Sun, Y., Wu, C. L., Joubert, L. M., Chin, R., Koh, A. L., Yu, Y., et al. (2017). Atomic structure of sensitive battery materials and interfaces revealed by cryo-electron microscopy. Science *358*, 506-510.

21 Zachman, M. J., Tu, Z., Choudhury, S., Archer, L. A., and Kourkoutis, L. F. (2018). Cryo-STEM mapping of solid-liquid interfaces and dendrites in lithium-metal batteries. Nature *560*, 345-349.

22 Goodenough, J. B., and Park, K. S. (2013). The Li-ion rechargeable battery: a perspective. J. Am. Chem. Soc. *135*, 1167-1176.

23 Becking, J., Gröbmeyer, A., Kolek, M., Rodehorst, U., Schulze, S., Winter, M., Bieker, P., and Stan, M. C. (2017). Lithium-metal foil surface modification: an effective method to improve the cycling performance of lithium-metal batteries. Adv. Mater. Interfaces *4*, 1700166.

24 https://materials.nrel.gov/queryStd.

25 Ling, C., Zhang, R., Takechi, K., and Mizuno, F. (2014). Intrinsic barrier to electrochemically decompose Li_2CO_3 and LiOH. J. Phys. Chem. C *118*, 26591-26598.

26 Ozhabes, Y., Gunceler, D., and Arias, T. A. (2015). Stability and surface diffusion at lithium-electrolyte interphases with connections to dendrite suppression. doi:arXiv:1504.05799.

27 Tasker, P. W. (1979). The surface energies, surface tensions and surface structure of the alkali halide crystals. Philosophical Magazine A *39*, 119-136.

28 Schweidler, S. et al. (2018). Volume changes of graphite anodes revisited: a combined operando X-ray diffraction and in situ pressure analysis study. J. Phys. Chem. C *122*, 8829-8835.

29 Lin, D., Liu, Y., and Cui, Y. (2017). Reviving the lithium metal anode for high-energy batteries. Nat. Nanotech. *12*, 194-206.

30 Monroe, C., and Newman, J. (2005). The impact of elastic deformation on deposition kinetics at lithium/polymer interfaces. J. Electrochem. Soc. *152*, A396-A404.

31 Mason, W. P. (1965). Physical acoustics: principles and methods. volume III-Part B, 61.

32 Shin, N., Ryu, K. H., Kim, Y.-G., and Lee, H.-T. (2014) Improved cyclic performances of li-sulfur batteries with sulfone-based electrolyte. SAE International, *01*,1844.

33 Su, C.-C., He, M., Amine, R., Rojas, T., Cheng, L., Ngo, A. T., and Amine, K. (2019). Solvating power series of electrolyte solvents for lithium batteries. Energy Environ. Sci.*12*, 1249-1254.

34 Su, C.-C., He, M., Amine, R., Chen, Z., and Amine, K. (2018). The relationship between the relative solvating power of electrolytes and shuttling effect of lithium polysulfides in lithium-sulfur batteries. Angew. Chem. Int. Ed. *130*, 12209-12212.

35 Chen, X., Li, H. R., Shen, X., and Zhang, Q. (2018). The origin of the reduced reductive stability of ion-solvent complexes on alkali and alkaline earth metal anodes. Angew. Chem. Int. Ed. *57*, 16643-16647.

36 Delp, S. A., Borodin, O., Olguin, M., Eisner, C. G., Allen, J. L., and Jow, T. R. (2016). Importance of reduction and oxidation stability of high voltage electrolytes and additives. Electrochimica Acta *209*, 498-510.

37 Parimalam, B. S., and Lucht, B. L. (2018). Reduction reactions of electrolyte salts for lithium ion batteries: $LiPF_6$, $LiBF_4$, LiDFOB, LiBOB, and LiTFSI. J. Electrochem. Soc. *165*, A251-A255.

38 Camacho-Forero, L. E., Smith, T. W., and Balbuena, P. B. (2016). Effects of high and low salt concentration in electrolytes at lithium–metal anode surfaces. J. Phys. Chem. C *121*, 182-194.

39 Chen, J., Fan, X., Li, Q., Yang, H., Khoshi, M. R., Xu, Y., Hwang, S., Chen, L., Ji, X., Yang, C., et al. (2020). Electrolyte design for LiF-rich solid–electrolyte interfaces to enable high-performance microsized alloy anodes for batteries. Nat. Energy *5*, 386-397.

40 Banerjee, A., Wang, X. F., Fang, C. C., Wu, E. A., and Meng, Y. S. (2020). Interfaces and interphases in all-solid-state batteries with inorganic solid electrolytes. Chem. Rev. *120*, 6878-6933.

41 Zhao, Q., Liu, X., Stalin, S., Khan, K., and Archer, L. A. (2019). Solid-state polymer electrolytes with in-built fast interfacial transport for secondary lithium batteries. Nat. Energy *4*, 365-373.

42 Lu, Y., Tu, Z., and Archer, L. A. (2014). Stable lithium electrodeposition in liquid and nanoporous solid electrolytes. Nat. Mater. *13*, 961-969.

43 Zhang, X. Q., Cheng, X. B., Chen, X., Yan, C., and Zhang, Q. (2017). Fluoroethylene carbonate additives to render uniform li deposits in lithium metal batteries. Adv. Funct. Mater. *27*, 1605989.

44 Li, W., Yao, H., Yan, K., Zheng, G., Liang, Z., Chiang, Y. M., and Cui, Y. (2015). The synergetic effect of lithium polysulfide and lithium nitrate to prevent lithium dendrite growth. Nat. Commun. *6*, 7436.

45 Zhao, Q., Lu, Y., Zhu, Z., Tao, Z., and Chen, J. (2015). Rechargeable lithium-iodine batteries with iodine/nanoporous carbon cathode. Nano Lett. *15*, 5982-5987.

46 Zhang, K., Guo, C., Zhao, Q., Niu, Z., and & Chen, J. (2015). High-performance organic lithium batteries with an ether-based electrolyte and 9,10-anthraquinone (AQ)/CMK-3 cathode. Adv. Sci. *2*, 1500018.

47 Chen, X. R., Yao, Y. X., Yan, C., Zhang, R., Cheng, X. B., and Zhang, Q. (2020). A diffusion--reaction competition mechanism to tailor lithium deposition for lithium-metal batteries. Angew. Chem. Int. Ed. *59*, 7743-7747.

48 Wang, Y., Lin, C. F., Rao, J., Gaskell, K., Rubloff, G., and Lee, S. B. (2018). Electrochemically controlled solid electrolyte interphase layers enable superior Li-S batteries. ACS Appl. Mater Interfaces *10*, 24554-24563.

49 Ota, H., Shima, K., Ue, M., and Yamaki, J.-i. (2004). Effect of vinylene carbonate as additive to electrolyte for lithium metal anode. Electrochimica Acta *49*, 565-572.

50 Zhao, Q., Tu, Z., Wei, S., Zhang, K., Choudhury, S., Liu, X., and Archer, L. A. (2018). Building organic/inorganic hybrid interphases for fast interfacial transport in rechargeable metal batteries. Angew. Chem. Int. Ed. *57*, 992-996.

51 Ding, F., Xu, W., Graff, G. L., Zhang, J., Sushko, M. L., Chen, X., Shao, Y., Engelhard, M. H., Nie, Z., Xiao, J., et al. (2013). Dendrite-free lithium deposition via self-healing electrostatic shield mechanism. J. Am. Chem. Soc. *135*, 4450-4456.

52 Yamada, Y., Wang, J., Ko, S., Watanabe, E., and Yamada, A. (2019). Advances and issues in developing salt-concentrated battery electrolytes. Nat. Energy *4*, 269-280.

53 Suo, L. M., Borodin, O., Gao, T., Olguin, M., Ho, J., Fan, X. L., Luo, C., Wang, C. S. , and Xu, K. (2015). "Water-in-salt" electrolyte enables high-voltage aqueous lithium-ion chemistries. Science *350*, 938-943.

54 Chen, S., Zheng, J., Mei, D., Han, K. S., Engelhard, M. H., Zhao, W., Xu, W., Liu, J. , and Zhang, J. G. (2018). High-voltage lithium-metal batteries enabled by localized high-concentration electrolytes. Adv. Mater. *30*, e1706102.

55 Ren, X., Chen, S., Lee, H., Mei, D., Engelhard, M. H., Burton, S. D., Zhao, W., Zheng, J., Li, Q., Ding, M. S., et al. (2018) Localized high-concentration sulfone electrolytes for high-efficiency lithium-metal batteries. Chem *4*, 1877-1892.

56 Zhao, Q., Liu, X., Zheng, J., Deng, Y., Warren, A., Zhang, Q., and Archer, L. (2020). Designing electrolytes with polymerlike glass-forming properties and fast ion transport at low temperatures. PNAS *117*, 26053-26060.

57 Hao, F., Verma, A., and Mukherjee, P. P. (2018). Mechanistic insight into dendrite–SEI interactions for lithium metal electrodes. J. Mater. Chem. A *6*, 19664-19671.

