Electrolyte Interphases in Aqueous Batteries

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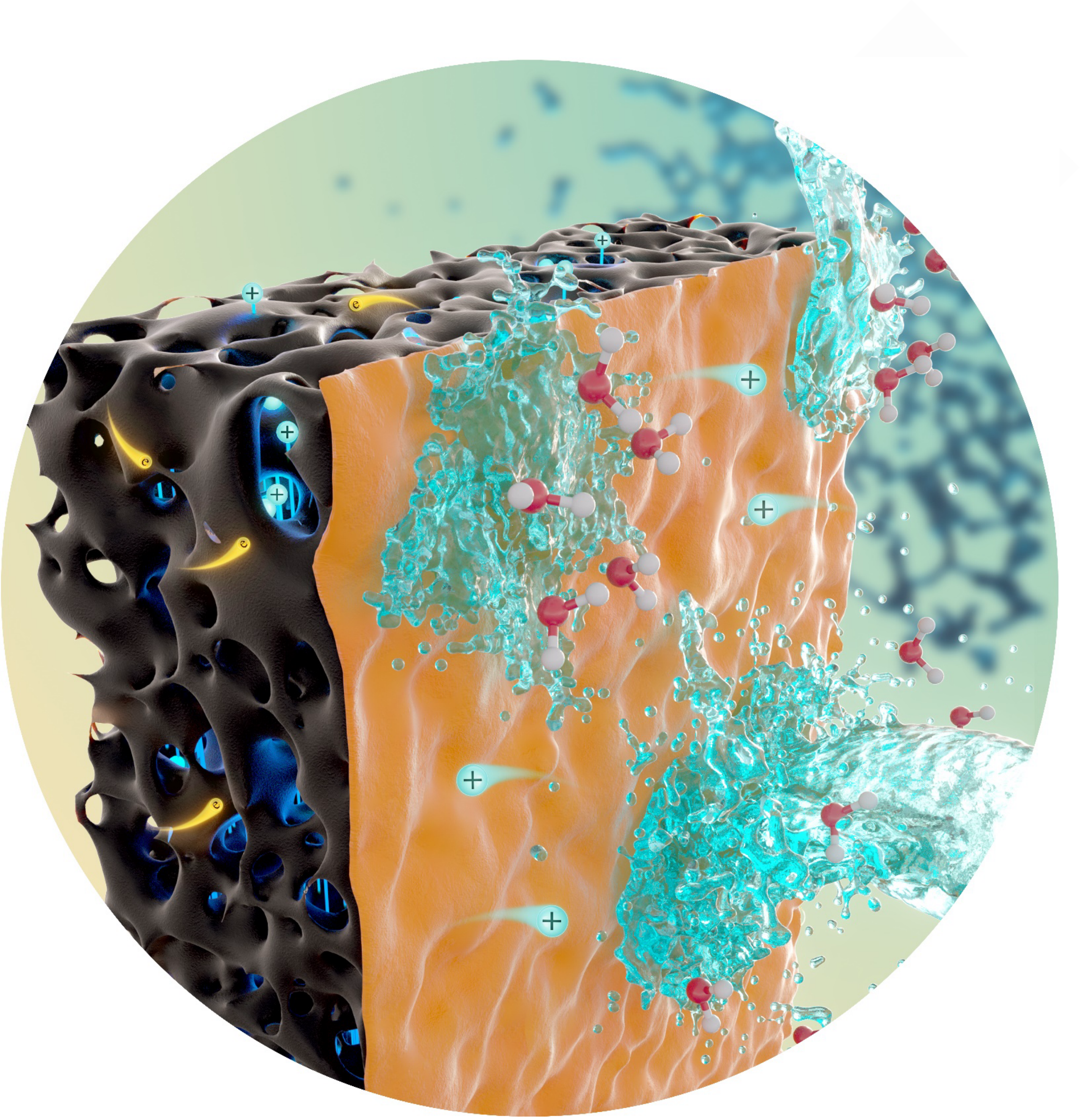

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Abstract: The narrow electrochemical stability window of water poses a challenge to the development of aqueous electrolytes. In contrast to non-aqueous electrolytes, the products of water electrolysis do not contribute to the formation of a passivation layer on electrodes. As a result, aqueous electrolytes require the reactions of additional components, such as additives and co-solvents, to facilitate the formation of the desired solid electrolyte interphase (SEI) on the anode and cathode electrolyte interphase (CEI) on the cathode. This review highlights the fundamental principles and recent advancements in generating electrolyte interphases in aqueous batteries.

1. Introduction

Aqueous electrolytes have the potential to shape the future of storage batteries, offering better safety, low cost, and sustainability.[1] However, one drawback is that aqueous electrolytes typically suffer from narrow electrochemical stability windows. Theoretically, a voltage of as low as 1.23 V can cause water to split into hydrogen (H_2) and oxygen (O_2) gases. This high reactivity of water limits the selection of suitable energetic electrodes, ultimately restricting the energy density of aqueous batteries.[2] Water electrolysis that can result in hydrogen evolution reaction (HER) or oxygen evolution reaction (OER) not only compromises the longevity of batteries but also raises safety concerns.

Significant progress has been made in extending the electrochemical stability of aqueous electrolytes beyond 3 V.[3] Two primary strategies have emerged to mitigate the electrolytic reactions of water. The first involves modifying the local chemical environment of water molecules to increase their inertness, mainly through the use of highly concentrated electrolytes containing salts with high solubility in water such as lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and $ZnCl_2$. By interrupting the hydrogen bonding network, it is believed that the O–H covalent bonds can be strengthened.[4] However, the underlying fundamental mechanisms are still a subject of debate, and the current thermodynamic control of water's reactivity seems insufficient to completely eliminate the parasitic reactions between water and electrodes. The second strategy focuses on kinetically suppressing the electrolysis of electrolytes by fostering the growth of electrolyte interphases on electrodes.[5] This approach takes inspiration from the successful formation of solid electrolyte interphase (SEI) on anodes and cathode electrolyte interphase (CEI) on cathodes in lithium-ion batteries. It is important to note that the names SEI and CEI may not align semantically, potentially confusing newcomers. An alternative name for SEI could be "anode electrolyte interphase" (AEI), but for consistency with existing literature, we will continue using SEI and CEI.

Numerous reviews have been published on the formation of solid electrolyte interphase (SEI) and cathode electrolyte interphase (CEI) in non-aqueous batteries.[6] These reviews provide detailed insights into the fundamental mechanisms of interphase growth. A common characteristic observed in non-aqueous battery systems is the decomposition of electrolyte solvents, such as ethylene carbonate (EC) during SEI formation and propylene carbonate (PC) during CEI formation. However, unlike organic solvents, water's reduction and oxidation products cannot directly contribute to the formation of SEI and CEI. Therefore, additional components, including anions, co-solvents, and additives, are introduced to facilitate the formation of these interphases in aqueous electrolytes. This Minireview article emphasizes the fundamental aspects of *in situ* electrolyte interphase (EI) formation in aqueous electrolytes and highlights progress made in this field. It is important to note that the scope of this article is limited to EIs formed through passivation reactions between electrolyte components and the electrode surface. Other solid phases applied onto the electrode surface, such as artificial SEI and CEI, will not be discussed here.

