REVIEW SUMMARY

BATTERIES

Designing better electrolytes

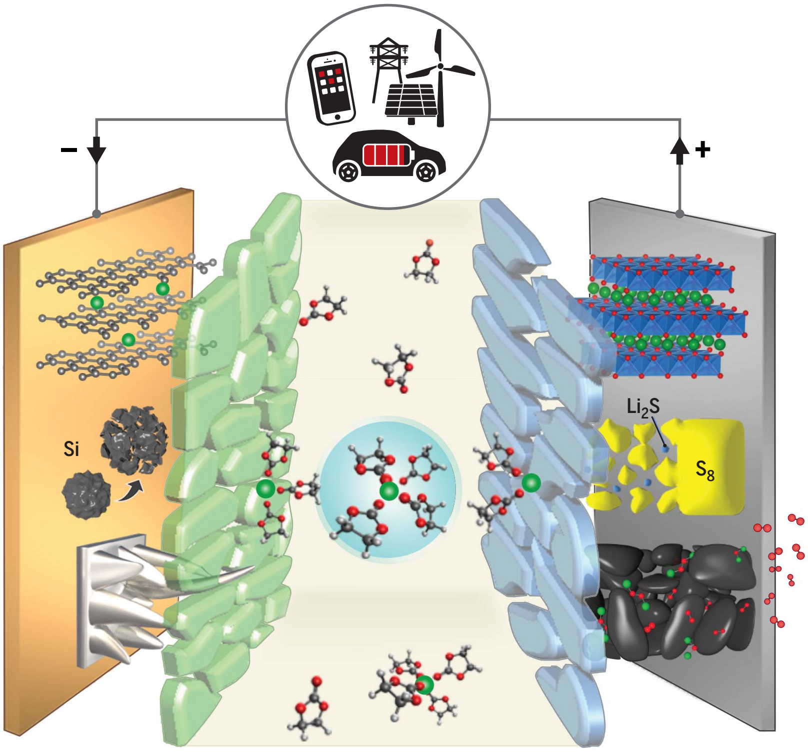
Y. Shirley Meng*, Venkat Srinivasan*, Kang Xu*

BACKGROUND: The electrolyte is an indispensable component in every electrochemical device, including lithium-ion batteries (LIBs). It physically segregates two electrodes from direct electron transfer while allowing working ions to transport both charges and masses across the cell so that the cell reactions can proceed sustainably. Whether powering our phones, driving our vehicles, or harvesting the intermittent energy from solar and wind farms, electrolytes in these LIBs determine how fast and how many times our devices can be recharged or how efficiently energy can be captured and stored over the grid. Occasionally, when an LIB is pushed away from the designed electrochemistry pathways by various factors such as excessive heat, mechanical mutilation, or internal short circuits induced under extreme charging conditions, electrolytes are also responsible for the fire and explosion accidents that we read about in the news.

The electrolyte is the most unique component in a battery. Because it must physically interface with every other component, it is obligated to satisfy numerous constraints simultaneously, including rapidly transporting ions and masses, effectively insulating electrons, and maintaining stability toward the strongly oxidative cathode and strongly reductive anode. Historically, the electrolyte-anode interfacing was the last piece of the puzzle to complete modern LIB chemistry.

ADVANCES: The commercial success of LIBs has attracted intense interest and investments in electrolyte research, which led to the identification of interphases as the key component responsible for the stable and reversible operations of cathode and anode materials far beyond the thermodynamic stability limits of any known electrolyte. These interphases, often with nanometer thickness, are formed by electrolytes in a self-limiting decomposition process, and they ensure fast rates of charging and discharging, maximum voltage, and reversibility of LIBs. In the past three decades, the chemistry, morphology, and formation mechanisms of interphases have been thoroughly investigated. Researchers have learned how such interphases are structured and what key ingredients they comprise and, most importantly, how to tailor them using electrolyte engineering. Today, it is widely accepted that designing better electrolytes also implies designing the associated interphases for the electrode materials. Although the accurate prediction of interphasial chemistry remains difficult, and key fundamental properties of interphases such as the rate and mechanism of ion transport across interphases are still unknown, the structure of the ion solvation sheath has been identified as an effective tool that directs the formation process of interphases. Such knowledge has been driving a series of new electrolyte concepts for emerging battery chemistries.

OUTLOOK: Efforts are being made to develop battery chemistries that promise high energy density, rapid charging, low cost, high sustainability, and independence from elements or materials of high geopolitical or ethical risks. Each individual chemistry may demand a unique electrolyte and corresponding interphase, but a few universal trends emerge: (i) a superconcentration of salts is used to leverage unusual properties arising from the altered ion-solvation structures; (ii) both polymeric and inorganic materials are used to solidify electrolytes so that the aggressive lithium-metal anode can be harnessed with higher safety; (iii) efforts are made to identify the most effective interphasial ingredients so that an interphase of singular composition can be designed and artificially applied; (iv) liquefied gaseous components are used to expand the low-temperature limits of conventional electrolytes; and (v) unusual electrochemical behaviors are explored by confining ion-solvation sheaths in nano- or sub-nano environments. ■



Electrolytes and the associated interphases play the central role in supporting diversified battery chemistries. On the anode side (left), the electrolyte must form an interphase that prevents graphitic anode from exfoliation, tolerates the drastic volume changes of a silicon electrode, and suppresses the growth of a dendritic form of lithium metal. On the cathode side (right), an interphase is critical in preventing the irreversible reactions with electrolytes, maintaining the lattice structure of transition metal oxides, suppressing the cross-cell shuttling of polysulfide species, and assisting the complicated triphasial reactions of an air-cathode. In all of these scenarios, interphases must enable ionic transport while insulating electronic transport.

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Electrolytes and the associated interphases constitute the critical components to support the emerging battery chemistries that promise tantalizing energy but involve drastic phase and structure complications. Designing better electrolytes and interphases holds the key to the success of these batteries. As the only component that interfaces with every other component in the device, an electrolyte must satisfy multiple criteria simultaneously. These include transporting ions while insulating electrons between the electrodes and maintaining stability against electrodes of extreme chemical natures: the strongly oxidative cathode and the strongly reductive anode. In most advanced batteries, the two electrodes operate at potentials far beyond the thermodynamic stability limits of electrolytes, so the stability therein has to be realized kinetically through an interphase formed from the sacrificial reactions between electrolyte and electrodes.