58 Lin, D., Liu, Y., Chen, W., Zhou, G., Liu, K., Dunn, B., and Cui, Y. (2017). Conformal lithium fluoride protection layer on three-dimensional lithium by nonhazardous gaseous reagent freon. Nano Lett. *17*, 3731-3737.

59 Li, N. W., Yin, Y. X., Yang, C. P., and Guo, Y. G. (2016). An artificial solid electrolyte interphase layer for stable lithium metal anodes. Adv. Mater. *28*, 1853-1858.

60 Wang, L., Zhang, L., Wang, Q., Li, W., Wu, B., Jia, W., Wang, Y., Li, J., and Li, H. (2018). Long lifespan lithium metal anodes enabled by Al_2O_3 sputter coating. Energy Storage Mater. *10*, 16-23.

61 Liu, Y., Tzeng, Y.-K., Lin, D., Pei, A., Lu, H., Melosh, N. A., Shen, Z.-X., Chu, S., and Cui, Y. (2018). An ultrastrong double-layer nanodiamond interface for stable lithium metal anodes. Joule *2*, 1595-1609.

62 Lin, D., Liu, Y., Liang, Z., Lee, H. W., Sun, J., Wang, H., Yan, K., Xie, J., and Cui, Y. (2016). Layered reduced graphene oxide with nanoscale interlayer gaps as a stable host for lithium metal anodes. Nat. Nanotech. *11*, 626-632.

63 Liang, X., Pang, Q., Kochetkov, I. R., Sempere, M. S., Huang, H., Sun, X., and Nazar, L. F. (2017). A facile surface chemistry route to a stabilized lithium metal anode. Nat. Energy *6*, 17119.

64 Tu, Z., Choudhury, S., Zachman, M. J., Wei, S., Zhang, K., Kourkoutis, L. F., and Archer, L. A. (2018). Fast ion transport at solid–solid interfaces in hybrid battery anodes. Nat. Energy *3*, 310-316.

65 Wei, S., Cheng, Z., Nath, P., Tikekar, M. D., Li, G., and Archer, L. A. (2018). Stabilizing electrochemical interfaces in viscoelastic liquid electrolytes. Sci. Adv. 4, eaao6243.

66 Liu, K., Pei, A., Lee, H. R., Kong, B., Liu, N., Lin, D., Liu, Y., Liu, C., Hsu, P. C., Bao, Z., et al. (2017). Lithium metal anodes with an adaptive "solid-liquid" interfacial protective layer. J. Am. Chem. Soc. *139*, 4815-4820.

67 Wang, G., Chen, C., Chen, Y., Kang, X., Yang, C., Wang, F., Liu, Y., and Xiong, X. (2020). Self-stabilized and strongly adhesive supramolecular polymer protective layer enables ultrahigh-rate and large-capacity lithium-metal anode. Angew. Chem. Int. Ed. *59*, 2055-2060.

68 Assegie, A. A., Cheng, J. H., Kuo, L. M., Su, W. N., and Hwang, B. J. (2018). Polyethylene oxide film coating enhances lithium cycling efficiency of an anode-free lithium-metal battery. Nanoscale *10*, 6125-6138.

69 Li, Q., Zeng, F.-L., Guan, Y.-P., Jin, Z.-Q., Huang, Y.-Q., Yao, M., Wang, W.-K., and Wang, A.-B. (2018). Poly (dimethylsiloxane) modified lithium anode for enhanced performance of lithium-sulfur batteries. Energy Storage Mater. *13*, 151-159.

70 Choudhury, S., Stalin, S., Vu, D., Warren, A., Deng, Y., Biswal, P., and Archer, L. A. (2019). Solid-state polymer electrolytes for high-performance lithium metal batteries. Nat. Commun. 10, 4398.

71 Kong, X., Rudnicki, P. E., Choudhury, S., Bao, Z. N., and Qin, J. (2020). Dendrite suppression by a polymer coating: a coarse-grained molecular study. Adv. Funct. Mater. *30*, 1910138.

72 Fu, C., Venturi, V., Kim, J., Ahmad, Z., Ells, A. W., Viswanathan, V., and Helms, B. A. (2020). Universal chemomechanical design rules for solid-ion conductors to prevent dendrite formation in lithium metal batteries. Nat. Mater. *19*, 758-766.

73 Choudhury, S., Agrawal, A., Wei, S., Jeng, E., and Archer, L. A. (2016). Hybrid hairy nanoparticle electrolytes stabilizing lithium metal batteries. Chem. Mater. *28*, 2147-2157.

74 Pang, Q., Zhou, L., and Nazar, L. F. (2018). Elastic and Li-ion-percolating hybrid membrane stabilizes Li metal plating. PNAS. *115*, 12389-12394.

75 Lee, H., Lee, D. J., Kim, Y.-J., Park, J.-K., and Kim, H.-T. (2015). A simple composite protective layer coating that enhances the cycling stability of lithium metal batteries. J.Power Sources *284*, 103-108.

76 Kozen, A. C., Lin, C.-F., Zhao, O., Lee, S. B., Rubloff, G. W., and Noked, M. (2017). Stabilization of lithium metal anodes by hybrid artificial solid electrolyte interphase. Chem. Mater. *29*, 6298-6307.

77 Zhao, Y., Amirmaleki, M., Sun, Q., Zhao, C. T., Codirenzi, A., Goncharova, L. V., Wang, C. H., Adair, K., Li, X., Yang, X. F., et al. (2019). Natural SEI-inspired dual-protective layers via atomic/molecular layer deposition for long-life metallic lithium anode. Matter *1*, 1215-1231.

78 Huang, W., Wang, H., Boyle, D. T., Li, Y. Z., and Cui, Y. (2020). Resolving nanoscopic and mesoscopic heterogeneity of fluorinated species in battery solid-electrolyte interphases by cryogenic electron microscopy. Acs Energy Lett. *5*, 1128-1135.

79 Yang, C. T., Lin, Y. X., Li, B., Xiao, X., and Qi, Y. (2020). The bonding nature and adhesion of polyacrylic acid coating on Li-metal for li dendrite prevention. ACS Appl. Mater Interfaces *12*, 51007-51015.

80 Bae, J., Qian, Y. M., Li, Y. T., Zhou, X. Y., Goodenough, J. B., and Yu, G. H. (2019). Polar polymer-solvent interaction derived favorable interphase for stable lithium metal batteries. Energy Environ. Sci. *12*, 3319-3327.

81 Yu, Z. A., Mackanic, D. G., Michaels, W., Lee, M., Pei, A., Feng, D. W., Zhang, Q. H., Tsao, Y. C., Amanchukwu, C. V., Yan, X. Z. (2019). A dynamic, electrolyte-blocking, and single-ion-conductive network for stable lithium-metal anodes. Joule *3*, 2761-2776.

82 Stalin, S., Tikekar, M., Biswal, P., Li, G., Johnson, H. E. N., Deng, Y., Zhao, Q., Vu, D., Coates, G. W., and Archer, L. A. (2020). Designing polymeric interphases for stable lithium metal deposition. Nano Lett. *20*, 5749-5758.

83 Gao, Y., Yan, Z., Gray, J. L., He, X., Wang, D., Chen, T., Huang, Q., Li, Y. C., Wang, H., Kim, S. H., et al. (2019). Polymer-inorganic solid-electrolyte interphase for stable lithium metal batteries under lean electrolyte conditions. Nat. Mater.*18*, 384-389.

84 Ramasubramanian, A., Yurkiv, V., Foroozan, T., Ragone, M., Shahbazian-Yassar, R., and Mashayek, F. (2019). Lithium diffusion mechanism through solid-electrolyte interphase in rechargeable lithium batteries. J. Phys. Chem. C *123*, 10237-10245.

85 Tewari, D. & Mukherjee, P. P. (2019). Mechanistic understanding of electrochemical plating and stripping of metal electrodes. J. Mater. Chem. A *7*, 4668-4688.

86 Song, J., Lee, H., Choo, M. J., Park, J. K., and Kim, H. T. (2015). Ionomer-liquid electrolyte hybrid ionic conductor for high cycling stability of lithium metal electrodes. Sci. Rep. *5*, 14458.

87 Tu, Z., Choudhury, S., Zachman, M. J., Wei, S., Zhang, K., Kourkoutis, L. F., and Archer, L. A. (2017). Designing artificial solid-electrolyte interphases for single-ion and high-efficiency transport in batteries. Joule *1*, 394-406.

88 Zhao, C. Z., Chen, P. Y., Zhang, R., Chen, X., Li, B. Q., Zhang, X. Q., Cheng, X. B., and Zhang, Q. (2018). An ion redistributor for dendrite-free lithium metal anodes. Sci. Adv. *4*, eaat3446.

89 Pang, Q., Liang, X., Shyamsunder, A., and Nazar, L. F. (2017). An in vivo formed solid electrolyte surface layer enables stable plating of Li metal. Joule *1*, 871-886.

90 Kim, M. S., Ryu, J.-H., Deepika, Lim, Y. R., Nah, I. W., Lee, K.-R., Archer, L. A., and Il Cho, W. (2018). Langmuir–Blodgett artificial solid-electrolyte interphases for practical lithium metal batteries. Nat. Energy *3*, 889-898.