2. Fundamentals of EIs

2.1. EI Formation Strategies

An aqueous electrolyte typically consists of three main components: strongly hydrated cations, weakly hydrated anions, and free water molecules. In a dilute electrolyte, these constituents usually do not react with the active mass of the electrode to form an EI. Within the electrical double layer (EDL) of a polarized anode during battery charging, hydrated cations are present, with the aqua ligands serving as the source for HER, and vice versa for OER from the EDL of the cathode in the presence of anions. For aqueous batteries, a successful EI should fulfill the same purpose as their non-aqueous counterparts, which is to extend the voltage window of electrolytes by passivating the electrodes from the electrolyte, while allowing electrochemical reactions of electrodes.[7] Consequently, the EI needs to be impermeable to water molecules while exhibiting high ionic conductivity for charge carriers and low electrical conductivity (**Figure 1**).[2,6a,8] The design of EIs primarily depends on the compositions of electrolytes. Currently, two main approaches are employed to enable EI formation on electrodes: (1) increasing the electrolyte concentration to incorporate anions within the solvation shells of cations, and (2) using reactive molecules as co-solvents or additives in the electrolyte. In aqueous electrolytes, the precursors for EI formation include anions, dissolved gases, and organic co-solvents or additives. These precursors ideally undergo reactions with the electrodes at potentials higher than that for HER but lower than that for OER. These reactions should be self-terminated to ensure effective passivation of the electrodes. Furthermore, effective EI formation may also benefit from thermodynamic strategies to extend the voltage window of aqueous electrolytes.

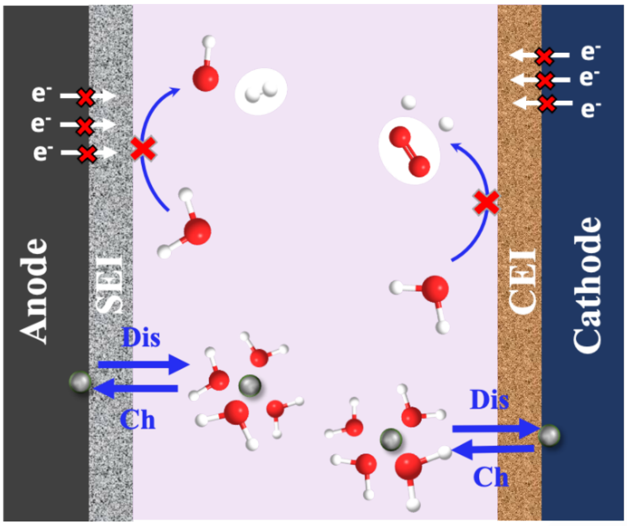

Figure 1. Schematic illustration of the functions of SEI and CEI.

Gas molecules dissolved in electrolytes have the potential to serve as sources for the formation of inorganic SEI.[9] In the case of 21 *m* LiTFSI aqueous electrolytes, O_2 and CO_2 gases can react to form Li_2O_2 and Li_2CO_3, respectively.[9a] It is worth noting that CO_2 exhibits a unique characteristic as it interacts strongly with the $TFSI^-$ anion. However, these resulting compounds are unstable in dilute aqueous electrolytes due to rapid hydrolysis and dissolution into water.[9b] To overcome this challenge, Yue *et al.* reported that a constant flow of CO_2 can stabilize Li_2CO_3 in a dilute 5 *m* LiTFSI aqueous electrolyte by mitigating its dissolution.[9a]

The reduction of anions on anodes, such as Zn, typically does not occur unless they are present within the anode's EDL. The proximity in the EDL enables the reduction of anions. However, during battery charging, the anode becomes negatively polarized, electrostatically attracting cations and repelling anions. In dilute electrolytes, fully hydrated cations and anions remain isolated from each other (**Figure 2a**). In contrast, super-concentrated aqueous electrolytes, also known as water-in-salt electrolytes (WiSE), introduced by Xu and Wang *et al.*, exhibit a distinct behavior due to insufficient hydration of cations.[3a,10] In WiSE, anions can enter the primary solvation shell of cations and the EDL of the anode, thereby increasing the likelihood of their reduction on the surface of the anode (**Figure 2b**).

Moreover, the higher local concentration of anions and the weakened bond strength within anions, resulting from the stronger interactions between cations and anions in WiSE, collectively contribute to an increase in the reduction potential of anions, thus facilitating the formation of SEI. This premise holds true when the anions are molecular and contain high-valent non-metal elements, making them more reducible. An outstanding example of such anions is $TFSI^-$. Density functional theory (DFT) simulations indicate that the decomposition potential of $TFSI^-$ anions shifts from 1.4 V vs. Li^+/Li in a free state within dilute LiTFSI electrolytes to 2.9 V in $Li_2(TFSI)\cdot H_2O$ aggregates within 21 *m* LiTFSI electrolytes.[3a] This demonstrates the significant impact of higher concentrations on the reduction potential. In contrast, anions present in concentrated $ZnCl_2$, such as $[ZnCl_4]^{2-}$ and its oligomers, exhibit cathodic stability, making them unsuitable for the mechanism discussed here.

Recently, an alternative mechanism has been proposed by Grimaud *et al.* in a 20 *m* LiTFSI aqueous electrolyte, suggesting that a chemical reaction between $TFSI^-$ and OH^- leads to the formation of inorganic LiF in the SEI.[11] More specifically, the HER product OH^- spontaneously attacks the electrophilic sulfur atoms in $TFSI^-$, generating F^- ions that precipitate with Li^+ ions to form LiF within the SEI (**Figure 2c-d**). Similarly, Guo *et al.* reported the use of a 1 *m* $Zn(OTF)_2$ aqueous electrolyte comprising 0.025 *m* $Zn(H_2PO_4)_2$, where $H_2PO_4^-$ ions react with OH^- ions coming from the HER on the anode surface, where the resulting PO_4^{3-} precipitate with Zn^{2+} ions to form $Zn_3(PO_4)_2$ within the SEI.[12] These findings indicate that the species released during the initial parasitic reactions can induce the decomposition of electrolyte components.[13] Specifically, during the HER, OH^- ions are produced on the anode, facilitating the chemical degradation of $TFSI^-$ and OTF^- ions to form fluorinated inorganic SEI, such as LiF and NaF.[9c,11,14] Furthermore, on the CEI side, Lee *et al.* discovered that the charged $LiNiO_2$ electrode releases active O^{2-} ions into the electrolyte.[15] These O^{2-} ions then react with Li^+, H_2O, and dissolved CO_2 to form LiOH and Li_2CO_3 within the CEI. The mechanism based on chemical reactions is promising since it is independent of the electrochemical stability of water and does not compromise the Coulombic efficiency (CE) of cells.