All electrochemical energy devices (fuel cells, batteries, and supercapacitors) operate by separating charges (1), and the electrolyte is the indispensable component to enforce such charge separation (2, 3). The electrolyte physically segregates two electrodes from direct electron transfer while allowing working ions to transport both charge and mass across the cell so that the cell's reactions can proceed sustainably. In a rechargeable battery, a qualified electrolyte not only conducts ions while insulating electrons (a property combination known as "electrolyte nature"), but also must remain inert to the cell reactions. The electrolyte dictates how fast the cell reaction can proceed (power density) and how many times a battery can be charged and discharged (reversibility). Although an electrolyte does not directly determine the energy of a battery (which is instead dictated by both electrodes), it does so indirectly by allowing or disallowing an electrode depending on whether electrochemical stability can be achieved between it and the electrolyte.

To maximize energy density, the electrodes in advanced batteries are often pushed to operate at extreme potentials, where no known electrolyte is thermodynamically stable. In advanced batteries such as lithium-ion batteries (LIBs), the stability between the electrolyte and electrodes (and consequently the reversibility of the battery) must be achieved kinetically. Thus, trace amounts of electrolytes are sacrificially decomposed, and their solid products are deposited on the electrode surfaces, forming a protection against further decomposition. This protection layer in batteries is called "interphase" (4). Interphase formed in this self-limiting manner is almost always identified on anode surfaces in LIBs, where it is referred to as a solid electrolyte interphase (SEI). When interphase occurs on a cathode surface, it is known as a cathode electrolyte interphase (CEI) (5), which is less definitive and complicated by several factors (3). First, most transition-metal oxide cathode materials already carry a native passivation layer of Li_2CO_3, which in turn reacts with acidic electrolytes in the battery environment through pure chemical pathways. Second, further evolution occurs through electrochemical pathway, leading to eventual CEI chemistry. Finally, the surface of the cathode material might also be involved in the evolution, creating an intermediate phase and thus smearing the clear definition of where CEI starts. Nevertheless, the electrolytes and interphasial chemistries are closely associated. Because the electrolyte is the only component in a battery that is in contact with every other component, designing better electrolytes implies tailoring and balancing a host of properties, ranging from bulk (e.g., ion solvation and transport and extended liquid structure) to interfacial structure and stability (e.g., preferential assembly and orientation of ions and molecules at Helmholtz planes and corrosion suppression) to interphasial chemistry and morphology. Although the irreversible reactions leading to interphase formation mainly occur during the initial activation cycles of batteries, the interphases thus formed will dictate the power, energy, and reversibility of the battery during its entire service life.

Differing from the two-dimensional interface in classical electrochemistry, interphase constitutes an independent, three-dimensional existence with special chemistry and morphology. With nanometer thickness (~2 to 20 nm) and extremely high sensitivity, interphases have been the least understood component in rechargeable batteries until recently, when various advanced characterization and computational techniques were developed to shed light on this critical component (6).

LIBs enabled by interphases

The energy density and rechargeability of LIBs rely on interphases (Fig. 1) (3). Because the potential of a graphitic anode in a LIB (~ 0.01 V versus Li) resides far beyond the thermodynamic stability window of the electrolyte, as marked by the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs), the reversible lithiation/de-lithiation chemistry relies on the protection from interphases (7). The electrolytes used in state-of-the-art LIBs vary with manufacturers and the cathode chemistry used; however, they almost exclusively follow a skeleton composition consisting of lithium hexafluorophosphate ($LiPF_6$) dissolved in a mixture of carbonate ester solvents, which is the result of balancing the requirements from every battery component (8), especially the graphitic anode at low potential (~0.01 V versus Li^+/Li) and transition-metal oxides or phosphates cathodes at high potential (~3.5 to 4.5 V versus Li^+/Li). It is now widely accepted that the SEI in LIBs mainly comes from the reductive decomposition of carbonate solvents and salt anions. These species are usually arranged in stratified structures, with the innermost layer being more inorganic (LiF and Li_2O) and the outer layer more organic (semicarbonates, oxalates, alkoxides, and polymers). Of special interest is the unbalanced contribution to SEI chemistry from one particular solvent, ethylene carbonate (EC) (9).

On the basis of numerous ex situ or in situ/in operando characterizations, the solvation sheath structure of Li^+ has been identified as being a key factor in SEI chemistry (9–11). In the very first cycle, as the negatively charged anode attracts the solvated Li^+ to its surface, it is the solvent molecules in the solvation sheath that initially experience reductive decomposition, thus becoming the precursors of the nascent SEI. EC happens to be the solvent that preferentially solvates Li^+. It is such solvation-interphase correlation that makes EC a preferred SEI contributor (9, 12, 13). Although the semicarbonate produced by EC decomposition constitutes the main SEI ingredient, recent studies have found that the nascent interphase can be electrochemically oxidizable (14), whereas long-term cycling turns it into monocarbonate (15).

The capability of EC in strongly solvating Li^+ and in forming a protective interphase on a graphitic anode make it almost an indispensable

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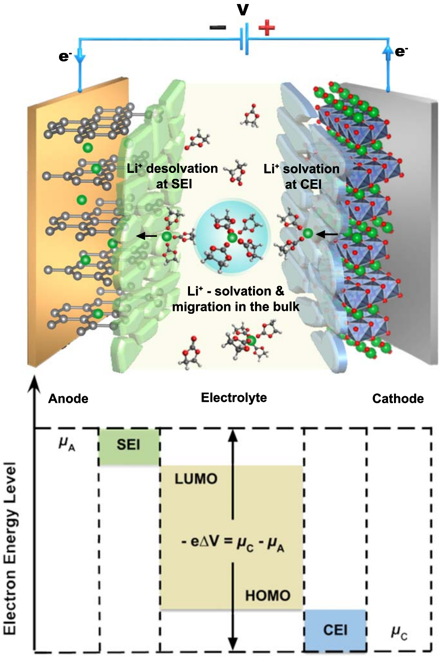

Fig. 1. How electrolytes work. The electrolyte must conduct ions, insulate electrons, and remain stable while simultaneously interfacing with all battery components. Substantial challenges arise when the cathode and anode operate at potentials beyond the region enclosed between LUMOs and HOMOs, where interphases must be formed to ensure the reversibility of the cell chemistry.

electrolyte component in all LIBs. However, the prevalent presence of EC in electrolytes also causes poor low-temperature performance and sluggish charging rates of LIBs because of its high melting point (36.5°C), high viscosity (2.0 cP at 25°C), and strong coordination with Li^+. Efforts have been made in recent years to replace EC with EC-free electrolytes based on acyclic carbonate such as ethylemethyl carbonate (melting point −53°C and viscosity 0.65 cP at 25°C) as the main solvent. When used in presence of fluoroethylene carbonate as a SEI-forming additive, this EC-free electrolyte could maintain most of the merits of EC-based electrolytes while circumventing the disadvantages (*16*, *17*).