91 Kim, M. S., Deepika, Lee, S. H., Kim, M. S., Ryu, J. H., Lee, K. R., Archer, L. A., and Il Cho, W. (2019). Enabling reversible redox reactions in electrochemical cells using protected LiAl intermetallics as lithium metal anodes. Sci. Adv. *5*, eaax5587.

92 Lopez, J., Pei, A., Oh, J. Y., Wang, G. N., Cui, Y., and Bao, Z. (2018). Effects of polymer coatings on electrodeposited lithium metal. J. Am. Chem. Soc. *140*, 11735-11744.

93 Shi, F., Pei, A., Vailionis, A., Xie, J., Liu, B., Zhao, J., Gong, Y., and Cui, Y. (2017). Strong texturing of lithium metal in batteries. PNAS *114*, 12138-12143.

94 Liu, W., Liu, P., and Mitlin, D. (2020). Review of emerging concepts in sei analysis and artificial sei membranes for lithium, sodium, and potassium metal battery anodes. Adv. Energy Mater. *10*, 2002297

95 Jackle, M., and Gross, A. (2014). Microscopic properties of lithium, sodium, and magnesium battery anode materials related to possible dendrite growth. J. Chem. Phys. *141*, 174710.

96 Yildirim, H., Kinaci, A., Chan, M. K., and Greeley, J. P. (2015). First-principles analysis of defect thermodynamics and ion transport in inorganic sei compounds: LiF and NaF. ACS Appl. Mater Interfaces *7*, 18985-18996.

97 Kuo, L.-Y., Moradabadi, A., Huang, H.-F., Hwang, B.-J., and Kaghazchi, P. (2017). Structure and ionic conductivity of the solid electrolyte interphase layer on tin anodes in Na-ion batteries. J. Power Sources *341*, 107-113.

98 Shi, S., Qi, Y., Li, H., and Hector, L. G. (2013). Defect thermodynamics and diffusion mechanisms in Li_2CO_3 and implications for the solid electrolyte interphase in li-ion batteries. J. Phys. Chem. C *117*, 8579-8593.

99 Soto, F. A., Marzouk, A., El-Mellouhi, F., and Balbuena, P. B. (2018). Understanding ionic diffusion through sei components for lithium-ion and sodium-ion batteries: insights from first-principles calculations. Chem. Mater. *30*, 3315-3322.

100 Hong, Y.-S., Li, N., Chen, H., Wang, P., Song, W.-L., and Fang, D. (2018). In operando observation of chemical and mechanical stability of Li and Na dendrites under quasi-zero electrochemical field. Energy Storage Mater. *11*, 118-126.

101 Mogensen, R., Brandell, D., and Younesi, R. (2016). Solubility of the solid electrolyte interphase (SEI) in sodium ion batteries. ACS Energy Lett. *1*, 1173-1178.

102 Seh, Z. W., Sun, J., Sun, Y., and Cui, Y. (2015). A highly reversible room-temperature sodium metal anode. ACS central Sci. *1*, 449-455.

103 Liu, W., Chen, Z., Zhang, Z., Jiang, P., Chen, Y., Paek, E., Wang, Y., and Mitlin, D. (2021). Lithium-activated SnS–graphene alternating nanolayers enable dendrite-free cycling of thin sodium metal anodes in carbonate electrolyte. Energy Environ. Sci. *14*, 382-395

104 Ma, J. L., Meng, F. L., Yu, Y., Liu, D. P., Yan, J. M., Zhang, Y., Zhang, X. B., and Jiang, Q. (2019). Prevention of dendrite growth and volume expansion to give high-performance aprotic bimetallic Li-Na alloy-O_2 batteries. Nat. Chem. *11*, 64-70.

105 Wang, H., Wang, C., Matios, E., and Li, W. (2018). Facile stabilization of the sodium metal anode with additives: unexpected key role of sodium polysulfide and adverse effect of sodium nitrate. Angew. Chem. Int. Ed. *57*, 7734-7737.

106 Zhang, Q., Lu, Y., Miao, L., Zhao, Q., Xia, K., Liang, J., Chou, S. L., and Chen, J. (2018). An alternative to lithium metal anodes: non-dendritic and highly reversible sodium metal anodes for Li-Na hybrid batteries. Angew. Chem. Int. Ed. *57*, 14796-14800.

107 Liu, P., and Mitlin, D. (2020). Emerging potassium metal anodes: perspectives on control of the electrochemical interfaces. Acc. Chem. Res. *53*, 1161-1175.

108 Davidson, R., Verma, A., Santos, D., Hao, F., Fincher, C., Xiang, S., Van Buskirk, J., Xie, K., Pharr, M., Mukherjee, P. P., et al. (2019). Formation of magnesium dendrites during electrodeposition. ACS Energy Lett. *4*, 375-376.

109 Son, S. B., Gao, T., Harvey, S. P., Steirer, K. X., Stokes, A., Norman, A., Wang, C., Cresce, A., Xu, K., and Ban, C. (2018). An artificial interphase enables reversible magnesium chemistry in carbonate electrolytes. Nat. Chem. *10*, 532-539.

110 Forero-Saboya, J., Davoisne, C., Dedryvere, R., Yousef, I., Canepa, P., and Ponrouch, A. (2020). Understanding the nature of the passivation layer enabling reversible calcium plating. Energy Environ. Sci. 1*3*, 3423-3431.

111 Wang, M., Jiang, C., Zhang, S., Song, X., Tang, Y., and Cheng, H. M. (2018). Reversible calcium alloying enables a practical room-temperature rechargeable calcium-ion battery with a high discharge voltage. Nat. Chem. *10*, 667-672.

112 Zhao, Q., Zachman, M. J., Al Sadat, W. I., Zheng, J., Kourkoutis, L. F., and Archer, L. (2018). Solid electrolyte interphases for high-energy aqueous aluminum electrochemical cells. Sci. Adv. *4*, eaau8131.

113 Zhao, Q., Huang, W., Luo, Z., Liu, L., Lu, Y., Li, Y., Li, L., Hu, J., Ma, H., and Chen, J. (2018). High-capacity aqueous zinc batteries using sustainable quinone electrodes. Sci. Adv. *4*, eaao1761.

114 Yadav, G. G., Wei, X., Huang, J., Gallaway, J. W., Turney, D. E., Nyce, M., Secor, J., and Banerjee, S. (2017). A conversion-based highly energy dense Cu^{2+} intercalated Bi-birnessite/Zn alkaline battery. J. Mater. Chem. A *5*, 15845-15854.

115 Banik, S. J., and Akolkar, R. (2015). Suppressing dendritic growth during alkaline zinc electrodeposition using polyethylenimine additive. Electrochimica Acta *179*, 475-481.

116 Zheng, J., Zhao, Q., Tang, T., Yin, J., Quilty, C. D., Renderos, G. D., Liu, X., Deng, Y., Wang, L., Bock, D. C., et al. (2019). Reversible epitaxial electrodeposition of metals in battery anodes. Science *366*, 645-648.

117 Zhao, Q., Stalin, S., Zhao, C. Z., and Archer, L. A. (2020). Designing solid-state electrolytes for safe, energy-dense batteries. Nat. Rev. Mater. *5*, 229-252.

118 Hao, J., Li, B., Li, X., Zeng, X., Zhang, S., Yang, F., Liu, S., Li, D., Wu, C., and Guo, Z. (2020). An in-depth study of zn metal surface chemistry for advanced aqueous zn-ion batteries. Adv. Mater. *32*, e2003021.

119 Nanda, J., Yang, G., Hou, T., Voylov, D. N., Li, X., Ruther, R. E., Naguib, M., Persson, K., Veith, G. M., and Sokolov, A. P. (2019). Unraveling the nanoscale heterogeneity of solid electrolyte interphase using tip-enhanced raman spectroscopy. Joule *3*, 2001-2019.

120 Avdeev, M. V., Rulev, A. A., Bodnarchuk, V. I., Ushakova, E. E., Petrenko, V. I., Gapon, I. V., Tomchuk, O. V., Matveev, V. A., Pleshanov, N. K., Kataev, E. Y., et al. (2017). Monitoring of lithium plating by neutron reflectometry. Appl. Surf. Sci. *424*, 378-382.

121 Hope, M. A., Rinkel, B. L. D., Gunnarsdottir, A. B., Marker, K., Menkin, S., Paul, S., Sergeyev, I. V., and Grey, C. P. (2020). Selective NMR observation of the SEI-metal interface by dynamic nuclear polarisation from lithium metal. Nat. Commun. *11*, 2224.

122 Xiang, Y., Zheng, G., Liang, Z., Jin, Y., Liu, X., Chen, S., Zhou, K., Zhu, J., Lin, M., He, H., et al. (2020). Visualizing the growth process of sodium microstructures in sodium batteries by in-situ (23)Na MRI and NMR spectroscopy. Nat. Nanotech. *15*, 883-890.

