

Progress and Challenges of Water-in-Salt Electrolytes: Exploring Physical Chemistry Properties and Solid Electrolyte Interphase Formation Mechanisms

Xuanze Wang^{+, [a, b]} Rossukon Jommongkol^{+, [a]} Jie Deng,^[c] Kexin Liu,^[b] Jiangfeng Qian,^{*[b]} Yachao Zhu,^{*[d, e]} and Olivier Fontaine^{*[f, g]}

"Water-in-salt" (WIS) electrolytes endow the possibility of commercial aqueous devices due to the extending electrochemical stability window (ESW). However, there is still a long way to address current issues until future practical applications, such as the high cost of salts, the cathodic limit, and the controversial mechanism of solid-electrolyte interphase (SEI). In this review, we first introduce cutting-edge WIS electrolytes and

display their current issues. After, the reported tactics of solving issues and achievements in our group are listed, including four sections: 1) physical structure; 2) SEI formation analysis; 3) additives contributions; and 4) devices. In the end, we focus on the current challenges and perspectives of WIS electrolytes for aiming at the practical applications of aqueous energy storage devices.

1. Introduction

Non-aqueous energy storage devices are prevailing thanks to their high energy density and cycling stability.^[1–2] Yet, the use of flammable organic electrolytes causes harsh safety issues and environmental pollution.^[3–4] In comparison, aqueous electrolytes using water solvent are low-cost, non-flammable, and non-toxic, being a great alternative for next-generation energy systems.^[5–6] Nevertheless, hydrogen evolution reaction (HER) (*i.e.* water decomposition) from water molecules with a low energy barrier is easy to initiate on the electrode interface before storing

charges via intrinsic redox centers, limiting a low electrochemical stability window (ESW) of 1.23 V.^[7] This limit severely hinders the further development of aqueous energy storage systems. Currently, a highly concentrated solution called water-in-salt (WIS) electrolyte appeared and granted the high ESW of aqueous electrolytes from 1.23 V to around 3 V, providing the possibility of future practical applications of aqueous energy storage devices.^[8] Nonetheless, it still has several issues that need to be solved. First, the use of many salts results in a high cost and it becomes worse when it applies a co-salts WIS electrolyte (water-in-bisalt electrolyte or hydrate-melt-electrolyte), where two or more salts dissolve in water.^[9–10] Second, water molecules cannot be totally blocked from approaching the electrode interface. The solvated water is still able to access the interface and is prone to be decomposed.^[11–12] Therefore, the ESW of WIS electrolytes is still insufficient to allow more anode materials like Li₄Ti₅O₁₂ or graphite to be applied in current aqueous systems. Third, the crucial factor of WIS electrolyte is the formation of solid-electrolyte interphase (SEI) that is able to protect the interface from further water decomposing (even not fully prevented).^[13–14] The confusion results from the controversial formation mechanism of SEI, including three main concepts. Suo *et al.* stated that the interphase is made up of opulent LiF species stemming from electrochemically reducing TFSI[–] anions and water at the same potential.^[15] Dubouis *et al.* described that the basic surroundings of OH[–] produced from water reduction and precipitated LiOH can instigate a nucleophilic attack on TFSI[–] anions, thereby generating the interphase composed of fluorinated species and some organic compounds.^[16] Bouchal *et al.* testified that the interphase is dynamic following concurrent LiTFSI precipitation and dissolution phenomenon.^[17] Besides, they claimed that the passivation layer on the interface is not uniform and functional enough to operate long-term aqueous systems.^[18]

[a] X. Wang,⁺ R. Jommongkol⁺
Molecular Electrochemistry for Energy Laboratory, School of Energy Science and Engineering, Vidyasirimedhi Institute of Science and Technology (VISTEC), Rayong, 21210, Thailand

[b] X. Wang,⁺ K. Liu, J. Qian
Hubei Key Laboratory of Electrochemical Power Sources, College of Chemistry and Molecular Sciences, Wuhan University, Wuhan, Hubei, 430072 China
E-mail: jfqian@whu.edu.cn