Compared with SEI, there has been much less understanding about CEI. In certain cases, even the existence of CEI has been debated (*18*). Although studies show that conventional electrolytes could support cell operations up to 5.6 V under certain conditions (*19*), in cells that must withstand long-term cycling, the need for a CEI is still fundamentally driven by the mismatch of thermodynamic factors (Fig. 1). Unlike SEIs, which fully cover an anode, the depositions on the cathode surface, mostly inorganic fluorides and oxides, have often been found to be scattered and discontinuous, raising suspicion about whether they indeed function as protection (*20*). This was partially because the operating potentials of most cathode materials used in LIBs (<4.2 V) do not deviate too far from the limits allowed by electrolyte HOMOs (~4.0 V), but also because CEI chemistry is much more complicated. It involves not only electrolyte but also the decomposition and phase transformation of the cathode itself, thus causing the problem of defining where the interphase should start and end. However, with the development and commercial adoption of various high-voltage (>4.5 V) cathode materials in LIBs, the necessity for CEI is no longer questionable, just like SEI (*21*).

Researchers have reached a consensus that electrolyte and interphase are convoluted, and that the solvation structure for Li^+ (or any other cations essential to the cell chemistry, such as Na^+, Mg^{2+}, Ca^{2+}, and Zn^{2+}) is of vital importance when designing new electrolyte systems (*22*). The most direct fruition of the solvation-interphase correlation is perhaps the superconcentration concepts that led to diversified new electrolyte systems, including water-in-salt electrolytes (WiSEs) (*23*–*25*).

Designing electrolytes and interphases for emerging battery chemistries

In an era where LIB has become a mature technology, emerging battery chemistries promising either extremely high energy or power or low cost and high sustainability are being actively pursued. Alternative working ions such as Na^+ (*26*), K^+ (*27*), Mg^{2+} (*28*), Ca^{2+} (*29*), and even Al^{3+} (*30*) are also under consideration. To support these more energetic and much more aggressive chemistries that either operate at extreme potentials with drastic morphological and volume changes (Li^0 and Si), or involve extremely reactive surfaces (Li^0 and air cathodes), or rely on working ions difficult to move (Mg^{2+}, Ca^{2+}, and Zn^{2+}), the designing of electrolytes and the associated interphases must address different challenges.

On the anode side, Si is gradually replacing graphite as anode host for Li^+, which theoretically could provide 10 times higher specific capacity than graphite. However, the manyfold volume change of Si accompanying such high capacity presents severe challenges to the electrolyte and the associated SEI, which must withstand not only the low potential of Si (~0.5 V vs. Li^0) but also the mechanical stress and incessant exposure to new Si surfaces (*31*). Although making Si nanosized or embedding it in carbonaceous matrices could relieve the stress and fragmentation (*32*), fluorinated solvents such as fluoroethylene carbonate and the highly fluorinated salt anion fluorosulfonyl imide have also been found to stabilize Si effectively, leading to highly fluorinated SEIs containing LiF and organic fluorides that help to prevent Si fragmentation (*33*).

Much more severe challenges are associated with lithium-metal (Li^0) anodes, which are being revisited as the ultimate anode material because of their energy density (*34*). The promised high energy of Li^0 is accompanied by extreme reactivity, which is associated with excessive and incessant interphase growth, leading to both low efficiency of the Li^0 electrode and dangerous morphologies such as dendritic and dead Li^0. Identifying an electrolyte with effective SEI chemistry has become a heavily invested research direction, with the goal that Li^0 deposition could proceed homogeneously at high Coulombic efficiency (CE%). It is of special importance to circumvent fractal-like, long-aspect-ratio crystals (Fig. 2), which could either penetrate the cell and create an internal short circuit or be easily cut off near the roots and form highly dangerous dead Li^0 (*35*). The best electrolytes identified so far are based on fluorinated ether molecules rather than esters, which can achieve CE% as high as 99.9% and suppress dangerous Li^0 morphologies during long cycling (*36*). The improved Li^0 reversibility from such general fluorination of both electrolyte composition and interphasial chemistry has been attributed to the high surface energy for Li^0 to nucleate on the LiF.

Metals corresponding to multivalent cations (Mg^{2+}, Ca^{2+}, Zn^{2+}, and even Al^{3+}) are of high interest as possible anode materials with the

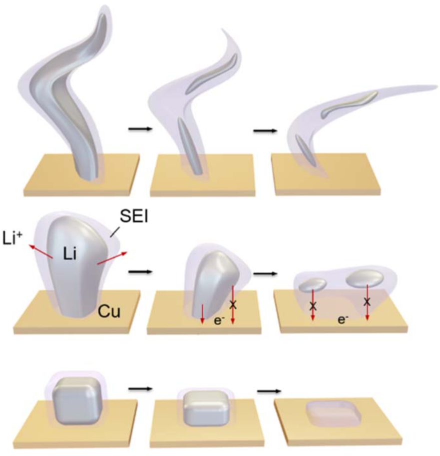

Fig. 2. The challenge of the Li^0 anode. Designing an electrolyte and the associated SEI to eliminate dangerous morphologies of dendritic and dead Li^0 is the key to enabling rechargeable lithium-metal batteries. Top: an inhomogeneous SEI encourages the growth of dendritic Li^0 at spots that are more conductive to Li^+, whereas dissolution near the root of the dendrite results in dead Li^0 that is electrically isolated from the current collector. Middle and bottom: designing better electrolytes and interphases guides the growth of dense Li^0 so that crystals of low aspect ratios are preferred, which means that they stay electrically attached during repeated plating and stripping.