123 Zhou, Y., Su, M., Yu, X., Zhang, Y., Wang, J. G., Ren, X., Cao, R., Xu, W., Baer, D. R., Du, Y., et al. (2020). Real-time mass spectrometric characterization of the solid-electrolyte interphase of a lithium-ion battery. Nat. Nanotech. *15*, 224-230.

124 Fang, C., Li, J., Zhang, M., Zhang, Y., Yang, F., Lee, J. Z., Lee, M. H., Alvarado, J., Schroeder, M. A., Yang, Y., et al. (2019). Quantifying inactive lithium in lithium metal batteries. Nature 5*72*, 511-515.

125 Kitz, P. G., Lacey, M. J., Novak, P., and Berg, E. J. (2019). Operando EQCM-D with simultaneous in situ eis: new insights into interphase formation in Li ion batteries. Analy. Chem.91, 2296-2303.

126 He, Y., Ren, X., Xu, Y., Engelhard, M. H., Li, X., Xiao, J., Liu, J., Zhang, J. G., Xu, W., and Wang, C. (2019). Origin of lithium whisker formation and growth under stress. Nat. Nanotech. *14*, 1042-1047.

127 Zhang, L., Yang, T., Du, C., Liu, Q., Tang, Y., Zhao, J., Wang, B., Chen, T., Sun, Y., Jia, P., et al. (2020). Lithium whisker growth and stress generation in an in situ atomic force

microscope-environmental transmission electron microscope set-up. Nat. Nanotech. *15*, 94-98.

128 Byun, K., Saha, J. K., and Jane, J. (2020). Role of a solid-electrolyte interphase in the dendritic electrodeposition of lithium: a brownian dynamics simulation study. J. Phys. Chem. C. *124*, 9124-9141.

129 Tikekar, M. D., Archer, L. A., and Koch, D. L. (2016). Stabilizing electrodeposition in elastic solid electrolytes containing immobilized anions. Sci.Adv. *2*, e1600320.

130 Jasinski, R. (1967) High energy batteries. Plenum Press: New York.

131 Chen, X., Hou, T.-Z., Li, B., Yan, C., Zhu, L., Guan, C., Cheng, X.-B., Peng, H.-J., Huang, J.-Q., and Zhang, Q. (2017). Towards stable lithium-sulfur batteries: Mechanistic insights into electrolyte decomposition on lithium metal anode. Energy Storage Mater. *8*, 194-201,.

132 Bhatt, M. D., and O'Dwyer, C. (2015). Solid electrolyte interphases at Li-ion battery graphitic anodes in propylene carbonate (PC)-based electrolytes containing FEC, LiBOB, and LiDFOB as additives. Chem. Phys. Lett. *618*, 208-213.

133 Xie, J., Liao, L., Gong, Y., Li, Y., Shi, F., Pei, A., Sun, J., Zhang, R., Kong, B., Subbaraman, R, et al. (2017). Stitching h-BN by atomic layer deposition of LiF as a stable interface for lithium metal anode. Sci. Adv. *3*, eaao3170.

134 Aurbach, D. (1996). A Comparative study of synthetic graphite and li electrodes in electrolyte solutions based on ethylene carbonate-dimethyl carbonate mixtures. J. Electrochem.Soc. *143*, 3809.

135 Ein-Eli, Y., Markovsky, B., Aurbach, D., Carmeli, Y., Yamin, H., and Luski, S. (1994). The dependence of the performance of Li-C intercalation anodes for Li-ion secondary batteries on the electrolyte solution composition. Electrochimica Acta *39*, 2559-2569.

136 Aurbach, D. (1989). The correlation between surface chemistry, surface morphology, and cycling efficiency of lithium electrodes in a few polar aprotic systems. J. Electrochem. Soc. *136*, 3198.

137 Li, Y., Sun, Y., Pei, A., Chen, K., Vailionis, A., Li, Y., Zheng, G., Sun, J., and Cui, Y. (2018). Robust pinhole-free li_3n solid electrolyte grown from molten lithium. ACS Central Sci. *4*, 97-104.

138 Xiong, S., Xie, K., Diao, Y., and Hong, X. (2014). Characterization of the solid electrolyte interphase on lithium anode for preventing the shuttle mechanism in lithium–sulfur batteries. J. Power Sources *246*, 840-845.

139 Tu, Z. Y., Zachman, M. J., Choudhury, S., Khan, K. A., Zhao, Q., Kourkoutis, L. F., and Archer, L. A. (2018). Stabilizing protic and aprotic liquid electrolytes at high-bandgap oxide interphases. Chem. Mater. *30*, 5655-5662.

140 Liu, F., Xiao, Q., Wu, H. B., Shen, L., Xu, D., Cai, M., and Lu, Y. (2017). Fabrication of hybrid silicate coatings by a simple vapor deposition method for lithium metal anodes. Adv. Energy Mater., *8*, 1701744.

141 Lin, L., Liang, F., Zhang, K., Mao, H., Yang, J., and Qian, Y. (2018). Lithium phosphide/lithium chloride coating on lithium for advanced lithium metal anode. J. Mater. Chem. A *6*, 15859-15867.

142 Zhang, R., Chen, X., Shen, X., Zhang, X.-Q., Chen, X.-R., Cheng, X.-B., Yan, C., Zhao, C.-Z., and Zhang, Q. (2018). Coralloid carbon fiber-based composite lithium anode for robust lithium metal batteries. Joule *2*, 764-777.

143 Ye, H., Zheng, Z. J., Yao, H. R., Liu, S. C., Zuo, T. T., Wu, X. W., Yin, Y. X., Li, N. W., Gu, J. J., Cao, F. F., et al. (2019). Guiding uniform li plating/stripping through lithium-aluminum alloying medium for long-life Li metal batteries. Angew. Chem. Int. Ed. *58*, 1094-1099.

144 Liu, Y., Lin, D., Liang, Z., Zhao, J., Yan, K., and Cui, Y. (2016). Lithium-coated polymeric matrix as a minimum volume-change and dendrite-free lithium metal anode. Nat. Commun. *7*, 10992.

145 Cha, E., Patel, M. D., Park, J., Hwang, J., Prasad, V., Cho, K., and Choi, W. (2018). 2D MoS_2 as an efficient protective layer for lithium metal anodes in high-performance Li-S batteries. Nat. Nanotech. *13*, 337-344.

Figure Legends

Figure 1. History of SEI on metallic Li anodes - from conceptual representations to direct visualization.
The first studies of Li metal batteries date back at least to the 1950s, where the aim was to create batteries with higher energy density.[130] In 1960-1970s, researchers began to recognize that a solid film was formed on the surface of Li, enabling the stability of Li metal in aprotic electrolytes even through the lowest potential of Li^+/Li.[10] This film was defined as a SEI in 1979 by Peled.[3] Since then, different models of SEI have been speculated.[11-14] Meanwhile, the components of SEI are gradually being understood and various artificial SEIs have been created according to the knowledge on the functionality of different SEI components.[15-21]

Figure 2. Formation, characteristics and components of SEI.
(A) A schematic diagram of SEI formation. The LUMO energy of electrolyte is lower than that of lithium, therefore the electrolyte will be reduced by the anode unless the reaction is blocked by SEI layer, which can extend the operating window of electrolytes. Correspondingly, the oxidation of electrolyte is related to the HOMO energy.[22] The working voltage of common cathodes (LFP, Ni-rich, LCO, Li-rich) are also listed.
(B) Band gap (electronic insulting) and diffusion barrier (ion conductive) of different SEI components on Li metal anode.[24,26]
(C) Comparison of SEI formed on Li-ion battery anode (graphite) and Li metal anode.[28] The plating and stripping without host leads to the nonplanar morphology of Li.
(D) Shear modulus[31] and surface energy[25,27,95] of different facets. The components within the SEI that possess both high shear modulus and surface tension are regarded as optimal for stable electrodeposition.

Figure 3. Design principles of SEI by regulating the recipes of electrolytes.
(A) Relative solvating power of common solvents used in lithium batteries. The esters and ethers are compared with the solvent of ethyl methyl carbonate (EMC),[33] and dioxolane (DOL),[34] respectively.
(B) Comparisons of LUMO energies of detailed solvents. The LUMO energy of Li^+-solvent (an optimized geometrical structure where one Li^+ is coordinated with one solvent molecule) is also listed to emphasize the differences of pure solvent and electrolytes.[4, 35,131,132]
(C) Reduction potentials of various salts, and corresponding reactions of typical Li-salts on the surface of Li metal.[36,37]
(D) Calculated bond dissociation energies of LiFSI with or without Li. The Figure shows the presence of Li induces an obvious thermodynamically favorable decomposition of salts.[38]

Figure 4. SEI regulated by additives and concentrations of electrolytes.
(A) Various additives and corresponding components/functionality of SEI formed on the surface of lithium metal.
(B) Schematic diagrams of SEI formation and Li^+ coordination environment in conventional, highly concentrated and locally concentrated electrolytes.

Figure 5. Design Principles for ASEI.