[c] J. Deng
Institute for Advanced Study, Chengdu University, Chengdu 610106, China

[d] Y. Zhu
Institute of Future Technology, Southwest Jiaotong University, Chengdu 610031, China
E-mail: yachao.scu@hotmail.com

[e] Y. Zhu
ICGM, Université de Montpellier, CNRS, ENSCM, 34293 Montpellier, France
E-mail: yachao.scu@hotmail.com

[f] O. Fontaine
Département de Chimie, Université de Montréal, Montréal, Québec postCode/> H2V 0B3, Canada
E-mail: olivier.fontaine.1@umontreal.ca

[g] O. Fontaine
School of Molecular Science and Engineering, Vidyasirimedhi Institute of Science and Technology (VISTEC), 555 Moo 1, Pa Yup Nai, Wang Chan, Rayong 21210, Thailand
E-mail: olivier.fontaine@vistec.ac.th

[+] These authors contributed equally.

In this review, we first comprehend the nature of WIS electrolytes and then focus on the strategies for solving the stated issues and detailing the accomplishment of WIS electrolytes in our group. Four main parts are included: physical analysis, SEI formation mechanism, additives, and storage device applications. Eventually, we point to the current challenges and future development of WIS electrolytes for promising applications of aqueous energy storage systems.

Our group has been focusing on the topic of water-in-salt electrolytes (WISE) since 2019. We aim to develop and gain a deep understanding of these highly concentrated electrolytes, which we have categorized into four sections over this timeline (as shown in Figure 1). First, we investigated the physical structure by studying the transport properties of WISE. Next, we focused on interface analysis, where our research aimed to understand the processes and phenomena behind water reduction and oxidation in water-in-salt electrolytes. In the

additive contribution section, we addressed the issue of the unstable SEI (solid-electrolyte interphase) layer by exploring the use of additives in WISE, such as the PDE polymer. A year later, we proposed using Diazonium. Additionally, we developed a new approach to estimate the water and salt populations in WISE. Further interface analysis was conducted, including investigations into the key components of the SEI layer. In the final section of our work, we focused on enhancing the performance of devices such as supercapacitors and batteries.

2. Physical Structure

As stated above, the ESW can be extended to a high enough to operate the aqueous system in WIS electrolytes. The reason for enlarged ESW is interesting to study when it involves water molecules that are prone to reduce at 1.23 V. Surely, physical



Xuanze Wang received his master's degree from University of Montpellier in 2022. He is a PhD degree candidate, the student of Prof. Olivier Fontaine in the School of Energy Science and Engineering, Vidyasirimedhi Institute of Science and Technology (VISTEC, Thailand). His research interests mainly focus on programming and deep learning applied in electrochemistry.



Rossukon Jommongkol received her bachelor's degree from Mahidol University in 2020. She is a Ph.D. degree candidate, the student of Prof. Olivier Fontaine in the School of Energy Science and Engineering, Vidyasirimedhi Institute of Science and Technology (VISTEC, Thailand). Her research interests mainly focus on advanced electrolytes for sustainable batteries.



Jie Deng received his PhD in Chemical Processing from Sichuan University. Currently he is a distinguished associate researcher at Chengdu University. His research focuses on the research of preparation of multifunctional nanomaterials and their applications in energy, including water electrolysis, hydrogen production, and metal oxides.



Kexin Liu received her B.S. degree from the College of Chemistry, Zhengzhou University, in 2022. She is currently a Ph.D. candidate at the College of Chemistry and Molecular Science, Wuhan University. Her research interests include the modification of lithium metal interfaces and the application of lithium salt additives in lithium-metal batteries.



Jiangfeng Qian received his PhD in Electrochemistry from Wuhan University. Currently he is a professor at Wuhan University (WHU). His research focuses on the research of new electrochemical energy storage materials and technologies, recycling and regeneration of lithium-ion and lithium metal batteries, new sodium ion batteries and two-dimensional materials, etc..