Notably, anions of fluoroalkyl sulfonylimide[3a, 16] and fluoroalkyl sulfonate[16a, 17] have been extensively studied for the formation of inorganic SEI in aqueous electrolytes. These anions are selected due to their high solubility, appropriate reduction potentials, and the low solubility of their reduction products, such as LiF, and ZnF_2.[18] In contrast, some reduction products, such as NaF[19] and Na_2CO_3[19a] suffer from high solubility in aqueous electrolytes. To improve the stability, one common strategy is to adopt high-concentration electrolytes to suppress their dissolution.[19] It is important to note that the research on the CEI in aqueous electrolytes is relatively limited compared to SEI studies, primarily due to the heightened need to address HER.[2] The oxidation of anions can contribute to the formation of CEI. The choice of anions is mostly limited to fluoroalkyl sulfonylimide *e.g.*, $TFSI^-$[20], and fluoroalkyl sulfonate anions, *e.g.*, OTF^-[21]. During charging, these anions are attracted to the positively charged cathode surface, where they undergo oxidation and form inorganic components within the CEI, such as LiF.

Recent research has highlighted the limited protective capabilities of purely inorganic SEI and CEI.[22] Such inorganic interphases do not "seal" the surface well.[23] Even in WiSE, numerous cycles are needed to form an effective SEI that can suppress the parasitic reactions (**Figure 2e**).[9b,9c,24] However, in Li-ion batteries, the benefits have been demonstrated from a dual-layer interphase structure, which consists of an inner layer predominantly composed of inorganic compounds and an outer layer with a notable organic nature (**Figure 3**).[25] This dual-layer structure synergistically offers the stability and the protective performance of the interphases. The dense inorganic layer facilitates rapid diffusion of charge carriers, while the porous organic layer, which possesses hydrophobic properties, shields the inorganic layer from corrosion by the electrolyte and promotes the de-solvation process. Moreover, this dual-layer interphase structure may possess unique self-repairing capabilities.

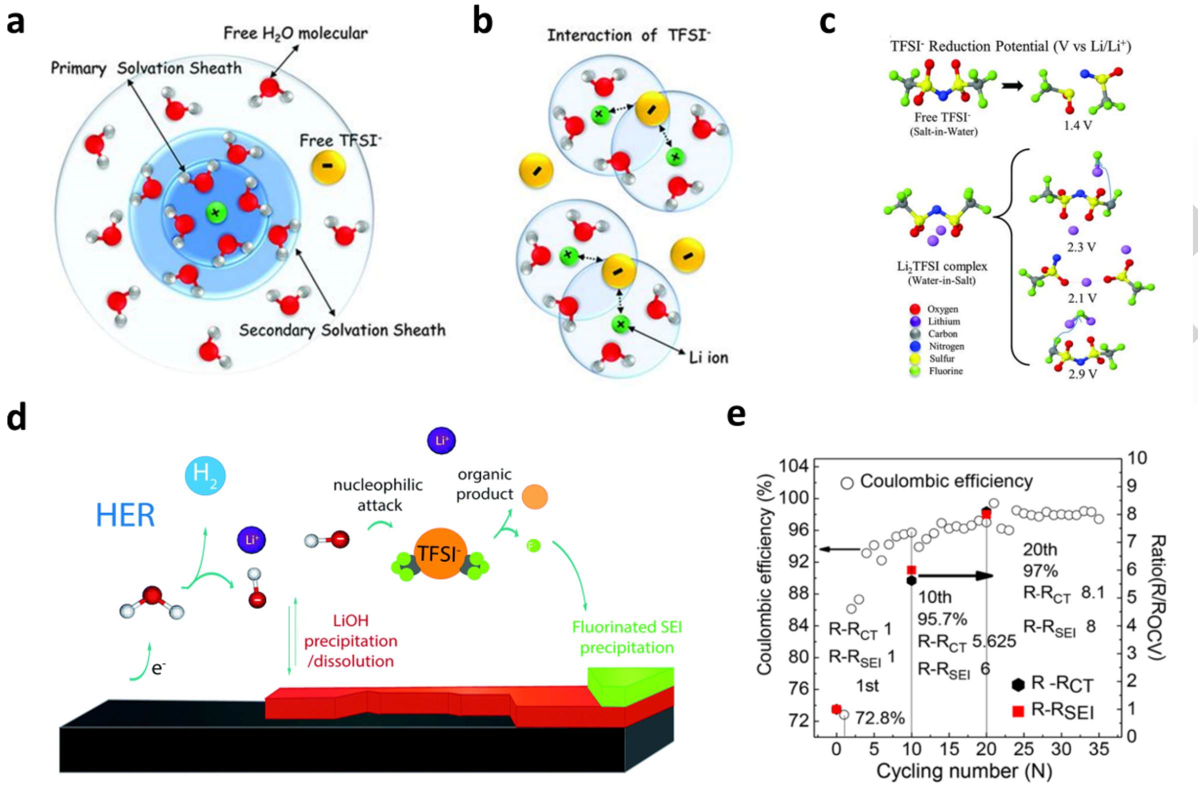

Figure 2. Solvation structure of a) WiSE, and b) dilute electrolytes.[3a] Schematic illustrating the TFSI⁻ decomposition mechanisms in c) conventional electroreduction mechanism[3a], and d) chemical reaction mechanism[11]. e) The evolving of SEI impedance as well the CE over the cycles of the Mo_6S_8 electrode.[9b]

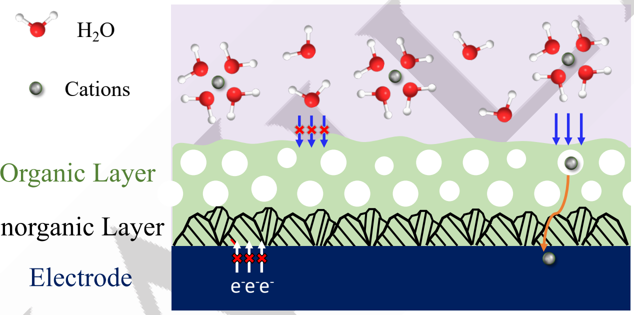

Figure 3. Schematic illustration of the dual-layer structure of EIs.

Organic co-solvents are commonly involved in the formation of the organic component of the SEI. In Li⁺-containing electrolytes, organic solvents like EC and PC can contribute to the formation of Li_2CO_3 in the SEI. However, the practical application of Li_2CO_3 is limited in aqueous batteries due to its relatively high solubility in water (ca. 0.17 *m*). Unlike anions, neutral organic molecules are not affected by the internal electric field within the cells. Nevertheless, their reduction is still influenced by their reduction potentials and the local concentration in the EDL of the anode. When co-solvents have a higher donor number (DN) than water, they tend to replace water in solvating cations and preferentially migrate to the surface of the anode (**Figure 4a**).[26] This behavior enables the co-solvents to form SEI even at low concentrations in the bulk electrolyte. These co-solvents typically exhibit high polarity and good miscibility with water. Examples of such co-solvents include dimethyl sulfoxide (DMSO)[26], trimethyl phosphate (TMP)[27], tetraethylene glycol dimethyl ether (TEGDME)[20], tetrahydrofuran (THF)[28], and N-methylpyrrolidone (NMP)[29].