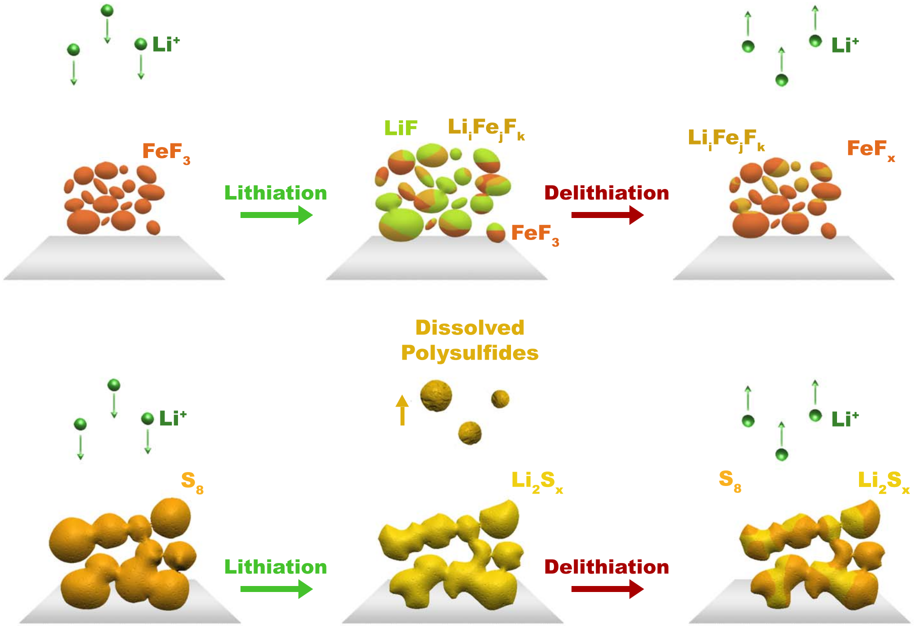

Fig. 3. Emerging conversion-reaction battery chemistries. Both iron fluorides (top) and sulfur (bottom) rely on drastic structure breaking and structure reforming to deliver high capacities and energy densities, but heir reversibility encounters severe difficulty because it is almost impossible to completely restore the original structure, and the active materials generated could be soluble in electrolytes and leave electrode bulk.

expectation that multiple electrons involved in their reactions would favor the specific capacity (*28*–*30*, *37*). However, the Coulombic force exerted by these multivalent cations on their environments (counterions, solvent molecules in bulk electrolyte, polyanions in lattice structure, or coordination sites in interphases) is so intense that either the multivalent salts have limited solubility in the electrolytes or the solvent molecules are so strongly bound to the multivalent ion that there is the possibility of their being electrostatically decomposed (*38*). Thus, desolvation at interphases becomes impossible or the multivalent cations are not able to travel across the interphases at all (*37*, *39*). Electrolyte design must resolve these problems, with the aim of forming (i) weakly coordinated electrolytes so that the cations are less solvated and the desolvation energy barrier could be more easily overcome, (ii) reduction-resistant electrolytes using various hydrides and organometallic Grignard reagents so that no SEI forms, or (iii) superconcentrated electrolytes in which networked anion clusters could assist in liberating cations for movement. Unlike LIB electrolytes, ethers rather than esters are exclusively favored here because of the intrinsic reactivity of the latter with these metals.

However, regardless of whether they are based on hydrides, Grignard reagents, or ethers, these reduction-resistant electrolytes raise new issues on the cathode side because they are all vulnerable against oxidation. Therefore, it remains to be seen whether these electrolytes can withstand the high voltage of multivalent cathode materials, which are still under development themselves. Prior experience with LIBs teaches us that the best approach to resolving such convoluted interests from the anode, cathode, and bulk electrolyte is an interphase that can effectively decouple them (*40*).

Among all multivalent cation chemistries that still largely remain remote from practical applications, Zn stands out as an exception. As the anode material in Alessandro Volta's first battery in 1799, Zn chemistries have powered us from the Industrial Revolution into the modern era, and they are still being used in the alkaline batteries available from drugstores. Zn reduction/oxidation potential sits at a moderate value (–0.76 V versus standard hydrogen potential) that allows for aqueous electrolytes; however, its poor reversibility has rendered these batteries essentially nonrechargeable. This situation has witnessed improvements in the past 5 years (*41*), when Zn^0 reversibility has progressed toward practical application, aided by advances in understanding Li^0 anode reversibility (*42*). The missing piece of a rechargeable Zn battery is a viable low-cost cathode material that could provide high reversibility and high capacity with Zn. The most promising candidates include air cathodes that use oxygen from the ambient air (*43*) and various intercalation hosts for Zn^{2+} (*44*).

On the cathode side, the pursuit for emerging chemistries has been focused on the search for either extremely high energy densities (*45*) or materials that are independent from Co or Ni, the two elements that LIB chemistries have been heavily reliant on, but are either extremely rare in the Earth's crust or are only available at high geopolitical or ethical risk.

As near-term goals, relatively more mature materials, such as improved versions of intercalation compounds, have been explored, some of which are already being gradually adopted by the LIB industry. Conceptually, they do not differ appreciably from the state-of-the-art LIB cathode materials, but the structural modifications of their lattices allow them to accommodate more Li$^+$ at higher potentials. The most popular approach to tailoring electrolytes for these aggressive cathodes are various electrolyte additives designed to have higher HOMOs so that even at a minor presence (from a parts-per-million level to a few percent) in the electrolyte, their oxidative decomposition could still dominate the CEI chemistry and form a better protection for both bulk electrolyte and the cathode itself (*46*). In some cases, the cathode structure is designed so that the redox reaction is no longer confined to the transition metals. Instead, the oxygen in the lattice could be harnessed for additional capacities. The electrolytes for such aggressive materials must display special stability against the reactive peroxide or superoxide species thus produced (*47*).