(A) Mechanical stability of various ASEI. Mechanical stability of the SEI is a key parameter for enabling uniform electroplating. Two factors are typically considered in designing the ASEI (i) Shear Modulus for countering stresses from the growing dendrites (i) Yield point that dictates conformality of the SEI for volume changes at the anode during electrodeposition.
(B) A schematic of chemical stability. Chemical stability of the ASEI prevents all faradaic and non faradaic reactions except the reduction of Lithium ions.
(C) Stable and uniform Li^+ ion transport. An ASEI should be designed to regulate mass and charge transfer. The Li^+ ion diffusivity ($D(Li^+)$) within the ASEI should be higher than that of the bulk and at the electrode/ASEI interface, the surface diffusivity should be high to promote lateral transport of ions. The electrodeposition should be overall reaction limited and not diffusion limited.

Figure 6. Comparisons of properties of various metals that are relevant to the desired characteristics of the SEI.
(A) Physical and chemical properties of various metals and metal ions.
(B) Diffusion barrier and surface energy of Li, Na, Mg, Al at different facets.[95]
(C) Comparisons of self-diffusion coefficient of Li-SEI and Na-SEI.[96-98] Li_i^+/ Na_i^+ stands for excess interstitial Li-ion/Na-ion. V_{Li}^- / V_{Na}^- stands for negatively charged Li/Na vacancy.
(D) Comparisons of migration energy barriers of hetero-diffusion via various approaches, including the diffusion of Li-ion in Na-SEI (NaF and Na_2CO_3) and the diffusion of Na-ion in Li-SEI (LiF and Li_2CO_3).[99]
(E) Comparison of charge capacity loss of Li metal anode and Na metal anode caused by the dissolution of SEI.[101]

Table 1 | Compositions and properties of various SEI

	Compounds	Formation methods	Characteristics/Properties	Ref.
B	*h*-BN[a]	CVD system with ammonia borane (H_3N-NH_3) [c]	2D material with high in-plane Young's modulus (1.0 Tpa)	133
C	Li_2CO_3[b]	Reduction of carbonates on Li	Highly insoluble in carbonate electrolytes	134
	$ROCO_2Li$ (R=alkyl) [b]	Reduction of carbonates on Li	Form Li_2CO_3 via the reaction with trace water	135
	ROLi (R=alkyl) [b]	Reduction of ether on Li	Form LiOH via the reaction with trace water	136
N	α-Li_3N[a]	Molten Li and N_2 gas	Pinhole-free layer with measured Li^+ conductivity (5.2×10^{-3}S cm^{-1})	137
	LiN_xO_y [b]	Reduction of $LiNO_3$ on Li	Prevent the shuttle reaction in Li-S batteries	138
F	LiF [b]	Reduction of F-salts and solvents on Li	Poorly soluble in electrolytes, chemical/electrochemical stable	42
Al	Al_2O_3[a]	ALD with trimethylaluminum as precursor[d]	Lithiophilic, high bandgap, extended oxidation stability.	139
Si	Si-O-alkyl [b]	Reaction between SEI and $SiCl_4$ additives	Viscoelastic characteristics that can accommodate Li volume change	50
	Li_xSiO_y with mercaptopropyl [a]	CVD with MPS and TEOS[e]	Strong inorganic Li_xSiO_y connect with soft mercaptopropyl	140
P	LiPON [a]	ALD process with LiOtBu, water,[f] trimethylphosphate, and nitrogen plasma	A thin film solid state electrolyte	76
	Li_3PO_4[a]	Reaction of PPA with Li and its native film [g]	High Young's modulus (10–11 Gpa)	59
	Li_3P with LiCl[a]	Reaction of PCl_3 and Li	Li_3P–fast Li-ion conductor (~10^{-4} S cm^{-1})	141
S	Li_2S_x ,$Li_2S_xO_y$ [b]	Reaction of polysulfides and Li with participation of $LiNO_3$	Prevent the shuttle reaction in Li-S batteries	138
Cl	LiCl [a]	Reaction of MCl_x (M= P, In, Zn, Sn, Bi et al.) and Li	Insulating LiCl with potential gradient for Li^+ diffusion.	63
Alloy	Li_xM_y (M=Al, Zn, Ag, In, Sn, Bi et.al) [a]	Reaction of metal salts and Li, metal and molten Li, or in-situ electrochemical reaction.	High Li^+ diffusion coefficient 4.7×10^{-8} cm^2 s^{-1} (LiZn, 300K) 3×10^{-6} cm^2 s^{-1} (Li_3Bi, 320K)	63,64,142, 143
Zn	ZnO[a]	ALD with diethyl zinc and water as precursors	Lithiophilic character that induce Li-ion diffusion	144
Mo	MoS_2[a]	Sputtering deposition with a MoS_2 target	2D lithiophilic materials with low Li-ion migration energy barrier (0.155 eV) on the surface.	145

Note: The table illustrates formation method and characteristics/properties of common SEI with selected examples. It should be noted that one single SEI can be formed with various methods. [a] Examples are artificial SEI built outside of electrochemical cells. [b] Examples are in-built SEI via the modification of electrolytes. [c] CVD is short for chemical vapor deposition. [d] ALD is short for atomic layer deposition. [e] MPS is short for 3-mercaptopropyl trimethoxysilane, [f] TEOS is short for tetraethoxysilane. [g] PPA is short for polyphosphoric acid.

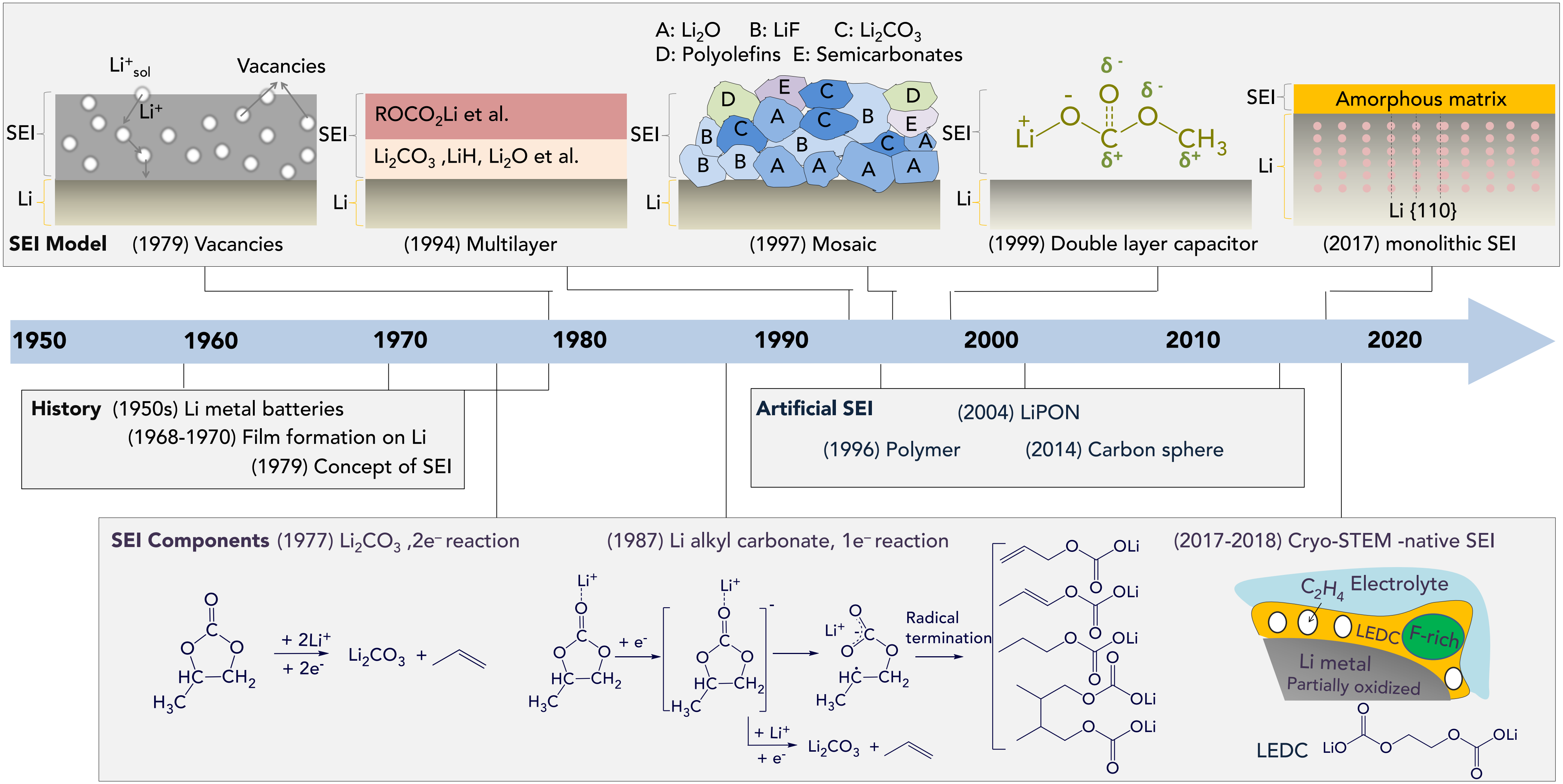
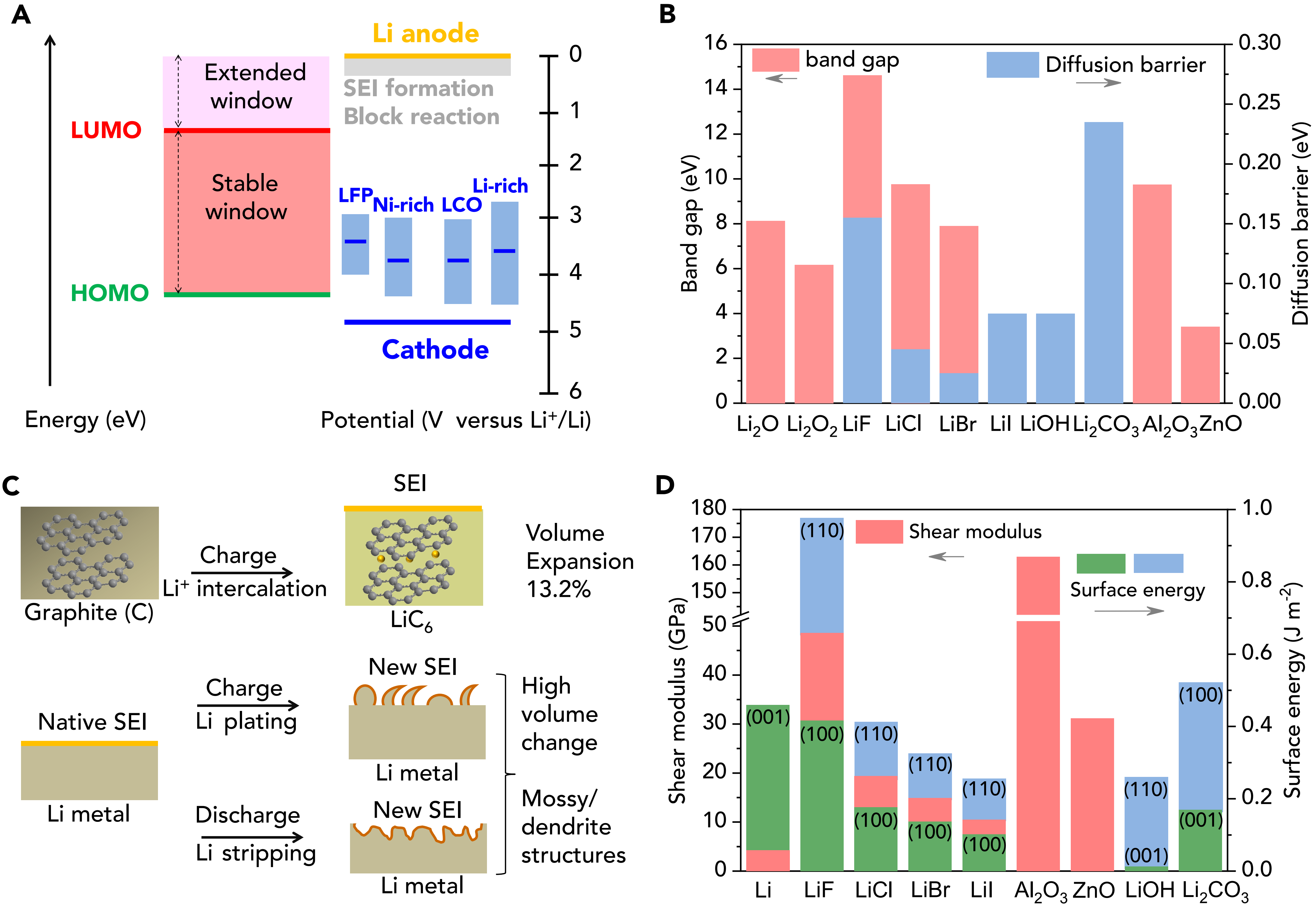