For solvents with low polarity, such as PC and dimethyl carbonate (DMC), they are typically immiscible with water. To achieve homogeneous solutions, one strategy is to utilize unique anions that possess both hydrophobic and hydrophilic groups, such as TFSI⁻[30] and OTF⁻[31] anions (**Figure 4b**). Additionally, our group has discovered that the presence of $[ZnCl_4]^{2-}$ in concentrated $ZnCl_2$ electrolytes improves the miscibility of DMC in water.[32] One possible explanation for this is that $[ZnCl_4]^{2-}$ is a centrosymmetric “non-polar” ion with a relatively low charge density, thereby facilitating the dissolution of DMC (**Figure 4c**).

Notably, low-polarity organic solvents are generally believed to exhibit high cathodic stability. For instance, the reduction potential of DMC by lithium metal is ca. 0.35 V vs. Li⁺/Li. Interestingly, in a concentrated hybrid electrolyte (H_1D_1) composed of 22 *m* LiTFSI in H_2O and 9.25 *m* LiTFSI in DMC in a 1:1 mass ratio, the reduction potential increases to 1.38 V by forming 2Li-DMC aggregates in the EDL of the anode (**Figure 4d**).[30] Furthermore, our group has reported that DMC contributes to an inorganic-organic dual-layer SEI on the zinc metal anode in a 30 *m* $ZnCl_2$ + 5 *m* LiCl + 10 *m* trimethylammonium chloride in H_2O and DMC (5:1, molar ratio) (ZLT-DMC) electrolyte, leading to a high CE of 99.95% tested at a low current density of 0.2 mA/cm^2 (**Figure 4e**).[32] The mechanism underlying the formation of the organic part in the SEI has been revealed by *ab initio* molecular dynamics (AIMD) calculations, indicating that DMC is first converted to $CH_3OOCO\cdot$ radicals, which then interact with Zn-Cl complexes to form ZnCl–O–$COOCH_3$ compounds within the SEI (**Figure 4f**). Although it is widely assumed that fluoride is the most suitable choice for anions in SEI layers, the SEI formed in this case is chloride rich. These results suggest that, in certain environments, chloride-containing solid phases can be engineered to deliver excellent EI performance.

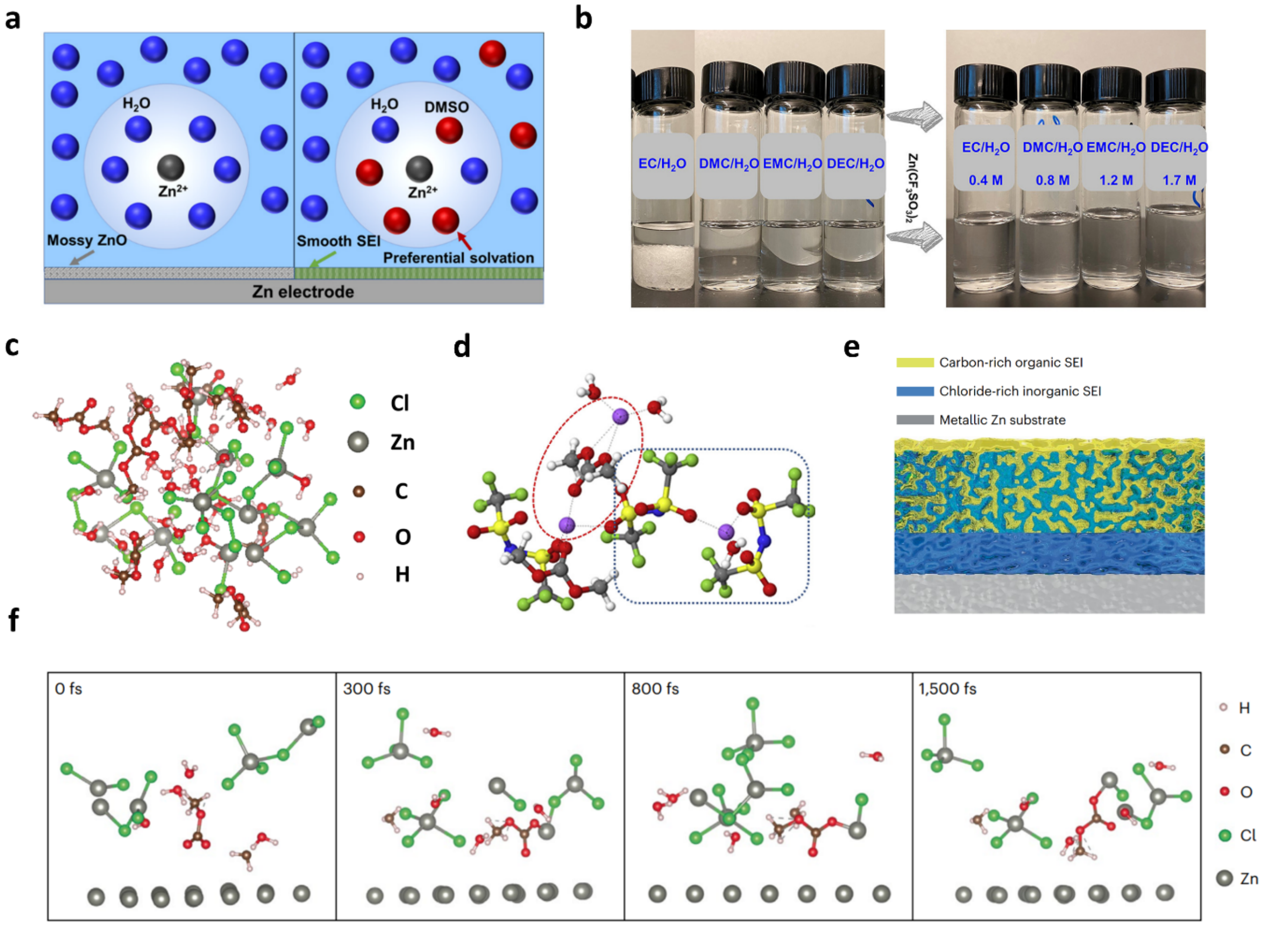

Figure 4. a) Solvation structure of pristine electrolytes (left) and with additional high DN co-solvents (right).[26] b) Photographs of the water and organic solvents mixtures before and after dissolving the $Zn(OTF)_2$ salt. c) Solvation structure of the 30 *m* $ZnCl_2$-DMC electrolyte provided by AIMD simulations. d) Solvation structure of the H_1D_1 electrolyte, where the 2Li-DMC aggregate is marked with red dashed circle.[30] e) Schematic illustration of the inorganic-organic hybrid SEI structure on zinc metal anode in the ZLT-DMC electrolyte.[32] f) AIMD simulation results illustrating the SEI formation process on zinc metal anode from ZLT-DMC electrolyte.[32]

2.2. Thermodynamic and Kinetic Factors of EI Formation

Electro-reduction and oxidation are the predominant mechanisms responsible for the formation of SEI and CEI, respectively. It is widely accepted that the formation potentials of SEI and CEI are determined by the frontier energy levels of the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) of the precursor molecules, respectively. In this context, we propose an alternative approach to predict the formation potential of EIs. From a thermodynamic standpoint, the onset potential of these reactions can be described by the following equation:

$$E_0 = -\frac{\sum G_{products} - \sum G_{reactants}}{nF} \qquad \textbf{Equation 1}$$

where $G_{products}$ and $G_{reactants}$ represent the Gibbs free energies of the reaction products and reactants, respectively. The values of these energies are closely related to the properties of the electrolyte. The $G_{reactants}$ depends on several factors, including the type of precursors involved and the local chemical environment of the precursors (**Figure 5**). The bond strength within the precursors can vary depending on the solvation structures. For example, $TFSI^-$ anions decompose at a potential of 1.4 V vs. Li^+/Li in a dilute electrolyte, but this potential shifts to approximately 2.9 V in $Li_2(TFSI)H_2O$ aggregates.[3a] In the case of anion precursors, their Gibbs energy is proportional to their concentration in the electrolyte according to the Nernst Equation. Higher concentrations of anion precursors will affect the SEI and CEI decomposition potentials, raising them for SEI and lowering them for CEI. On the other hand, the $G_{products}$ is determined by the specific type of products formed in the EI.

