Interfaces and interphases in batteries

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HIGHLIGHTS

- Interfaces and interphases are two separate but closely corrected concepts.
- Interface has been well understood in classical electrochemistry.
- Interphase still presents many unanswered questions to us.
- Knowing how to design interphase holds the key future batteries.

GRAPHICAL ABSTRACT
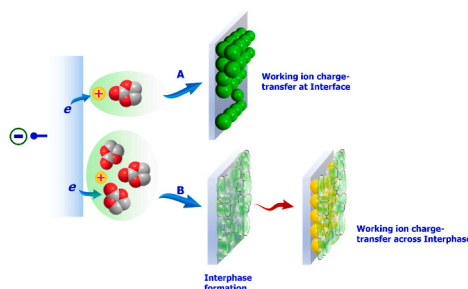
ABSTRACT

Lithium-ion battery (LIB) is the most popular electrochemical device ever invented in the history of mankind. It is also the first-ever battery that operates on dual-intercalation chemistries, and the very first battery that relies on interphases on both electrodes to ensure reversibility of the cell chemistries. Although it was the commercial success of LIBs that highlighted the importance of interphases, its occurrence far predated the birth of LIBs, and its existence goes far beyond the scope of lithium-based battery chemistries.

This perspective intends to shed light on the evolution of our knowledge about interfaces and interphases in batteries. As two intimately intertwined components in electrochemical devices, interface has been thoroughly described in classical electrochemistry, while interphase still presents many unanswered questions to us. The efforts of understanding and eventually tailor-designing the latter will hold the key to enable the next generation battery chemistries.

1. The classical interface: two-dimensional entity

In battery literature, the two words "interface" and "interphase" are often used interchangeably, yet they represent two very distinct concepts.

Interface is where electrode and electrolyte meet. Its importance for an electrochemical device cannot be over-emphasized. Since all electrochemical reactions are based on coupled oxidations and reductions, electron exchange must occur among the reactants, and interface provides the only legitimate location for such electron exchange. In other words, it is interface that distinguishes electrochemistry from conventional chemistry [1].

Perhaps Faraday was the first one to recognize the importance of interface for electrochemistry [2]. In his famous treatise in 1834, he wrote that "*The (electrode) surfaces, at which the electric current enters and leaves … are most important places of action, and require to be distinguished apart from the (electrode) poles …*". In this incredibly prescient paper, he also created a series of new terms that we still use today: "electrolytes", "ions", "cations", "anions", "electrodes", "cathodes" and "anodes".

In modern perspective, interface is where both phases (bulk electrode and bulk electrolyte) experience a sudden phasial discontinuity, the consequence of which is the uneven charge distribution and abrupt potential change. These properties dictate the kinetics and energetic efficiencies of cell reactions, which, for batteries, are reflected as rate

capability, power density as well as energy efficiencies of the device. In classical electrochemistry, an ideal interface should have zero thickness, which implies that there is no decomposition reaction that leads to permanent deposition of the electrode surface, hence the electrode surface remains completely clean [3]. The uneven charge distribution in one phase (e.g., electrode) thus should induce a corresponding response in charge distribution in the other phase (the electrolyte), so that the interfacial region as a whole still maintains the electroneutrality. In other words, the interface consists of a pair of parallel sheets of excess charges of the same quantity but opposite sign. In this sense, interface should be electrified, with very few exceptions. A simple rendition of an electrified interface is often called the "*electric double layer*", or "*Helmholtz-Perrin Model*" [4] (Fig. 1). The potential drop across such electric double layer is linear, because the interface in this case behaves as a double-layer capacitor.