SEI Model
(1979) Vacancies
Li^+_{sol}
Li^+
Vacancies
SEI
Li
(1994) Multilayer
$ROCO_2Li$ et al.
Li_2CO_3 ,LiH, Li_2O et al.
(1997) Mosaic
A: Li_2O B: LiF C: Li_2CO_3
D: Polyolefins E: Semicarbonates
(1999) Double layer capacitor
δ -
δ+
(2017) monolithic SEI
Amorphous matrix
Li {110}
1950
1960
1970
1980
1990
2000
2010
2020
History (1950s) Li metal batteries
(1968-1970) Film formation on Li
(1979) Concept of SEI
Artificial SEI (2004) LiPON
(1996) Polymer
(2014) Carbon sphere
SEI Components (1977) Li_2CO_3 ,2e⁻ reaction
(1987) Li alkyl carbonate, 1e⁻ reaction
(2017-2018) Cryo-STEM -native SEI
+ 2Li⁺
+ 2e⁻
Li_2CO_3 +
+ e⁻
+ Li⁺
+ e⁻
Radical termination
OLi
C_2H_4 Electrolyte
LEDC
F-rich
Li metal
Partially oxidized
LEDC
LiO

Figure 2


A
Energy (eV)
LUMO
HOMO
Extended window
Stable window
Li anode
SEI formation
Block reaction
LFP
Ni-rich
LCO
Li-rich
Cathode
0
1
2
3
4
5
6
Potential (V versus Li+/Li)
B
band gap
Diffusion barrier
Band gap (eV)
Diffusion barrier (eV)
0
2
4
6
8
10
12
14
16
0.00
0.05
0.10
0.15
0.20
0.25
0.30
Li2O
Li2O2
LiF
LiCl
LiBr
LiI
LiOH
Li2CO3
Al2O3
ZnO
C
Graphite (C)
Charge
Li+ intercalation
SEI
LiC6
Volume Expansion 13.2%
Native SEI
Li metal
Charge
Li plating
New SEI
Li metal
High volume change
Discharge
Li stripping
New SEI
Li metal
Mossy/ dendrite structures
D
Shear modulus
Surface energy
Shear modulus (GPa)
Surface energy (J m-2)
0
10
20
30
40
50
150
160
170
180
0.0
0.2
0.4
0.6
0.8
1.0
(001)
(110)
(100)
(110)
(100)
(110)
(100)
(110)
(100)
(110)
(001)
(100)
(001)
Li
LiF
LiCl
LiBr
LiI
Al2O3
ZnO
LiOH
Li2CO3