More radical materials leveraging conversion-reaction chemistries are being considered as long-term targets (*48*), including metal fluorides, sulfides (*49*), elemental sulfur (*50*), or even oxygen (*51*), which had been unsuccessfully explored in the early days of the rechargeable battery research. Unlike intercalation-type electrodes with minimal structural change, these electrode materials experience complete restructuring during the discharge, enabling significantly higher capacities, but at the expense of reversibility because it is almost impossible to completely restore the original electrode structures (Fig. 3). Because of advances made in the synthesis of nanostructured materials, these once-inaccessible chemistries could be revisited with higher feasibilities. The corresponding electrolytes and interphases are thus required to resist the strong catalytic activity from the nanosized metallic particles generated from the metal fluorides or sulfides, suppress the parasitic shuttling of soluble polysulfides across the cell, and remain inert to the reactive peroxide or superoxide intermediates from oxygen reduction (*48*–*51*). There have been limited improvements made thus far in addressing these challenges, leaving a wide space for researchers to explore.

New concept electrolytes and interphases

Substantial efforts are being made not only in designing and synthesizing new electrolyte components (solvents, salts, and additives), but also in making use of already-existing components in an innovative manner. These can be condensed into a few general approaches that have been effectively applied to a wide spectrum of battery chemistries from Si and Li^0 to multivalent metals and from improved intercalation to conversion-reaction materials.

Superconcentrating

Traditionally, electrolytes were confined to a salt concentration around 1 molarity (or 1 molality) to maximize ion transport. This limit was lifted after researchers realized that an extra-high salt concentration could bring a series of benefits that offset the loss in ion transport due to the viscosity increase (52, 53). These benefits include nonflammability, anticorrosion at high voltage, high cation transference, and, most importantly, new interphasial chemistries. The rationale underneath such changes lies in the solvation sheath structures of both cation and anion, which are significantly altered at these unusual salt concentrations. One extreme example is the WiSE (23–25), in which 21 molality or higher lithium salts dissolved in water enable the formation of an SEI in water and expand the electrochemical stability window of aqueous electrolytes from 1.23 V into the regime of >3.0 V to support high-voltage aqueous LIBs. At such extra-high salt concentrations, not only are solvation sheaths restructured, but in extended length scales, the hydrogen bonding between water molecules completely disappears and an anion-cation network forms. The superconcentration concept applies to aqueous, nonaqueous, and even hybrid electrolyte systems. One particular modification is the so-called localized high-concentration electrolytes, in which a noncoordinating co-solvent (usually polyfluorinated ethers) is introduced to further disrupt the liquid structure of the parent electrolyte so that the overall salt concentration would be near 1.0 M but locally the cation still sees a solvation structure similar to a superconcentration regime (54).

Singularizing

Because it has been widely established that interphases formed in situ on an electrode are highly inhomogeneous in both chemistry and morphology, efforts are being made to identify which chemical is the single most effective ingredient in ensuring cell reversibility. On the basis of this knowledge, efforts could then be made to enrich such chemistry in interphases or even make the interphases in singular composition. Currently, the attention has been focused on two distinct inorganic salts, LiF and Li_2O, as effective yet manipulable SEI components.

The presence of various fluorides, either organic or inorganic, has been long identified in both SEIs and CEIs, but no simple linear relation could be established between fluoride content and interphase performance. Fluorine is the most resistive element toward both oxidation and reduction, so it should make an ideal ingredient for interphases designed to support aggressive battery chemistries. However, fluorides are excellent insulators not only to electrons but also to ions, so it is counterintuitive that a pure fluoride-based interphase could function at all. Simulations reveal that when fluorides interface with other impurities such as oxides or carbonates at nanometric scale, highly conductive pathways for Li^+ can be created along the grain boundaries (55). It becomes increasingly apparent that fluoride distribution in the interphases and interactions with other species are more critical than the fluoride content alone (56). Thus far, knowledge about precisely tailoring the nanometric morphology of these fluoride species is still missing. A semi-empirical approach adopted as the design philosophy is that fluorine must be prestored in the structures of various solvents, additives, or anions, and would then become available only when electrochemically activated. Fluorides formed in this manner would exist in nanometric scales and well interfaced with other interphasial ingredients. Highly fluorinated interphases have been made with impressive performances, examples of which include the almost pure LiF- or NaF-based SEIs formed in WiSE from TFSI anions and the LiF-enriched CEIs formed in fluorinated ether electrolytes (23, 24).

Li_2O was identified recently as an alternative interphasial ingredient on Li^0 on the basis of observation and analysis achieved under cryogenic electron microscopy (57, 58). Unexpectedly, highly fluorinated ether electrolytes that have led to fluorinated CEI on a NMC cathode simultaneously generated Li_2O-based, monolithic SEIs on a Li^0 surface without any detectable fluorides (58, 59). More pure interphases of singular chemical composition were thus attempted, in which both LiF and Li_2O were artificially applied on Li^0 surfaces using a suspension of corresponding nanoparticles (60). It is anticipated that with increasing understanding about interphasial chemistry and morphology, we will witness further such efforts with new chemical ingredients. However, caution should be exercised here because we actually know very little about how LiF or Li_2O functions in an interphase. The correlation between their presence in interphases and their effect on electrochemical performance remains superficial and highly empirical. More fundamental knowledge is needed before we can determine whether an ideal interphase should be singular or heterogeneous.

Solidifying

Making electrolytes solid has always been desirable because solid electrolytes (SEs) provide nonflammability, zero leakage, and mechanical resistance against Li^0-dendrite growth, thus offering more convincing feasibility of enabling Li^0 anodes in wide range of operating temperatures (61). Decades ago, researchers started seeking suitable materials with an excellent electrolyte nature, i.e., high ionic conductivity ($\sigma_{Li+} > 0.1$ mS/cm) but low electronic conductivity ($\sigma_e < 10^{-7}$ mS/cm). These efforts have covered organic materials such as polymeric, inorganic ceramic or glassy materials such as oxides, halides, and sulfides as well as composites that combine all of them (61, 62).

Polymeric ion conductors are of interest because of their flexibility and processibility, but the coupling between the segmental motion of the oligoether chain and the ion transport constitutes an insurmountable barrier to achieving sufficient ion conductivities at ambient temperature (63). The average conductivity of ~10^{-5} S/cm at 25°C restricts the use of these polymer electrolytes in batteries to niche applications at elevated temperatures, such as the solid lithium-metal batteries adopted in certain electric vehicles in Europe. Fundamental breakthroughs are needed to decouple ion transport from polymeric segmental relaxation, which requires a new ion transport mechanism. One recent advance in which cellulose chains are artificially expanded by bridging copper ions so that Li^+ can travel independently from the polymeric chain represents one such direction (64).