In reality, the structure of an interface is much more complicated, especially on the electrolyte side if the electrolyte is a liquid (which represents the majority of electrochemical devices). This is mainly because, unlike electrode materials that are often excellent electronic conductors, the electrolyte consists of discrete ions solvated by solvent molecules [5]. The thermal motions of the ions and solvent molecules in random manner tends to disrupt the attempt of the ions to assemble orderly at the interface on the electrolyte side. The result of this disruption is a rather diffused ionic layer on the electrolyte side of the interface, hence the potential change across such an interface would no longer be linear, and the assembly of excess charges on the electrolyte side should scatter in a wide range from the electrode surface. Based on this assumption, there has been many versions of modification to the Helmholtz-Perrin Model, the most famous of which include *Gouy--Chapman Model* [6], where the diffused charge distribution results into a non-linear potential profile across the interfacial that can be described by a mathematical approximation closely similar to Debye-Huckel theory, *Stern Model*, which combined *Helmholtz-Perrin* and *Gouy-Chapman Models* and argued that the charge distribution consists of a dense layer close to the electrode surface and a diffused layer farther away [7], *Grahame Model* that took into account the specific adsorption of certain ions such as chloride on electrode surface [8], and *Bockris-Devanathan-Müllen Model* that treated the electrode as a giant two-dimensional ion, hence the immediate layer (also called the *inner-Helmholtz Layer*) next to the electrode is a two-dimensional solvation sheath consisting of oriented solvent molecules [9].

With the interfacial structure models evolving closer to reality, it also became more difficult to describe the interfacial distributions of charge and potentials with mathematical accuracy. Till today, the simplest model, i.e., Helmholtz-Perrin Model, still serves as the foundation for the theoretical description of interfaces, on which the famous *Butler-Volmer Equation* has been derived as the core of classical kinetics for electrochemical reactions [10], as well as the quantum rendering of the interfacial charge-transfer process derived by Marcus [11].

An ideal interface in classical electrochemistry should be conceptually two-dimensional, hence its thickness can be considered as zero. This sets a rather strict requirement for the electrochemical devices in order for such an ideal interface to be created. Most important of all, the electrodes must operate within the electrochemical stability window of the electrolyte, so that no irreversible reactions occur, and no solid deposition on the electrodes form. In other words, an ideal interface must be "clean" of any "impurities" resulting from the irreversible reactions between the electrodes and the electrolytes. Disobeying this requirement, an ideal interface cease to exist, and the junction between electrode and electrolyte could (but not always) transform into a new entity, i.e., *interphase* as named by Peled [12].

1.1. An independent phase: Peled's SEI

Interphase is the result of irreversible reactions between electrode and electrolyte. Because of the reactions, the junction between electrode and electrolyte is no longer clean, as the solid "impurities" produced by the reactions deposit on electrode surface and constitutes an independent phase. Although such an independent phase has been known to exist in all Li^0-based primary batteries commercialized in 1960s, it was Peled who formally studied it in 1979 when examining the rechargeability of Li^0-based secondary batteries, and established the basic property an interphase must possess: an ionic conductor but an electron insulator [12].

Lithium (Li^0) is the most electropositive metal ever known among all the elements, as represented by the lowest potential (-3.04 V) of it against standard hydrogen electrode (SHE). Such electropositivity reflects the extreme activity of Li^0, which reacts with almost anything upon contact [13]. However, as early as 1950s, people already know that lithium-metal often, although not always, stably exists in a number of non-aqueous and aprotic solvents, after a "*passivation layer*" develops on its surface. This passivation layer stops reaction between Li^0 and electrolyte, but still allows the passivated Li^0 electrode to operate as pristine Li^0, i.e., maintaining its electrochemical potential and activity. Peled was the first one who suggested that the passivation layer thus developed on Li^0 surface has *electrolyte nature*, i.e., insulating electron transport between Li^0 and electrolytes but allowing Li^+ to transport [12, 14]. This combination could well explain the above dual function: stopping chemical reaction but allowing electrochemical reactions.

Peled thus made up a new name for this passivation layer on Li^0, *solid-electrolyte-interphase* (SEI) [12]. Here "*Solid*" indicates the insoluble nature of this layer that results from the reaction between Li^0 and electrolyte. Of course, this nature only matters when the default electrolyte is in liquid state, which represent majority of electrolytes used in today's electrochemical devices; "*Electrolyte*" refers to its ion-conducting/electron-insulating nature mentioned above; and
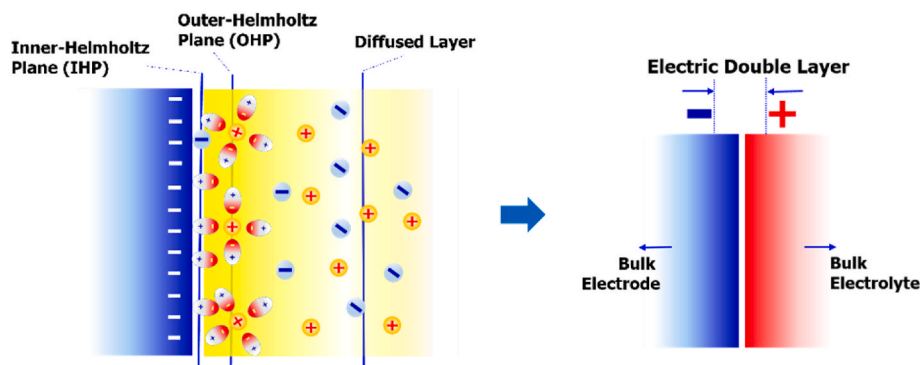