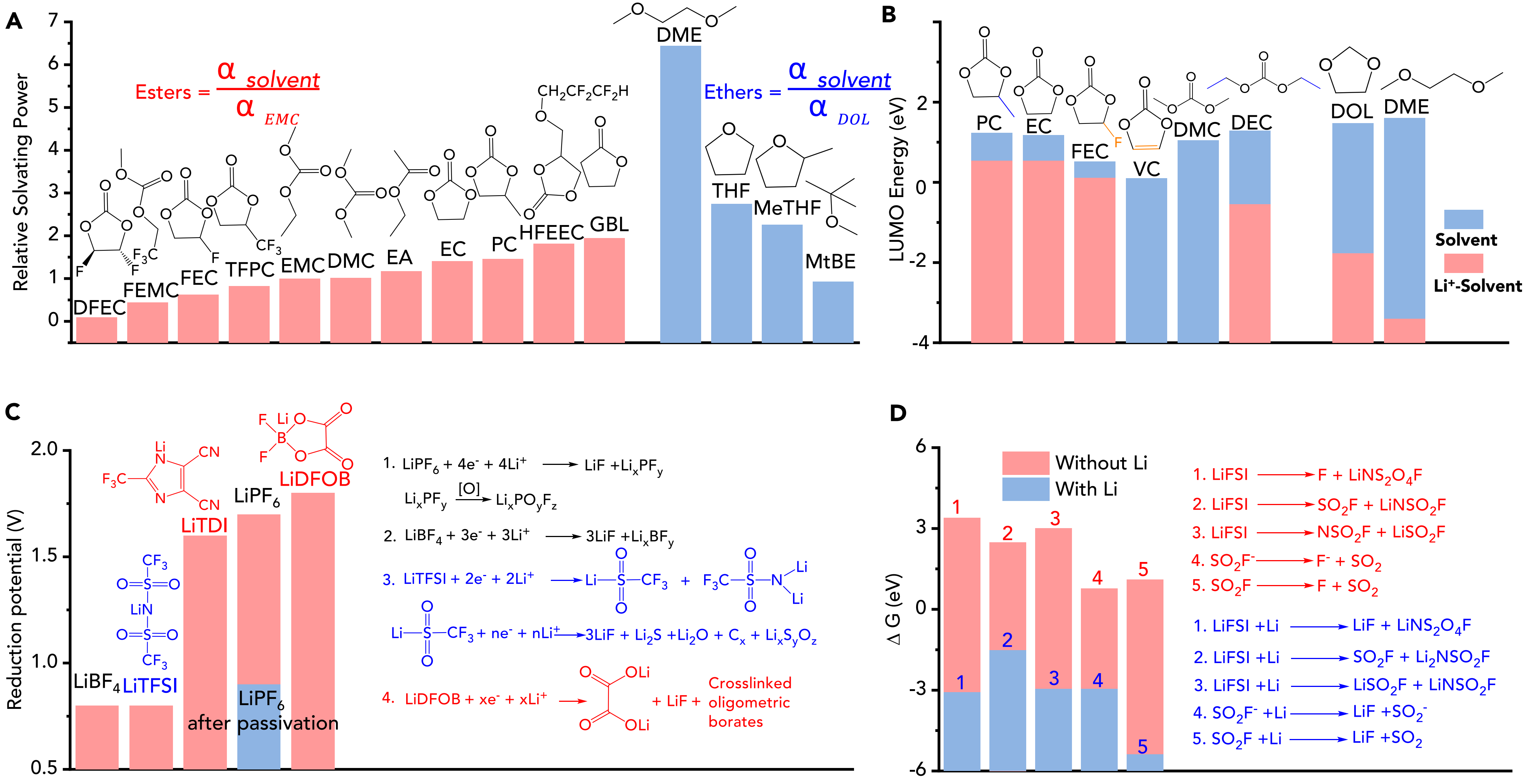

A
Relative Solvating Power
0
1
2
3
4
5
6
7
Esters = α solvent / α EMC
Ethers = α solvent / α DOL
DFEC
FEMC
FEC
TFPC
EMC
DMC
EA
EC
PC
HFEEC
GBL
DME
THF
MeTHF
MtBE
F_3C
CF_3
$CH_2CF_2CF_2H$
B
LUMO Energy (eV)
-4
-2
0
2
PC
EC
FEC
VC
DMC
DEC
DOL
DME
Solvent
Li⁺-Solvent
C
Reduction potential (V)
0.5
1.0
1.5
2.0
$LiBF_4$
LiTFSI
LiTDI
$LiPF_6$
LiDFOB
$LiPF_6$ after passivation
1. $LiPF_6 + 4e^- + 4Li^+ \longrightarrow LiF + Li_xPF_y$
$Li_xPF_y \xrightarrow{[O]} Li_xPO_yF_z$
2. $LiBF_4 + 3e^- + 3Li^+ \longrightarrow 3LiF + Li_xBF_y$
3. $LiTFSI + 2e^- + 2Li^+ \longrightarrow Li{-}SO_2{-}CF_3 + F_3C{-}SO_2{-}NLi_2$
$Li{-}SO_2{-}CF_3 + ne^- + nLi^+ \longrightarrow 3LiF + Li_2S + Li_2O + C_x + Li_xS_yO_z$
4. $LiDFOB + xe^- + xLi^+ \longrightarrow$ + LiF + Crosslinked oligometric borates
D
Δ G (eV)
-6
-3
0
3
6
Without Li
With Li
1
2
3
4
5
1. LiFSI → F + $LiNS_2O_4F$
2. LiFSI → $SO_2F + LiNSO_2F$
3. LiFSI → $NSO_2F + LiSO_2F$
4. SO_2F^- → $F^- + SO_2$
5. SO_2F → $F + SO_2$
1. LiFSI +Li → LiF + $LiNS_2O_4F$
2. LiFSI +Li → $SO_2F + Li_2NSO_2F$
3. LiFSI +Li → $LiSO_2F + LiNSO_2F$
4. SO_2F^- +Li → LiF $+SO_2^-$
5. SO_2F +Li → LiF $+SO_2$

Figure 4

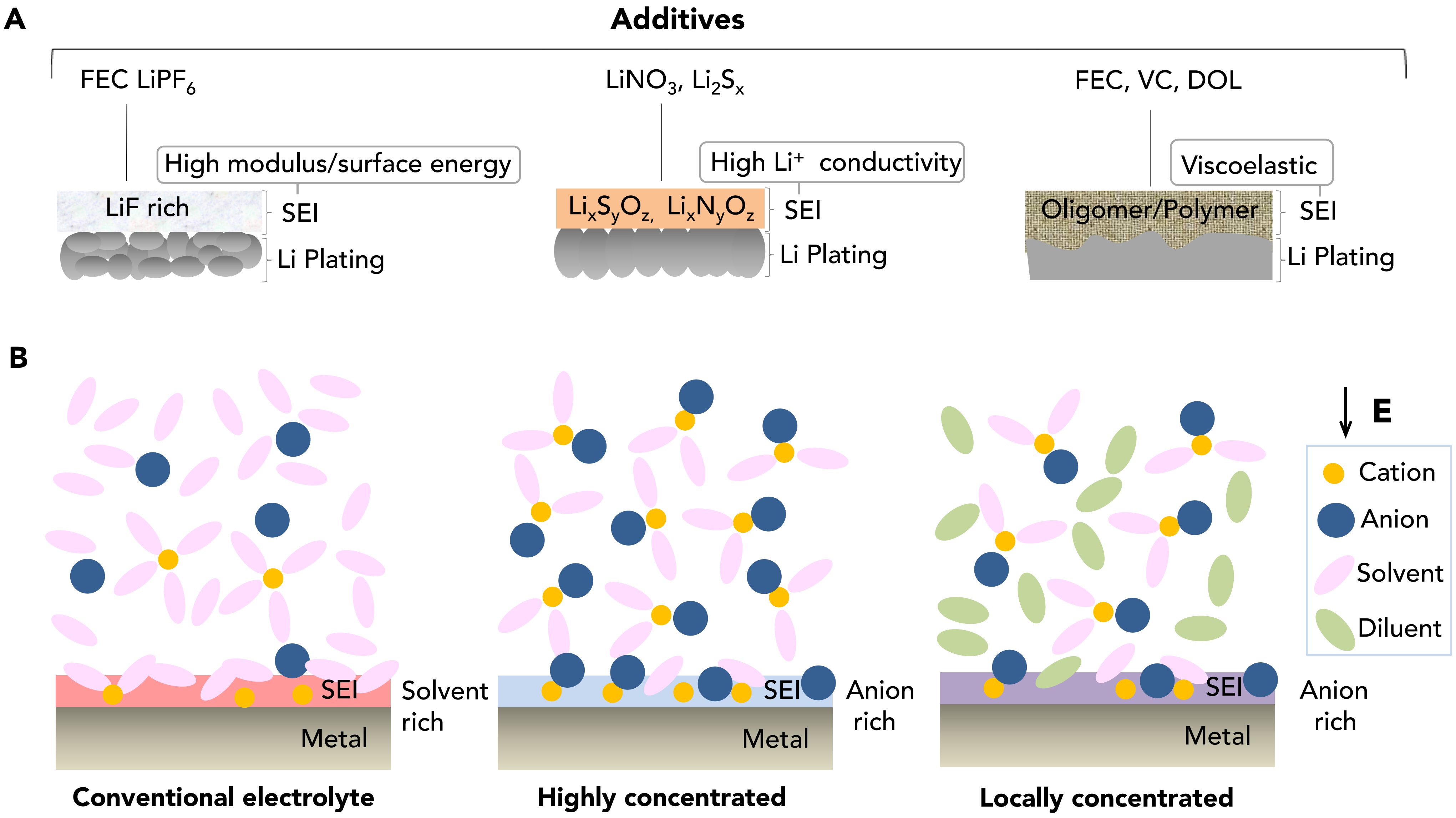

A
Additives
FEC LiPF$_6$
High modulus/surface energy
LiF rich
SEI
Li Plating
LiNO$_3$, Li$_2$S$_x$
High Li$^+$ conductivity
Li$_x$S$_y$O$_z$, Li$_x$N$_y$O$_z$
SEI
Li Plating
FEC, VC, DOL
Viscoelastic
Oligomer/Polymer
SEI
Li Plating
B
SEI
Metal
Solvent rich
Conventional electrolyte
SEI
Metal
Anion rich
Highly concentrated
SEI
Metal
Anion rich
Locally concentrated
E
Cation
Anion
Solvent
Diluent