Among the inorganic solid materials, sulfides have emerged as a top contender, with high ionic conductivities at room temperature (>10^{-3} S/cm) and high compliance to be processed into ultrathin dense layers, but their moderate electrochemical stability requires extra interphasial protection against extreme potentials of numerous cathode and anode chemistries (61). Argyrodite Li_6PS_5Cl (LPSCl) has been revealed to form interphases with both Li^0 and Si, which is dominated by electronic insulating yet ionic conductive salts such as LiCl, Li_2S, and Li_3P (65). For high-voltage cathodes such as layered transition-metal oxides, sulfides are usually protected by artificial interphases that are formed by coating on sulfide SEs a layer of ceramic with high oxidative stability, examples of which are lithium niobates and lithium borates. With tailored composition and interfacial engineering, sulfide-based SEs could work at voltages >4.2 V (66).

Various types of scalable, low-cost, uniform coating strategies on cathode materials are still being explored, because the mismatch in chemical and mechanical properties between the cathode active materials and the SE could lead to uncontrolled impedance growth that negatively affects cell performance (67). Coating layers not only chemically and electrochemically protects the interfaces from decomposition, but also serves as a mechanical buffer to stabilize solid-solid interfaces. The formation of dendritic

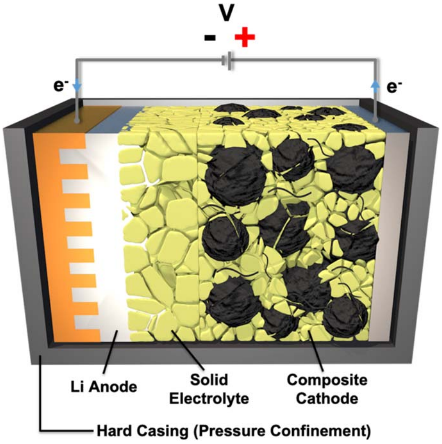

Fig. 4. Interfacing solid with solid. Interfacing solid materials in an all-solid battery encounters both challenges and opportunities with the solid-solid contact points of active anode/cathode materials and the SEs.

and dead Li^0 continues to plague Li metal anodes because of imperfections and inhomogeneity at metal-SE interface, leading to these dangerous Li^0 morphologies that become exacerbated at higher current densities. Recently, the inhomogeneous stripping of lithium and the subsequent formation of voids have also become a focus of research (68). Plastic deformation of the metal through mechanical compression shows promise in preventing dendritic and dead Li^0 (69, 70). However, obtaining these pressures may require significant cell-level penalties because of the need for special fixturing.

The paramount challenge for SEs still comes from solid-solid interfaces, because SEs cannot flow or infiltrate into the porosity structure of the electrodes. A common approach to overcoming the physical contact issue is the addition of a controlled amount of liquid electrolytes to fill the voids and gaps. This renders the system less solid and results in a hybrid electrolyte or semi-SE (71). Conversely, the solid-solid contact challenge could also be turned into an advantage to enable three-dimensional (3D) architectures for the Li or Si anodes, because the interphasial reactions can only occur at those contact points, whereas large volume expansion and shrinkage can be accommodated with appropriate 3D design and dynamic pressure control (Fig. 4) (72). The single-ion conducting nature of SEs eliminates concentration polarization and allows accommodation of local effects that cause nonuniform reaction and eventual capacity fade (73). Although it remains a key hurdle for the battery field to quantify the coupled electrochemical-mechanical phenomena, recent work has been rather encouraging, showing a stable and long cycle-life of laboratory-scale batteries.

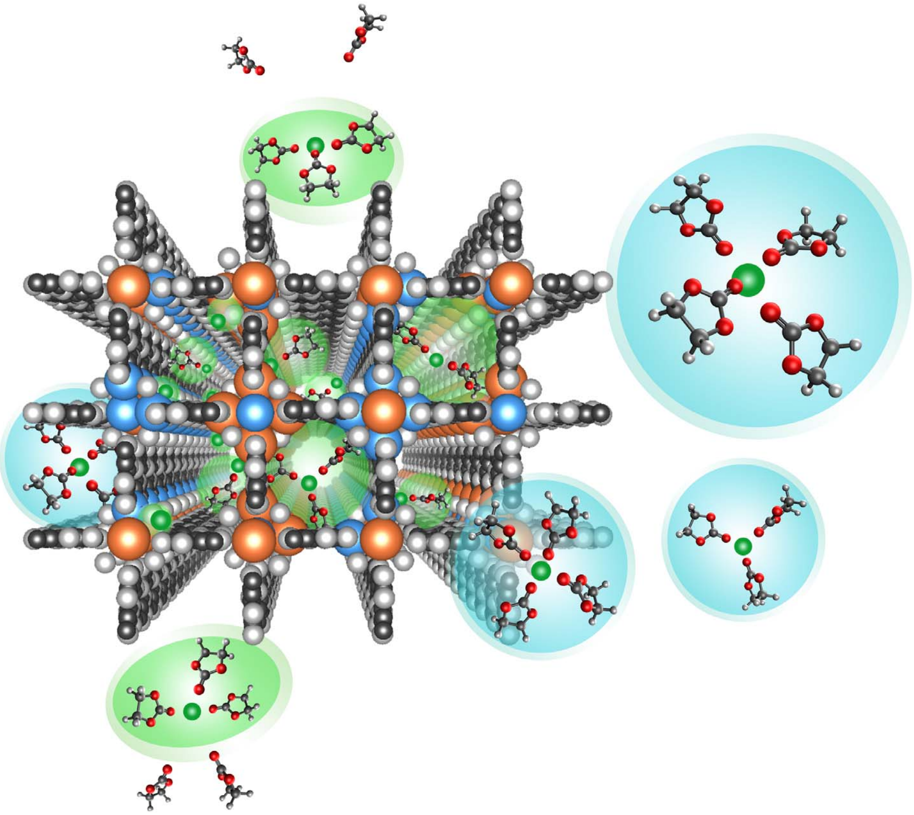

Fig. 5. Solvation in nanoconfinement. When the host environment becomes comparable in size with the ion solvation sheaths, forced interaction between the host and ion or its solvent members becomes inevitable, which induces partial or complete desolvation of the ions and generates a series of unusual properties.