Fig. 1. The complicated structure of electrode-electrolyte interface is often simplified into an electrified double-layer, which behaves as a simple capacitor. The ideal interface should be "clean", i.e., the electrode surface is not free of any solid impurities produced by the electrodic reaction. The spheres carry "+" and "-" signs represent cations and anions, respectively, while the solvent molecules are represented by an oval-shaped dipole.

"*Interphase*" implies that it is an independent phase between the electrode and the electrolyte, with its own thickness, chemical composition and morphology.

SEI is by no means unique on Li^0. In fact, on the surface of any electrode that operates at potentials beyond the stability of electrolyte, there could be (and again, not always) SEI formed, examples of which includes sodium, potassium, magnesium and calcium [15,16]. Only in presence of SEI can the reversible electrochemical reactions based on these alkaline or alkaline earth metals operate reversibly far away from the equilibrium defined by the thermodynamics (Fig. 2).

We have repeatedly mentioned above that the formation of an SEI is not always the case. In fact, the condition required by the formation of an effective SEI is rather restrictive and very hard to meet. Many alkaline or alkaline earth metal electrodes have electrochemical potentials that are situated beyond the stability limits of the conventional electrolytes, but majority of the cases leads to sustained and catastrophic reactions between the electrode and electrolyte components, with interphase-formation as the extreme minority. One typical example is a piece of Li^0 thrown into water or alcohol, where no effective SEI could be formed because the reaction products (LiOH or LiOR) is too soluble in aqueous or alcoholic media to terminate the reactions. The reactions hence proceed until either Li^0 or water is completely consumed.

In a more general term, for an effective interphase to form, a host of strict requirements must be met, with the electrode potential going beyond the stability of electrolyte being the condition of necessity but not condition of sufficiency. Because when the potential of an electrode ventures beyond the electrochemical stability window of its electrolyte, the irreversible reactions thus induced do not always produce solid products that will deposit on the electrode surface. In such scenarios, no SEI could form.

Furthermore, if the solid deposition does not possess the electrolyte nature, i.e., ion-conducting but electron-insulating, then the new phase formed cannot effectively stop the sustained reactions between the electrode and electrolyte. In such scenarios, no SEI could form either.

Finally, it should be noted here that, although interphase is often associated with rechargeable battery chemistries, it is by no means confined therein only. Instead, it exists universally in almost all electrochemical devices that operate above 3 V. For example, the lithium-metal primary batteries ($Li/SOCl_2$, $LiMnO_2$ or Li/CF_x) commercialized in 1960s were already based on interphases on lithium-metal surface formed by either inorganic electrolytes such as thionyl chloride ($SOCl_2$) or organic electrolytes such as ethers, where LiCl or Li_2O serves as the interphasial ingredients. In broad sense, interphase is just a special layer

of products generated by the reactivity between electrode and electrolyte materials.

1.2. Transplanting SEI concept to lithium-ion batteries

Although SEI concept was initially proposed by Peled for Li^0 surface only, it gained popularity when Dahn and colleagues expanded its application to graphitic electrodes that also operates at extreme potentials [17].