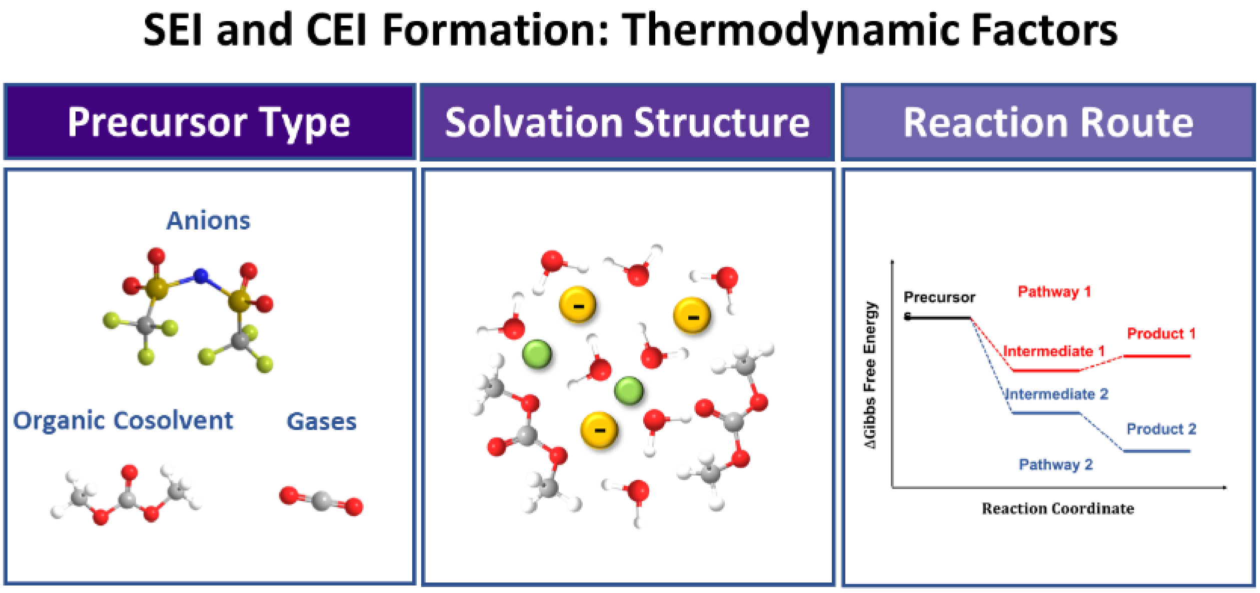

Figure 5. Thermodynamic impact factors on the EI formation potential.

The relative formation kinetics between the organic and the inorganic layer strongly influences the functionality of EIs. In our research, we observed the formation of a hybrid SEI with a uniform thickness of ca. 150 nm on zinc metal anode in a hybrid aqueous electrolyte containing DMC as the co-solvent (**Figure 6a**).[32] However, when we replaced DMC with diethyl carbonate (DEC), a much thicker SEI with a thickness ranging from 500 nm to 1.5 μm was formed, accompanied by a thinner organic layer on the outer surface (**Figure 6b**). We hypothesize that this variation is due to the lower reaction rate of S_N2 ester cleavage in DEC, which has bulkier side chains compared to DMC. The S_N2 reaction refers to a nucleophilic substitution reaction where two components are involved in the rate-determining step. As a result, the inorganic layer grows thicker, consuming more electrolytes, and leading to a lower CE value of 99.86%.

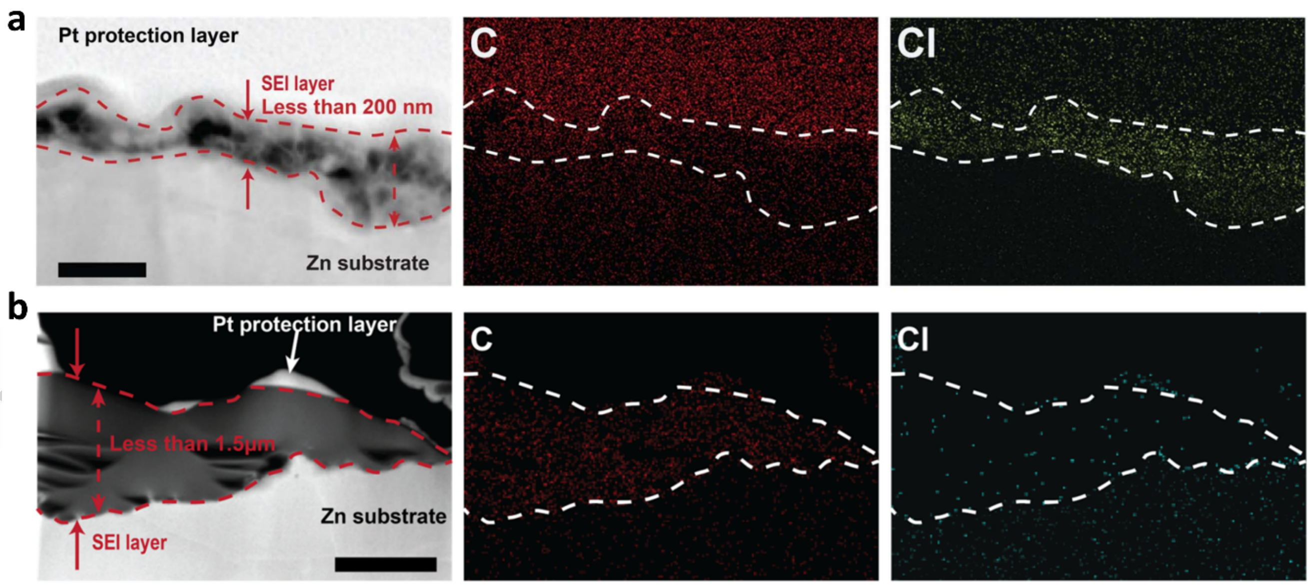

Figure 6. Dark field Scanning Transmission Electron Microscopy cross-section image and Energy Dispersive X-Ray mapping of the SEI formed on zinc metal anodes in a) ZLT-DMC electrolyte, scale bar: 200 nm and b) ZLT-DEC electrolyte, scale bar: 1 μm.[32]

Several organic co-solvents have been reported to form stable CEI in aqueous electrolytes. These co-solvents include urea[24], NMP[29], tetramethylene sulfone (TMS) [33], TMP[34], and TEGDME[20]. In most cases, these organic co-solvents undergo oxidation to form a hydrophobic organic CEI on the cathode surface. However, TMP is an exception as it decomposes to form inorganic $Zn_3(PO_4)_2$ in a 30 *m* $ZnCl_2$ electrolyte.