Yachao Zhu received his PhD in Chemical Engineering from Université Toulouse III - Paul Sabatier. Currently he is a distinguished associate researcher at Southwest Jiaotong University. His research focuses on the research of new electrolyte for supercapacitors and lithium-ion batteries, in-depth study of the essential differences between pseudocapacitor and battery materials.



Olivier Fontaine received his PhD in Electrochemistry from Paris Diderot University (Paris VII). Currently he is a professor at Université de Montréal (UdeM) and Institut Universitaire de France (IUF). His research focuses on the research of synthesis of new electrode materials, structure of electrolytes, and electrochemical analysis integrated with artificial intelligence method.

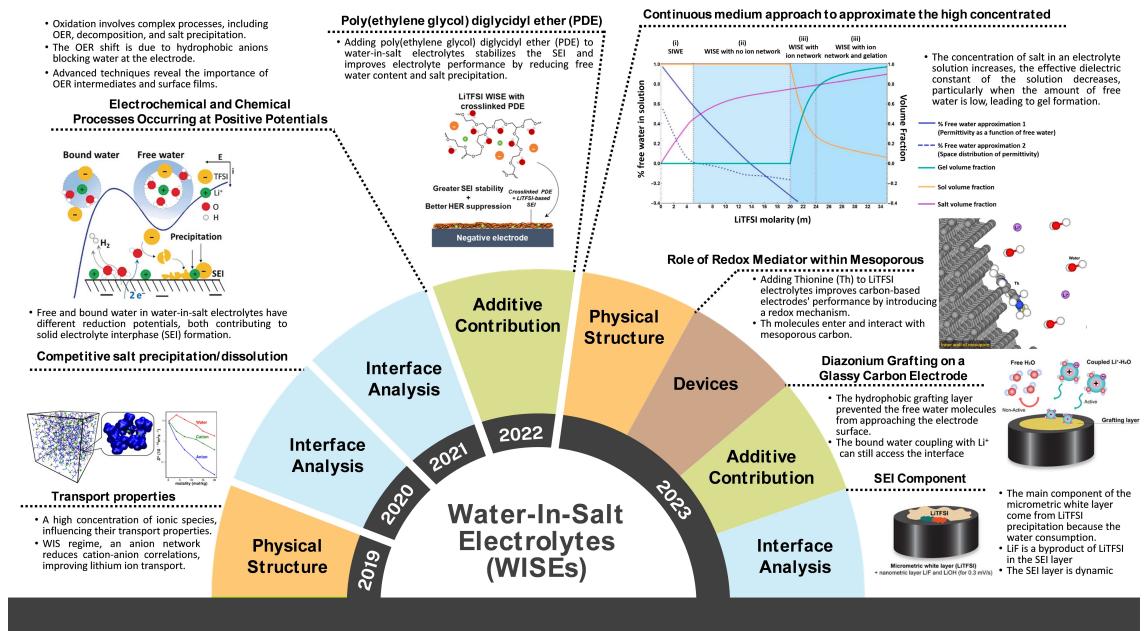


Figure 1. Timeline illustrates our work on water-in-salt electrolytes, from the past to the present.^[17–23] Reproduced with permission: Copyright 2020, Angewandte Chemie International Edition,^[17] Copyright 2023, Small,^[18] Copyright 2022, Journal of The Electrochemical Society,^[19] Copyright 2023, The Journal of Chemical Physics,^[20] Copyright 2023, ACS Applied Materials & Interfaces,^[21] Copyright 2023, Energy Storage Materials,^[22] Copyright 2019, The Journal of Physical Chemistry B.^[23]

chemistry is one of the most important keys corresponding to this extension. Unfortunately, there are rare articles in detail discussing this regime. So, what are salt-in-water (SIW) and water-in-salt (WIS) electrolytes?