In early 1990s the first generation of lithium-ion battery (LIB) was commercialized by Sony based on the initial technological foundation set by Yoshino and co-workers at Asahi Kasei [13]. This new battery differed from any previous batteries because its energy storage mechanism relies on the reversible intercalation/de-intercalation of Li^+ in a pair of intercalation hosts. At the time the anode material was a "soft carbon" called petroleum coke, whose amorphous structure prevents full utilization of carbonaceous capacity to accommodate Li^+ at optimized potentials. In order to fully leverage the capacity of carbon, the most crystalline form of carbonaceous materials became the natural goal. However, although the fully lithiated form of graphite LiC_6, had been known since 1950s [18], its electrochemical formation has been extremely difficult. No one has succeeded in doing so during the four decades, until Fujimoto and co-workers at Sanyo accidently found in 1991 that, if the electrolyte contains ethylene carbonate (EC), then LiC_6 can be synthesized in a reversibly manner [19]. This discovery laid the foundation of the modern LIB configuration: graphitic anode, an EC-containing electrolyte and an intercalation cathode, which remained almost constant since 1994 [20] (Fig. 3).

But why only EC can ensure the electrochemical synthesis of LiC_6?

Dahn and colleagues explained that, since graphite intercalates Li^+ at potentials (~ 0.01 V vs. Li^0) close to that of Li^0, an SEI must be formed to protect the graphite from being disintegrated [17]. This SEI, as result from the reaction between graphite and electrolyte, has to rely on some ingredients produced by the reduction reaction of EC. Transplanting SEI concept from Li^0 surface to graphitic anode represented a significant advance in our understanding of electrolytes and interphases. Since the work by Dahn and colleagues, the development of electrolytes must not only consider the physical properties such as salt solubility and ion transport, but also the interphasial chemistries that could be generated by the electrolyte.

The interphase concept was also extended to the other side of the battery, i.e., the cathode, because researchers noticed that, once the potential of the cathode goes beyond certain threshold, e.g., > 4.0 V vs.
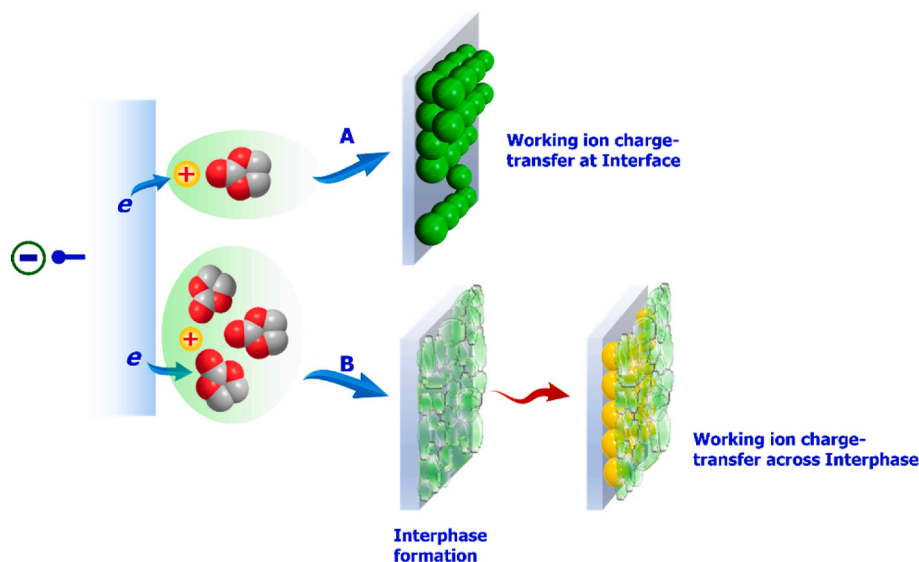