2.3. Other Aspects

Characterizing EIs has always presented a challenge. The properties of EIs are strongly influenced by the solvation structure of electrolytes in the EDLs on electrode surfaces, which change as a function of potential. In addition, the growth of EIs is a dynamic process involving complex structural and compositional reorganization. However, most current studies primarily focus on analyzing the solvation structures in bulk electrolytes using *ex situ* techniques such as nuclear magnetic resonance (NMR), Fourier-transform infrared spectroscopy (FTIR), and Raman spectroscopy. Furthermore, some components within EIs are chemically unstable and may decompose when subjected to heating or electron beam irradiation in conventional techniques like transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). This can result in an incomplete or inaccurate understanding of the EIs. Therefore, it becomes necessary to explore more *in situ* techniques such as cryo EM, electrochemical atomic force microscopy, and electrochemical quartz crystal microbalance (EQCM) to characterize the properties of EIs.[35] These *in situ* techniques can be integrated with molecular dynamics (MD) and density functional theory (DFT) simulation studies to unveil the formation mechanisms of EIs.

Generally, EI forming agents should exhibit suitable oxidation/reduction potentials, and their products should collectively demonstrate excellent stability in electrolytes, effective passivation of electrodes, high ionic conductivity, and homogeneous ion conduction across EIs. However, the options are constrained by the narrow electrochemical stability window of water. Consequently, many studies utilize WiSE to generate stable EIs and expand the range of available forming agents. WiSE typically exhibits lower solubility towards inorganic compounds in EIs compared to their dilute counterparts, thereby enhancing stability and protection capabilities.[36] However, the excessive use of salts and the associated cost in WiSE pose significant barriers to their commercialization. Moreover, various organic solvents have been introduced into aqueous electrolytes to form EIs. The organic species derived in EIs generally display superior stability when compared to the inorganic components derived from anions in dilute aqueous electrolytes. However, the high flammability and toxicity of these organic solvents undermine the advantages of aqueous electrolytes. Hence, it is necessary to explore more cost-effective and environmentally friendly salts and additives that can facilitate the formation of homogeneous and robust SEI and CEI with good stability in low-concentration aqueous electrolytes. For instance, Wang *et al.* reported a low-concentration eutectic electrolyte consisting of 4.5 *m* LiTFSI and 0.1 m KOH in H_2O/urea (8.6:1, V: V) with a stable formation of inorganic/organic hybrid SEI and a wide electrochemical stability window of 3.3 V.[14] In this electrolyte, the inexpensive co-solvent urea serves as both the precursor for forming the organic layer in SEI and the diluent to reduce the LiTFSI concentration in the bulk electrolyte without compromising its properties. The addition of KOH is expected to catalyze the decomposition of LiTFSI into the inorganic compound LiF within the SEI.

3. Conclusions and Perspectives

In summary, unlike EIs in non-aqueous batteries, EIs in aqueous batteries require specific chemical reactions between the electrodes and electrolyte components other than water. As shown in **Table I**, we summarize the EI properties in the representative works based on various charge carriers. The primary goal of these EIs is to be waterproof and chemically stable, effectively passivating the electrode and preventing further reactions with water molecules. EIs in aqueous batteries need to be more impermeable than those in non-aqueous electrolytes because water, being a smaller and more reactive molecule than most organic solvents, is inherently more corrosive. Reactions involving anions like $TFSI^-$ can produce fluorinated salts that are considered effective constituents of SEI layers. However, a key question remains unanswered: can a pure inorganic SEI adequately passivate a metal anode, given the significant volume changes that occur during electrode plating and stripping? The addition of organic co-solvents and additives appears to be a promising solution. However, for these organic components to function effectively, their solubility in aqueous electrolytes is crucial. Therefore, efforts are needed to engineer the local structure of aqueous electrolytes to enhance the solubility of these additives. Another question arises as to whether an inorganic-organic dual-layer structure is indispensable for passivating the electrode in aqueous electrolytes. In this case, the inorganic layer directly contacts the electrode surface, while the organic layer interfaces with the aqueous electrolyte. Ideally, the organic layer would be hydrophobic, serving as a waterproof coating. However, there is still a fundamental knowledge gap regarding the mechanism of reactions between the electrode and species in the electrolyte, particularly their thermodynamic driving forces of the reactions and the formative process of EIs. Advanced characterization techniques such as cryo-EM can provide valuable insights. In the broader battery field, substantial efforts have been made to generate artificial EIs through coating and deposition methods. However, these artificial EIs often tend to be too thick, often reaching micrometer-scale in thicknesses. Consequently, an important consideration is whether this approach is economically viable and practically compatible with manufacturing processes. The ideal EIs for aqueous batteries would be very thin, on the order of tens of nanometers, while remaining chemically and mechanically stable. Moreover, they should possess a hydrophobic outer surface to effectively passivate the electrodes. In addition, we should develop a more fundamental understanding of the impact of environmental and testing conditions, such as pressure, temperature and cycling current, on the EI properties, which dictate the practicality of the EI formation strategies. Research on EIs in aqueous environments holds significant promise for the future of storage batteries, and this field is expected to experience exponential growth in the near future.

Table 1. Summary of exemplary EI works based on different charge carriers.