Simply put, the most fundamental difference between salt-in-water and water-in-salt is the concentration or the molecular amount of free water in the solution. This will affect the effective permittivity and water activity of the solution, thereby affecting OER and HER overpotentials. Some of us^[20] studied the qualitative contribution of reducing the concentration of free water molecules to the solution permittivity as the salt concentration increases in water-in-salt electrolytes (WISE) and the effect of water activity on the OER and HER overpotentials. Two models were compared, *i.e.* the effective permittivity as a function of the percentage of free water and the spatial distribution of the effective permittivity. Three types of electrolyte structures were obtained: dilution, water content gradient, and aggregation. Theoretical calculations of the OER and HER redox potentials were also compared with the experimentally determined electrochemical properties of the aqueous LiTFSI electrolyte.

First, it is found that the amount of water decline can lead to the decrease of solvation degree of the ions in the aqueous LiTFSI electrolyte. Assuming that there is a moment when water completely disappears, then theoretically, the solvation of ions will also completely disappear at this time. In this case, the ion can be considered an unsolvated ion because the solvation is completely gone. The size and properties of the ion are similar to the theoretical values for the unsolvated condition. Secondly, the relationship between the concentration and effective permittivity constant, as well as water activity, was interestingly

disclosed. In detail, the concentration has a vigorous influence on the amount of free water and the distance between ions in the LiTFSI solution, and we also researched this ion distance influence on solution effective permittivity. An equation linking the effective solution permittivity with the free water molecules is built as below.

The pure aqueous solution can be assimilated to a solution containing 100% free water molecules if only electrostatic interactions are considered. Assuming that the permittivity of an electrolyzed aqueous solution is a function of the free water concentration in WISE, the permittivity of the solution can be determined (Eq. 1).

$$\epsilon_{\text{eff}} = \epsilon_{\text{H}_2\text{O}} \cdot \%n_{\text{H}_2\text{O}_{\text{free}}} \quad (1)$$

This equation is in accordance with the fact that the salt quantity in the water can be negligible in the diluted solution, and the permittivity of the solution is assimilated to the permittivity of the water. ($\epsilon_{\text{eff}} = \epsilon_{\text{H}_2\text{O}} \cdot \%n_{\text{H}_2\text{O}_{\text{free}}} = \epsilon_{\text{H}_2\text{O}} \cdot 100\%$)

Knowing that the number of free water molecules ($n_{\text{H}_2\text{O}_{\text{free}}}$) is proportional to the concentration of free water molecules ($C_{\text{H}_2\text{O}_{\text{free}}}$), the effective solution permittivity (ϵ_{eff}) is a simple function of the concentration of free water molecules ($C_{\text{H}_2\text{O}_{\text{free}}}$). Thus, in our model, the effective permittivity can be calculated as below.

$$\epsilon_{\text{eff}} = \frac{\epsilon}{1 + \left(\frac{\epsilon}{\epsilon^*} - 1\right) \cdot e^{-d'_{\text{ion}}}} \quad (2)$$

where ϵ^* is the short wavelength permittivity, ϵ_{eff} is the effective permittivity, ϵ is the long wavelength permittivity, d'_{ion}

is the variable distance between two cations (nm or \AA). Equation 2, derived primarily from the work of A. A. Kornyshev in 1981^[24] describes the non-local shielding of ions in structurally polar liquids, focusing on the variation of the permittivity of the solvent as a function of the distance between the ions. In a solution, $\frac{\epsilon_{\text{eff}}}{\epsilon} = 1$ corresponds to pure free water in solution. The above information exhibits the influence of ion distance on effective permittivity, and that is the space distribution of effective permittivity. Besides, in the Debye-Hückel theory,^[22] the solvent is usually considered as a dielectric continuum with a fixed dielectric constant in the system. However, as increasing the solution concentrations, the presence of ions affected the physical properties of the medium and thus the permittivity. Therefore, a model of permittivity versus ion concentration is urgently developed.