Fig. 2. Illustration of the difference between *Interface* and *Interphase*. In the former case, the electrode surface is clean, and the working ion experiences charge-transfer, such as the reduction and deposition of the ion. In the latter case, the electrode operates beyond the stability limit of electrolyte, whose decomposition results into the formation of an interphase. The charge-transfer reaction of the working ion must occur across such interphase. Many transition metal ions ($Cu^{+/2+}$, $Fe^{2+/3+}$ etc.) belong to the former case, while alkaline (Li^+, Na^+ and K^+) and alkaline earth metal (Be^{2+}, Mg^{2+}, Ca^{2+}) ions belong to the latter case given their high electropositivity. Note the natural correlation between working ion solvation sheath structure and the interphasial chemistry. The spheres carry "+" sign represent working cations, and the spheres without sign represents the deposited metal from the working ion. Ethylene carbonate (EC) is used here to represent a general non-aqueous solvent molecule.
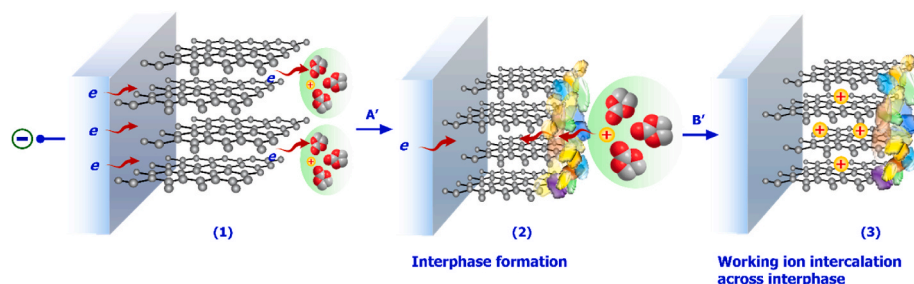
Fig. 3. The reversible intercalation/de-intercalation of Li^+ into/from graphitic structure relies on the formation of an interphase by EC. This interphasial chemistry enables the graphite anode for modern LIBs. Figure reproduced from Ref. 1 with permission of the Royal Society of Chemistry Press, London, Copyright 2023.

Li^0, an independent phase would also exist with similar functions to SEI. Winter and colleagues named this interphase "*cathode-electrolyte-inter-phase*" (CEI) [21]. The role of CEI becomes increasingly critical when more aggressive cathode materials (high voltage > 4.5 V, or high nickel content) are being adopted by LIB industry.

Nowadays, almost all new battery chemistries under development are designed to rely on interphases to work.

1.3. Understanding interphases

Compared with the studies on ion solvation and ion transport, the understanding of interphase is still in its infancy. The knowledge of how interphases forms, how they are structured and composed, and how one could tailor design an interphasial chemistry, remains topics that continue to be explored.

The discoveries made by Fujimoto et al. and Dahn et al. identified EC as a key electrolyte solvent responsible for SEI formation. Aurbach advanced our knowledge by establishing a single-electron reduction pathway cleaves EC at its alkaline C–O site, leading to a semi-carbonate, lithium ethylene dicarbonate (LEDC) [22]. This identification was supported by numerous work that followed, including various spectroscopic characterization as well as in-vitro synthesis of LEDC [23–26]. Onuki et al. later also identified an alternative two-electron pathway that cleaves EC at its acyl C–O site, leading to alkoxides and oxalates as minor ingredients in SEIs [27]. More recently, Wang et al. found that, upon long-term cycling and storage, LEDC loses one carbonyl group and releases CO_2, leading to lithium ethylene monocarbonate (LEMC) as the main SEI ingredients [28]. Semi-carbonates like LEDC and LEMC could also experience further reduction if they are close enough to the electrode, leading to products in more reduced form, such as lithium carbonate (Li_2CO_3) and lithium oxide (Li_2O). Compared with graphitic anode in LIBs, a Li^0 metal anode could engender much more complicated and diversified products, such as carbides, hydrides [29–32].

Polymerization also occurs, especially in the presence of unsaturated or fluorinated solvents/additives such as vinylcarbonate (VC) and fluoroethylene carbonate (FEC), leading to oligomers or polymers of varying lengths. Fluorine, on the other hand, has been a persistent ingredient in the SEI, mostly from the chemical or electrochemical decomposition of the lithium salt anion, hexafluorophosphate (PF_6^-), or from the electrochemical decomposition of the fluorinated solvents/additives, if there is any [33,34].

According to various advanced characterization techniques, SEIs in LIBs were found to be often layer-structured, with more inorganic species in the inner-layer closer to the graphitic electrode, and more organic species in the outer-layer closer to the electrolyte side [35]. However, choice of new electrolyte composition as well as electrode nature could result into different architectural arrangements of these chemical species. For example, a "monolithic" SEI has been reported to form on Li^0 surface in highly fluorinated electrolytes [36].

In summary, the chemical composition of SEI is rather diversified and heterogenous, consisting of mixed organic (semi-carbonates) and inorganic (oxides, carbonates, fluorides). Both the chemical composition and structure SEIs are highly dependent on the electrolyte composition and the forming condition (current density, voltage cut-off, temperature, external pressure, etc.) adopted. The latter has been well-guarded trade-secrets of various LIB manufacturers.