Charge Carriers	Electrolytes	EI Type & Composition	Mechanism	Refere-nce

Li^+	5 *m* LiTFSI rich in CO_2 gas	SEI: Li_2CO_3 and LiF	Electrochemical Reduction of gas and anion	[9a]
Li^+	21 *m* LiTFSI	SEI: Li_2CO_3, LiF, and Li_2O	Electrochemical reduction of gas and anion	[9b]
Li^+	20 *m* LiTFSI	SEI: LiF and LiOH	Chemical reaction between anion and OH^-	[11]
Li^+	LiTFSI-TEGDME ether-in-water electrolyte	SEI: bi-layer structure with LiF-rich inner layer and organic-rich outer layer	Electrochemical reduction of organic cosolvent and anion	[20]
Na^+	9.3 *m* $Na(otf)_2$	SEI: NaF	Electrochemical reduction of anion	[17a]
Na^+	17 *m* $NaClO_4$+ 2 *m* Naotf	SEI: NaF–Na_2O–NaOH	Electrochemical reduction of anion	[19a]
K^+	2 m KFSI/ DMF:H_2O (mass ratio, 1:1)	SEI: KF and -CF_x	Electrochemical reduction of anion	[37]
Zn^{2+}	ZLT-DMC	SEI: bi-layer structure with chloride-rich inner layer and carbon-rich outer layer	Electrochemical/ chemical reactions between anode and electrolyte	[32]
Zn^{2+}	$Zn(TFSI)_2$+acetamide eutectic electrolyte	SEI: bi-layer structure with ZnF_2-rich inner layer and organic-rich outer layer	Electrochemical reduction of organic cosolvent and anion	[16b]
Zn^{2+}	1 *m* Zn $(otf)_2$ + 25 × 10^{-3} *m* $Zn(H_2PO_4)_2$)	SEI: $Zn_3(PO_4)_2$•$4H_2O$	Precipitation Reaction	[12]
Zn^{2+}	1 *m* $ZnCl_2/H_2O$: DMSO (molar ratio,17:1)	SEI: $Zn_{12}(SO_4)_3Cl_3(OH)_{15}\cdot 5H_2O-ZnSO_3-ZnS$	Electrochemical reduction of organic cosolvent	[26]
Zn^{2+}	1 *m* ZnOtf/H_2O-THF	SEI: bi-layer structure with ZnF_2 and $ZnCO_3$-rich inner layer and organic-rich outer layer	Electrochemical reduction of organic cosolvent and anion	
Al^{3+}	5 *m* Al $(otf)_3$	SEI: AlF_3 and Al_2O_3	Electrochemical reduction of anion, chemical oxidation	[17b]
Li^+	4.5 *m* LiTFSI–KOH–$CO(NH_2)_2$–H_2O	CEI: bi-layer structure with LiF-rich inner layer and organic-rich outer layer	Electrochemical oxidation of organic cosolvent and anion	[14]
Zn^{2+}	2 *m* $ZnSO_4$ + 0.1 *m* $MnSO_4$" electrolyte	CEI: $CaSO_4$	Precipitation Reaction	[13]
Zn^{2+}	31 *m* $ZnCl_2/H_2O$:TMP (molar ratio, 1:9)	CEI: $Zn(PO_4)_2$	Electrochemical oxidation of organic cosolvent	[34]
Mg^{2+}	0.8 *m* $Mg(TFSI)_2$-85%PEG-15%H_2O	CEI: MgF_2	Electrochemical oxidation of anion	[23]

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Keywords: electrolyte interphase • aqueous battery • electrolytes • gas evolution

References

[1] Y. Sui, M. Yu, Y. Xu, X. Ji, *J. Electrochem. Soc.* **2022**, *169*, 030537.

[2] Y. Sui, X. Ji, *Chem. Rev.* **2021**, *121*, 6654-6695.

[3] a. L. Suo, O. Borodin, T. Gao, M. Olguin, J. Ho, X. Fan, C. Luo, C. Wang, K. Xu, *Science* **2015**, *350*, 938-943; b. Y. Yamada, K. Usui, K. Sodeyama, S. Ko, Y. Tateyama, A. Yamada, *Nat. Energy* **2016**, *1*, 16129; c. J. Xie, Z. Liang, Y.-C. Lu, *Nat. Mater.* **2020**, *19*, 1006-1011; d. Z.-Q. Lin, G. Fan, T. Zhang, F. Huo, Q. Xi, J. Wang, T. She, X. Zeng, J. Weng, W. Huang, *Adv. Energy Mater.* **2023**, *13*, 2203532; e. A. von Wald Cresce, K. Xu, *Carbon Energy* **2021**, *3*, 721-751; f. S. Chen, M. Zhang, P. Zou, B. Sun, S. Tao, *Energy Environ. Sci.* **2022**, *15*, 1805-1839; g. H. Zhang, X. Liu, H. Li, I. Hasa, S. Passerini, *Angew. Chem. Int. Ed.* **2021**, *60*, 598-616.

[4] a. J. Zheng, G. Tan, P. Shan, T. Liu, J. Hu, Y. Feng, L. Yang, M. Zhang, Z. Chen, Y. Lin, J. Lu, J. C. Neuefeind, Y. Ren, K. Amine, L.-W. Wang, K. Xu, F. Pan, *Chem* **2018**, *4*, 2872-2882; b. Z. Tian, W. Deng, X. Wang, C. Liu, C. Li, J. Chen, M. Xue, R. Li, F. Pan, *Funct. Mater. Lett.* **2017**, *10*, 1750081; c. C. Zhang, W. Shin, L. Zhu, C. Chen, J. C. Neuefeind, Y. Xu, S. I. Allec, C. Liu, Z. Wei, A. Daniyar, J.-X. Jiang, C. Fang, P. Alex Greaney, X. Ji, *Carbon Energy* **2021**, *3*, 339-348.

[5] R. Jayakumar, D. M. Harrison, J. Xu, A. V. Suresh Babu, C. Luo, L. Ma, *J. Mater. Chem. A* **2023**, *11*, 8470-8496.

[6] a. P. Zou, Y. Sui, H. Zhan, C. Wang, H. L. Xin, H.-M. Cheng, F. Kang, C. Yang, *Chem. Rev.* **2021**, *121*, 5986-6056; b. K. Xu, *Chem. Rev.* **2014**, *114*, 11503-11618; c.