Liquefying

In addition to liquids and solids, a new frontier has been created in which a quasi-gases are harnessed as electrolyte solvents. These efforts enable operation at lower temperatures not otherwise possible with typical electrolytes. Relatively polar gaseous hydrofluorocarbon molecules such as fluoromethane (CH_3F) can be liquefied under moderate pressure (74), which dissolves salts at room temperature to form liquefied gas electrolytes. These electrolytes are nontoxic and have relatively strong covalent bonds that allow for a wide electrochemical window. Because of their small molecular size and weak intermolecular attraction, these solvents display exceptionally low viscosity that enables a superior solvent dielectric-fluidity factor that is higher than that of typical electrolyte solvents such as esters and ethers. The solvents also have extremely low melting points that render batteries operational below –60°C. Additives such as tetrahydrofuran (THF) (75) can be introduced to alter the Li^+-solvation structure, which has been fully populated with CH_3F molecules. The intrinsic fluorine-rich chemistry and the self-equilibrated pressure enable Li^0 reversibility even at very high current densities (10 mA/cm^2) and low temperatures. Other types of co-solvent could also be used to widen the operation temperature range, especially at the upper limit, where salt precipitates and ion transport shutdown occurs. More recent use of difluoromethane (CH_2F_2) in combination with dimethoxyethane co-solvent have shown such an improvement (76), and the concept was also extended to multivalent chemistries such as Zn (77). These unconventional electrolytes, although confined to limited applications because they require a hermetical stainless steel case, have significant potential for further development.

Nano-confining

The size of most ion solvation sheaths ranges from an angstrom to nearly a nanometer, depending on the solvent molecules and the solvation numbers. With the emergence of diversified nanomaterials, an interesting question arises: How would the solvated ions behave in these sub-nano structures? There have been numerous reports on the unusual properties of electrolytes in nano-confinement. For example, anomalous capacitance arose when solvated tetraalkyl ammonium cations were forced into pores as small as 0.65 nm (78). Significantly different interphasial behaviors and morphologies of Li^0 anode emerged when infusing conventional LIB electrolytes

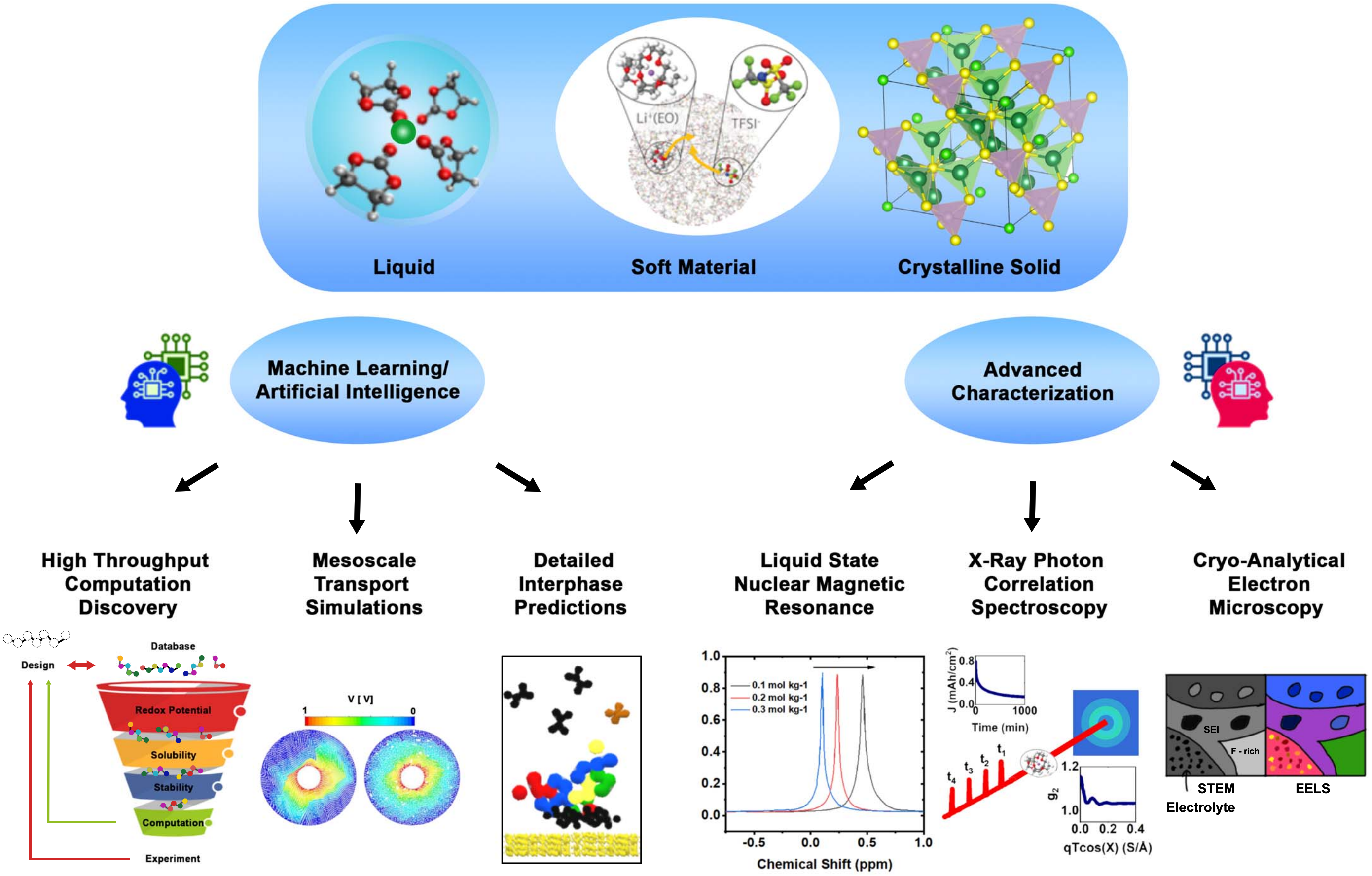

Fig. 6. Seeing electrolyte dynamics at molecular resolution. Advanced ex situ and in situ/in operando characterizations assisted by computational simulation and modeling bring a new horizon to the understanding and discovery of electrolytes and their interphases.

into nanopores of a ceramic-polymer composite host of mean diameter ~40 nm (79). The electrochemical stability window was significantly expanded when ether-based electrolytes were frozen into the sub-nano channels of 0.29 nm created by metal-organic framework structures (80, 81). Finally, extraordinarily fast ion transport far above the corresponding bulk polymer electrolyte occured along the ceramic-polymer interfaces when the same polymer was embedded into the channels of a ceramic host as small as 40 nm in diameter (82). Although these scattered phenomena do not seem to be related at first glimpse, and the investigators in each study offered widely different rationales, there is a converging factor in all of them: In the nanostructured environment, the solvated ions were likely to interact with the surfaces of the host materials (Fig. 5), during which partial or even complete desolvation of the ions occured, producing electrolytes at chemical states that are not fully understood yet. Therefore, there might be opportunities to leverage these conditions.