Beside chemical ingredients, SEI formation mechanism is of higher importance, as we desire to tailor design new interphases to cater to the battery chemistries that keep emerging. It is now widely accepted that the solvation sheath structure of the working cation plays a key role in determining the source of interphasial chemistry [37–40]. For example, in LIBs, where graphitic carbon is universally used as the anode host lattice, Li^+ usually "kidnaps" those solvent molecules preferentially recruited by its Coulombic field to the graphitic structure. At the edge sites of the graphitic structure, those solvent molecules in the Li^+-solvation sheath, which are usually EC in state-of-the-art electrolyte compositions, become the major chemical contributor to the resultant SEI. Replacing the graphitic structure with metallic electrode, similar mechanism works, as the working ions in their solvation sheath are the species that approaches the inner-Helmholtz layer on the electrode before any charge-transfer occurs. Thus, knowing how to alter the solvation sheath structure of working cation constitutes the key to manipulate SEI chemistries, although the exact mechanism of how those solvent molecules react to form a solid deposition layer remains to be understood. This concept has been confirmed by numerous characterization techniques, and has been widely adopted to design new electrolytes for various battery chemistries, the example of which include the family of concentrated electrolytes that rely on anion-derived interphases, such as "solvate ionic liquid" electrolytes [41], super-concentrated electrolytes [42], water-in-salt electrolytes or locally concentrated electrolytes [43,44]. The common foundation of these "concentration" approaches is the attempt to leverage the interphasial chemistry contributed from the decomposition of anions instead of solvent molecules.

While "solvation sheath structure" concept has been mainly pursued in research, interphase additives are more extensively used in LIB industry [45]. The use of trace amount of additives to alter interphasial chemistry seems to be more effective and economical, as the main physical and chemical properties of the mature electrolyte composition would suffer little impact. The basic philosophy of additive-approach is that, if a molecular or ionic compound that possesses lower electrochemical stability limits than the main electrolyte composition is present in the electrolyte system, this "unstable" compound would be preferentially decomposed, whose product would dictate the interphase and potentially provide better protection. For this reason, most additive molecules contain functionalities that promote earlier decomposition, such as unsaturated bonds, fluorination as well as ring-like structures. VC, vinylethylene carbonate (VEC) and FEC are perhaps the most extensively used molecular additives for interphase formation, while lithium bis(oxalate)borate (LiBOB) and its derivative lithium difluorooxalato borate (LiDFOB) or lithium difluoro bis(oxalate)phosphate (LiDFBOP) represent the additives in ionic form [33,34].

It is computationally possible to predict what compounds can be decomposed earlier than the main electrolyte components based on the

theory of molecular orbital energy levels, i.e., highest-occupied-molecular-orbital (HOMO) and lowest-unoccupied-molecular-orbital (LUMO), which defines the thermodynamic stability limit of a given electrolyte system [46,47]. But in reality, it is still impossible to precisely predict what cascade of reactions would follow, and whether these decomposition products could serve as ingredients for a better SEI. Overall, additive approach remains semi-empirical.

2. Conclusion: what we have known and what we Don't know yet

Given the critical importance carried by interphase, there have been focused efforts dedicated to their study. Thus far we have well understood the correlation between the electrolyte composition and interphasial chemistries, the role of solvation sheath structure of cation played in the formation process, as well as how to manipulate the solvation sheath structure of cation in order to alter the interphasial chemistries. Through extensive surface analysis we have also learned what the most desired species are likely. This knowledge has enabled us to tailor design interphases to some extent, and in some cases even to artificially apply pre-made interphases ingredients such as LiF and Li_2O.

However, interphase remain the "least understood" battery component, due to its in-situ and sensitive nature and its nanometric presence closely intertwined with the electrode chemistry and structure [48]. One particular case is CEI on cathode surface. Although the existence of CEI was contended in certain cases, it has been well established for those cathode materials operating at high voltages (>4 V). The definition of CEI, however, could still be ambiguous. Like SEI, CEI is the result of the irreversible reaction between electrolyte and the electrode (cathode) material. As the electrolyte components experience decomposition, so does the active species in cathode, which is often reflected as the phase transformation of cathode lattice near the interfacial region, such as the layered structure of transition metal oxides turning into rock salt structure. Whether this interfacial region of cathode lattice should be considered as part of CEI, or only the part contributed by the electrolyte decomposition be counted, could be subject of debate.