X.-B. Cheng, R. Zhang, C.-Z. Zhao, F. Wei, J.-G. Zhang, Q. Zhang, *Adv. Sci.* **2016**, *3*, 1500213; d. M. Li, C. Wang, Z. Chen, K. Xu, J. Lu, *Chem. Rev.* **2020**, *120*, 6783-6819.
[7] X. Fan, C. Wang, *Chem. Soc. Rev.* **2021**, *50*, 10486-10566.
[8] Q. Zhang, J. Luan, Y. Tang, X. Ji, H. Wang, *Angew. Chem. Int. Ed.* **2020**, *59*, 13180-13191.
[9] a. J. Yue, J. Zhang, Y. Tong, M. Chen, L. Liu, L. Jiang, T. Lv, Y.-s. Hu, H. Li, X. Huang, L. Gu, G. Feng, K. Xu, L. Suo, L. Chen, *Nat. Chem.* **2021**, *13*, 1061-1069; b. L. Suo, D. Oh, Y. Lin, Z. Zhuo, O. Borodin, T. Gao, F. Wang, A. Kushima, Z. Wang, H.-C. Kim, *J. Am. Chem. Soc.* **2017**, *139*, 18670-18680; c. T. Jin, X. Ji, P. F. Wang, K. Zhu, J. Zhang, L. Cao, L. Chen, C. Cui, T. Deng, S. Liu, *Angew. Chem. Int. Ed.* **2021**, *133*, 12050-12055.
[10] a. J. Han, A. Mariani, S. Passerini, A. Varzi, *Energy Environ. Sci.* **2023**, *16*, 1480-1501; b. O. Borodin, J. Self, K. A. Persson, C. Wang, K. Xu, *Joule* **2020**, *4*, 69-100.
[11] N. Dubouis, P. Lemaire, B. Mirvaux, E. Salager, M. Deschamps, A. Grimaud, *Energy Environ. Sci.* **2018**, *11*, 3491-3499.
[12] X. Zeng, J. Mao, J. Hao, J. Liu, S. Liu, Z. Wang, Y. Wang, S. Zhang, T. Zheng, J. Liu, P. Rao, Z. Guo, *Adv. Mater.* **2021**, *33*, 2007416.
[13] S. Guo, S. Liang, B. Zhang, G. Fang, D. Ma, J. Zhou, *ACS Nano* **2019**, *13*, 13456-13464.
[14] J. Xu, X. Ji, J. Zhang, C. Yang, P. Wang, S. Liu, K. Ludwig, F. Chen, P. Kofinas, C. Wang, *Nat. Energy* **2022**, *7*, 186-193.
[15] C. Lee, Y. Yokoyama, Y. Kondo, Y. Miyahara, T. Abe, K. Miyazaki, *Adv. Energy Mater.* **2021**, *11*, 2100756.
[16] a. L. Suo, O. Borodin, W. Sun, X. Fan, C. Yang, F. Wang, T. Gao, Z. Ma, M. Schroeder, A. von Cresce, *Angew. Chem. Int. Ed.* **2016**, *128*, 7252-7257; b. H. Qiu, X. Du, J. Zhao, Y. Wang, J. Ju, Z. Chen, Z. Hu, D. Yan, X. Zhou, G. Cui, *Nat. Commun.* **2019**, *10*, 5374.
[17] a. L. Suo, O. Borodin, Y. Wang, X. Rong, W. Sun, X. Fan, S. Xu, M. A. Schroeder, A. V. Cresce, F. Wang, C. Yang, Y.-S. Hu, K. Xu, C. Wang, *Adv. Energy Mater.* **2017**, *7*, 1701189; b. T. Dong, K. L. Ng, Y. Wang, O. Voznyy, G. Azimi, *Adv. Energy Mater.* **2021**, *11*, 2100077.
[18] C. Wang, Y. S. Meng, K. Xu, *J. Electrochem. Soc.* **2019**, *166*, A5184.
[19] a. T. Jin, X. Ji, P.-F. Wang, K. Zhu, J. Zhang, L. Cao, L. Chen, C. Cui, T. Deng, S. Liu, N. Piao, Y. Liu, C. Shen, K. Xie, L. Jiao, C. Wang, *Angew. Chem. Int. Ed.* **2021**, *60*, 11943-11948; b. H. Wang, T. Liu, X. Du, J. Wang, Y. Yang, H. Qiu, G. Lu, H. Li, Z. Chen, J. Zhao, G. Cui, *Batter. Supercaps* **2022**, *5*, e202200246.
[20] Y. Shang, N. Chen, Y. Li, S. Chen, J. Lai, Y. Huang, W. Qu, F. Wu, R. Chen, *Adv. Mater.* **2020**, *32*, 2004017.
[21] S. Liu, D. Liu, S. Wang, X. Cai, K. Qian, F. Kang, B. Li, *J. Mater. Chem. A* **2019**, *7*, 12993-12996.
[22] a. L. Droguet, G. M. Hobold, M. F. Lagadec, R. Guo, C. Lethien, M. Hallot, O. Fontaine, J.-M. Tarascon, B. M. Gallant, A. Grimaud, *ACS Energy Lett.* **2021**, *6*, 2575-2583; b. J. Xu, C. Wang, *J. Electrochem. Soc.* **2022**, *169*, 030530.
[23] Q. Fu, X. Wu, X. Luo, S. Indris, A. Sarapulova, M. Bauer, Z. Wang, M. Knapp, H. Ehrenberg, Y. Wei, *Adv. Funct. Mater.* **2022**, *32*, 2110674.
[24] Y. Huang, W. Sun, K. Xu, J. Zhang, H. Zhang, J. Li, L. He, L. Cai, F. Fu, J. Qin, H. Chen, *Energy Storage Mater.* **2022**, *46*, 577-582.
[25] a. E. Peled, S. Menkin, *J. Electrochem. Soc.* **2017**, *164*, A1703; b. J. Xu, *Nanomicro Lett.* **2022**, *14*, 166.
[26] L. Cao, D. Li, E. Hu, J. Xu, T. Deng, L. Ma, Y. Wang, X.-Q. Yang, C. Wang, *J. Am. Chem. Soc.* **2020**, *142*, 21404-21409.
[27] G. Ma, S. Di, Y. Wang, W. Yuan, X. Ji, K. Qiu, M. Liu, X. Nie, N. Zhang, *Energy Storage Mater.* **2022**, *54*, 276-283.
[28] G. Liang, Z. Tang, B. Han, J. Zhu, A. Chen, Q. Li, Z. Chen, Z. Huang, X. Li, Q. Yang, C. Zhi, *Adv. Mater.* **2023**, *35*, 2210051.
[29] K. Wang, F. Liu, Q. Li, J. Zhu, T. Qiu, X.-X. Liu, X. Sun, *Chem. Eng. J.* **2023**, *452*, 139577.
[30] F. Wang, O. Borodin, M. S. Ding, M. Gobet, J. Vatamanu, X. Fan, T. Gao, N. Eidson, Y. Liang, W. Sun, S. Greenbaum, K. Xu, C. Wang, *Joule* **2018**, *2*, 927-937.
[31] F. Ming, Y. Zhu, G. Huang, A.-H. Emwas, H. Liang, Y. Cui, H. N. Alshareef, *J. Am. Chem. Soc.* **2022**, *144*, 7160-7170.
[32] H. Jiang, L. Tang, Y. Fu, S. Wang, S. K. Sandstrom, A. M. Scida, G. Li, D. Hoang, J. J. Hong, N.-C. Chiu, K. C. Stylianou, W. F. Stickle, D. Wang, J. Li, P. A. Greaney, C. Fang, X. Ji, *Nat. Sustain.* **2023**, *6*, 806-815.
[33] Y. Shang, S. Chen, N. Chen, Y. Li, J. Lai, Y. Ma, J. Chen, F. Wu, R. Chen, *Energy Environ. Sci.* **2022**, *15*, 2653-2663.
[34] W. Wang, C. Yang, X. Chi, J. Liu, B. Wen, Y. Liu, *Energy Storage Mater.* **2022**, *53*, 774-782.
[35] a. A. v. Cresce, S. M. Russell, D. R. Baker, K. J. Gaskell, K. Xu, *Nano Lett.* **2014**, *14*, 1405-1412; b. M. Wang, Z. Feng, *Chem. Commun.* **2021**, *57*, 10453-10468.
[36] J. Xie, Y. Guan, Y. Huang, Y.-C. Lu, *Chem. Mater.* **2022**, *34*, 5176-5183.
[37] X. Yuan, Y. Li, Y. Zhu, W. Deng, C. Li, Z. Zhou, J. Hu, M. Zhang, H. Chen, R. Li, *ACS Appl. Mater. Interfaces.* **2021**, *13*, 38248-38255.

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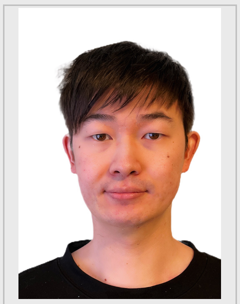

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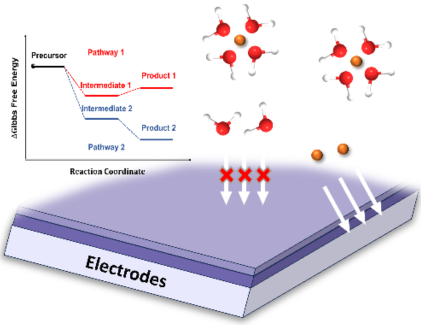
Entry for the Table of Contents



This Minireview highlights the fundamental aspects and the recent progress made in the emerging field of the formation of electrolyte interphases (EIs) in aqueous electrolytes.

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