Figure 5

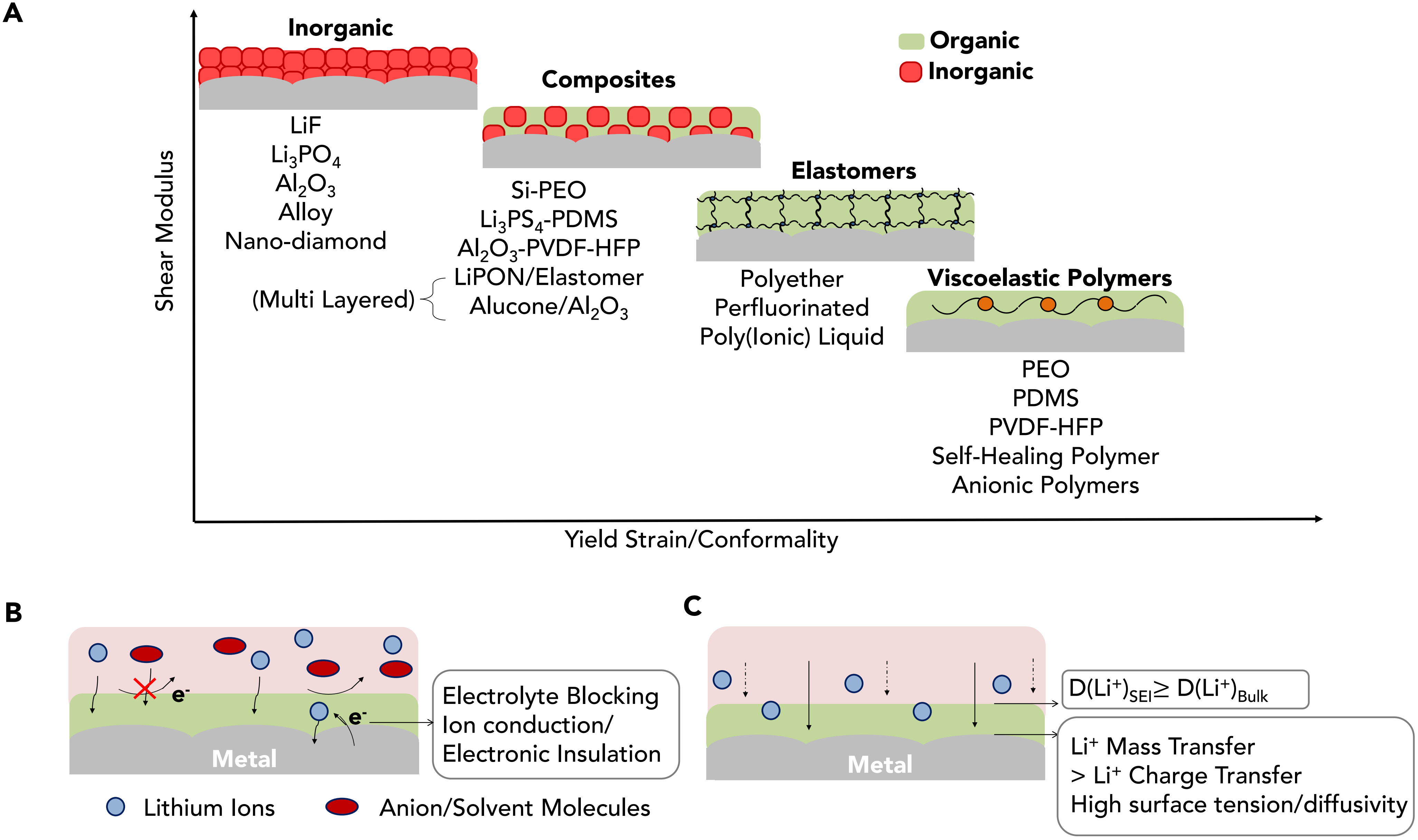
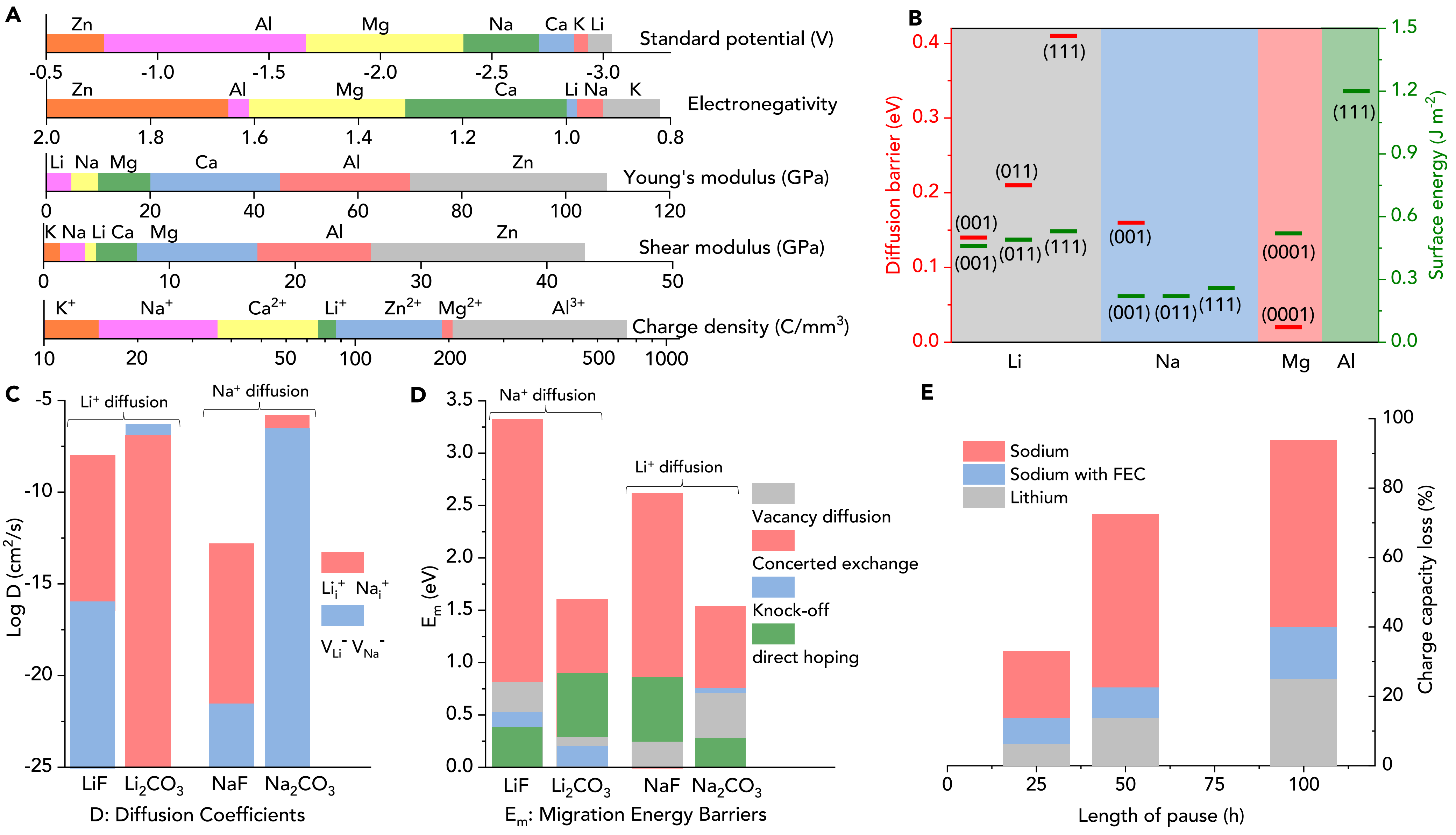

A
Shear Modulus
Yield Strain/Conformality
Organic
Inorganic
Inorganic
LiF
Li_3PO_4
Al_2O_3
Alloy
Nano-diamond
Composites
Si-PEO
Li_3PS_4-PDMS
Al_2O_3-PVDF-HFP
LiPON/Elastomer
Alucone/Al_2O_3
(Multi Layered)
Elastomers
Polyether
Perfluorinated
Poly(Ionic) Liquid
Viscoelastic Polymers
PEO
PDMS
PVDF-HFP
Self-Healing Polymer
Anionic Polymers
B
e^-
e^-
Metal
Electrolyte Blocking
Ion conduction/
Electronic Insulation
Lithium Ions
Anion/Solvent Molecules
C
Metal
$D(Li^+)_{SEI} \geq D(Li^+)_{Bulk}$
Li^+ Mass Transfer
> Li^+ Charge Transfer
High surface tension/diffusivity

Figure 6


A
Zn
Al
Mg
Na
Ca K Li
Standard potential (V)
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
Zn
Al
Mg
Ca
Li Na
K
Electronegativity
2.0
1.8
1.6
1.4
1.2
1.0
0.8
Li Na Mg
Ca
Al
Zn
Young's modulus (GPa)
0
20
40
60
80
100
120
K Na Li Ca Mg
Al
Zn
Shear modulus (GPa)
0
10
20
30
40
50
K⁺
Na⁺
Ca²⁺
Li⁺
Zn²⁺
Mg²⁺
Al³⁺
Charge density (C/mm³)
10
20
50
100
200
500
1000
B
Diffusion barrier (eV)
0.0
0.1
0.2
0.3
0.4
Surface energy (J m⁻²)
0.0
0.3
0.6
0.9
1.2
1.5
(001)
(001)
(011)
(011)
(111)
(111)
(001)
(001)
(011)
(111)
(0001)
(0001)
(111)
Li
Na
Mg
Al
C
Log D (cm²/s)
-5
-10
-15
-20
-25
Li⁺ diffusion
Na⁺ diffusion
Li_i⁺ Na_i⁺
V_Li⁻ V_Na⁻
LiF
Li₂CO₃
NaF
Na₂CO₃
D: Diffusion Coefficients
D
E_m (eV)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
Na⁺ diffusion
Li⁺ diffusion
Vacancy diffusion
Concerted exchange
Knock-off
direct hoping
LiF
Li₂CO₃
NaF
Na₂CO₃
E_m: Migration Energy Barriers
E
Sodium
Sodium with FEC
Lithium
Charge capacity loss (%)
0
20
40
60
80
100
0
25
50
75
100
Length of pause (h)