More importantly, there is a long list of key interphasial properties that we still do not have sufficient knowledge about, which includes.

(1) The structure and morphology of SEIs and CEIs.

The chemical composition of interphases is relatively easy to determine, thanks to the various surface-sensitive characterization techniques such as X-ray photoelectron spectra, electron microscopes and absorption/scattering spectra. However, how these interphasial ingredients are spatially arranged within the interphases remains difficult to ascertain, because of the high fragility of interphases toward any ex-situ techniques and the absence of reliable in-situ/operando techniques. In some sense, how the interphasial ingredients are arranged is as important as what they are (chemical compositions). For example, fluorides are commonly believed to be an effective interphasial ingredient, but simple application of fluorides on electrode surface would not work; Instead, these fluorides have to be scattered as nanoscale particles in the interphase and sufficiently interface with other species (oxides, carbonates) [49,50].

(2) How working ions travel across interphase.

Mechanistic understanding of this topic was never satisfactorily achieved. With the exception of oligomer/polymer species, almost all the identified interphasial ingredients, no matter fluorides, oxides, carbonates, alkoxides or oxalates, are poor ionic conductors, but yet alkaline working ions (Li$^+$, Na$^+$ or K$^+$) can easily transport across interphases built upon such "insulating" species, as evidenced by the reasonable charge/discharge rates of the corresponding batteries. Do these ions replace their counterparts previously immobilized in these fluorides, oxides, carbonates, alkoxides or oxalates? Or do they transport along certain "defects" such as grain-boundary between particles? There have been various theoretical explanation and modeling, but none has been directly supported by experiments [51,52].

(3) The conductivity of working ion in interphase

Although we know that interphases must conduct working ions at reasonable conductivity, so far no one has been able to directly measure the conductivity or diffusivity of working ions through the interphases. Modeling gave us estimates of these numbers at 10^{-15}– 10^{-17} m^2/s, which remain hypothetical and to be verified [53–55].

(4) Interphases for multivalent working ion and possible intermediates

Multivalent ions (Mg^{2+}, Ca^{2+}, Zn^{2+} or Al^{3+}) are being explored in recent years as possible working ions for the next generation batteries. Differing from their monovalent counterparts (Li$^+$, Na$^+$ or K$^+$), these ions bear twice or thrice as much charge with comparable or even smaller ionic radii, hence they are heavily solvated by solvent molecules in order to compensate for the strong Coulombic field strength. A direct consequence of such strong solvation is the difficulty in desolvation, which must happen at the electrode/electrolyte interface before charge-transfer could take place. A series of interesting questions therefore arise: Can these multivalent working ions travel across interphases because of their strong interaction with the environment? Do they experience partial reduction, generating meta-stable intermediates such as Mg^+, Ca^+, Zn^+, before being reduced to elemental form?

(5) The potential profile and ion concentration distribution across interphases

As discussed in the first section, in order to quantitatively describe the kinetics of ion transport across interphases, one needs to know the potential profile and ion concentration distribution across such heterogenous phase. This has not been possible because (a) We cannot yet precisely determine the architecture and morphology of the interphasial species; (b) We do not know the nature of interactions among each species. This knowledge gap prevents us from acquiring a mathematical model for these quantities within interphase. To make things more complicated, since interphase is an independent phase, each interphase has its own interfaces with electrode and electrolyte, respectively.

The list goes on, which include how an interphase creates its own interfaces with electrolyte or electrode, what the energetic barriers are across such interfaces, how the solvation sheath structure of the working ions vary in the nano-structured environment of the interphases, etc, etc.

As we are endeavoring to design and develop electrolytes for the next generation battery chemistries, knowing the answer to these questions might constitute the key to success. The emerging applications of data science together with new characterization techniques will further assist us in understanding this least understood component in a battery device.

Credit Author Statement

Kang Xu Conceived and wrote the paper.

Declaration of competing interest

Data availability

No data was used for the research described in the article.

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