Outlook: A bright future with apprehensions

A battery is a multicomponent system consisting of at minimum a positive electrode (cathode), a negative electrode (anode), and an electrolyte. For the battery chemistry to work, all of these components must synchronize with each other. The failure of a battery often occurs not as a result of a single malfunctioning component but rather because of the interactions between different components.

Constrained by such a synchronization requirement, the electrolyte has often been the languishing component (8) because it must simultaneously interface with every other component in a battery, be it active components such as the cathode and anode or inactive components such as separators, current collectors, and cell packaging. A significant amount of knowledge has been generated about electrolytes and their relation to interphase. Nevertheless, many basic questions remain unanswered, such as: (i) How exactly do ions travel across interphases consisting of intrinsically insulating materials? (ii) How can one precisely measure electronic and ion conductivity within the interphases? (iii) Which components are effective and functional in the interphases and which are unnecessary and redundant? This list of questions will surely grow as new systems are developed and explored. In the meantime, new insights are being provided by various analytical methods that were previously unavailable. For example, combined chemical analysis, cryogenic electron microscopy, and pair distribution function (PDF) acquired from a synchrotron revealed that the interphasial chemistry on Li^0 is much more complicated than was once believed, with the exotic interphasial components such as glassy Li^0 and lithium hydride still under debate (83, 84).

To answer all of these questions, characterization techniques, especially those operational under in situ/in operando conditions and those with extremely high spatial and temporal resolutions, are needed. In the past decades, although many advanced characterization tools have been developed to probe and quantify the interphasial species, tools that directly probe the electrolyte are still absent. Given the noncrystalline and fast ion dynamics nature of typical electrolytes, spectroscopic methods with high chemical sensitivity and total scattering for local structure are most suitable because they are tolerant to long-range disordered arrangements. As shown in Fig. 6, a comprehensive understanding about solvation structure in electrolytes, the associated interphase chemistry, and its distribution along 2D and 3D length scales, as well as how the chemistry evolves during electrochemical processes, could be achieved by the study of large datasets collected using a combination of a host of techniques. These include liquid and solid nuclear magnetic resonance (*13*), differential PDF derived from x-ray or neutron scattering (*85*), and cryogenic analytical electron microscopy equipped with tomography and electron energy loss spectroscopy (*86*).

As highly powerful supercomputing capabilities become more accessible, complicated processes in electrolyte bulk and interfaces are increasingly available for modeling with improved accuracy. Computational methods increasingly play a role in the discovery of new electrolytes and additives by using density functional theory to screen the thermodynamic oxidative and reductive stability of various organic molecules (*87*), in predicting ion mobility in SEs using methods such as nudged elastic band coupled with ab initio molecular dynamics (*88*), as well as in understanding interfacial and interphasial processes (*89*, *90*). These approaches have led to the development of infrastructures and associated databases to provide electrolyte information to the wider research community (*91*). With the increased interest in automated high-throughput experimentation (so-called robotic labs), these computation screening approaches are now aided by large volumes of experimental data, lending themselves to analysis using machine learning approaches (*92*).

Computation predictions complement experimental characterization methods by offering insight into the detailed and transient processes at interfaces. The recent molecular dynamic simulations of WiSE and its derivatives on electrified surfaces have revealed the possibility of predicting interphasial chemistries based on how the solvents and ions assemble and position in the inner-Helmholtz layers of the electrode before interphase formation (*89*). Further, molecular dynamic simulations also shed light on the reduction reactions responsible for interphase formation producing solid and gaseous products including C_2H_4, Li_2CO_3, LiF, and LEDC (*93*).

Finally, the increasing interest in developing electrolytes with enhanced transport properties has shed light on scale-bridging approaches linking ion correlations at the atomic scale to transport properties at the continuum scale using Stefan-Maxwell formalism (*94*). These methods have recently incorporated additional phenomena such as solvent motion (*95*) and its role in the precise definition of ion transference and the role of morphological effects at the nanoscale on conductivity (*96*), both of which use large-scale computations.

Although computational methods have blossomed over the past decade, further efforts are needed to move beyond thermodynamic calculations into the prediction of chemical reactions so that the cascade of reactions leading to the formation of interphases can be precisely described and tighter coupling between experimental methods and predictions can be forged. Artificial intelligence and machine learning methods will eventually grow to a leading role in these endeavors. Validation of modeling requires further support from advanced characterization.

The past decade has witnessed the explosive growth of research activities on battery chemistry and materials, with electrolyte development taking a substantial role. This emphasis on an area of vital importance to the future of our planet and civilization will be sustained and driven further by anxieties over both geopolitical and supply chain risks. Given that a battery is a system consisting of multiple components, complications often arise when evaluating a single component in different environments and settings. To enforce the reproducibility and comparability of the battery performance data in the literature, rigorous practice and standardized protocols by researchers are strongly encouraged. Some efforts have already been made in this direction (*97*, *98*), and we view these as indispensable guidelines that the battery, chemistry, and materials research community should follow strictly.

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Designing better electrolytes

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Progress and challenges for electrolytes
Compared with the development of new cathodes and anodes, there has been less of a focus on the development of electrolytes. However, it is the electrolyte that controls the flow of ions and charges, and it is the only component in intimate contact with all the others. With the push toward higher energy and power densities, electrolytes are also involved in kinetically formed interphases that aid in the stability of a battery but can also hamper its operation. In a review, Meng *et al*. captures a number of trends that have emerged in the development of advanced battery electrolytes. —MSL

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