Figure 2 comprehensively demonstrates the various physicochemical properties of LiTFSI water-in-salt (WIS) electrolytes and how they influence the overall behavior of the system.

In Figure 2a, the weight-averaged degree of ion aggregation (ξ) is plotted as a function of salt volume fraction (ϕ). As the salt volume fraction increases, the degree of ion aggregation rises significantly, indicating that ions tend to form larger aggregates rather than exist independently in high-concentration environments. This aggregation behavior can have a substantial impact on the physical and chemical properties of the electrolyte, especially in the transport processes at the interface. This behavior is directly related to the electrolyte concentration, and the double logarithmic plot in the inset further describes that, near the gel point, the change in the degree of aggregation follows a critical exponent of -1 . This suggests that, as the solution approaches the gel state, the correlation between ions increases significantly, and the system exhibits more complex dynamic characteristics. These observations imply that the aggregated ion clusters may alter the rheological properties and transport characteristics of the electrolyte, thereby affecting the overall performance of the battery.

In Figure 2b, the effect of LiTFSI concentration on the redox potentials of water (oxygen evolution reaction, OER, and hydrogen evolution reaction, HER) is studied in detail. Two different effective permittivity models are used to calculate the effect of concentration changes on the decomposition potential of water: the effective permittivity model based on the free water fraction and the spatial distribution model of effective permittivity. As the LiTFSI concentration increases, both the oxidation and reduction potentials of water shift in more positive and negative directions, respectively, indicating that high-concentration LiTFSI electrolytes can effectively expand the electrochemical stability window (ESW) of aqueous solutions. Specifically, from 1 molal to 21 molal LiTFSI solutions, the oxidation and reduction potentials shift by about 0.12 V in total. This phenomenon indicates that reducing the activity of free water plays an important role in expanding the electrochemical stability window. Moreover, the potential changes caused by concentration also indicate significant changes in the interaction between free water molecules and the electrode interface, especially at high potentials, which may have profound

effects on electrode stability and long-term cycling performance.

Figure 2c shows 1D and 2D plots of water activity in the solution under different molalities (e.g., 20 mol/kg and 0.3 mol/kg). The green regions represent free water, while the orange parts represent solvated water. The results show that as the ion distance decreases, the proportion of free water decreases, and water activity also decreases, consistent with the observed decrease in water availability with increasing concentration. These changes indicate that the solvation state of water molecules is significantly affected in high-concentration electrolytes, leading to reduced water activity, which further explains the expanded electrochemical stability window of high-concentration LiTFSI solutions. Specifically, at high concentrations, the balance between solvated and free water is disrupted, making it more difficult for water molecules to reach the electrode surface, thereby suppressing undesirable side reactions such as hydrogen evolution reaction (HER). This is crucial for improving the stability of electrolytes. The gel point calculated by Maffre et al. is when the mole fraction of salt is between 0.12 and 0.18. This is slightly different from the result obtained by McEldrew et al. (between 0.17 and 0.18), but it is within an acceptable range and is mathematically correct.

In Figure 2d, the simulated viscosity, conductivity, and self-diffusion coefficients are compared with experimental results for LiTFSI solutions. The simulated results are in good agreement with the experimental data, indicating that classical molecular dynamics simulations with simple nonpolarizable force fields can effectively reproduce the transport properties of WIS electrolytes. Notably, these transport properties make LiTFSI-based WIS electrolytes kinetically similar to ionic liquids rather than traditional solvent-based electrolytes. This high-concentration environment can increase the lithium ion transference number, thereby enhancing the potential of WIS electrolytes for future battery applications. In addition, the simulations reveal how increasing LiTFSI concentration affects the viscosity and ion diffusion behavior of the solution – at high concentrations, the increase in viscosity leads to a reduction in ion migration speed, but at the same time, due to the strong correlation between ions, the lithium ion transference number increases. This unique characteristic makes WIS electrolytes perform well in applications with high power demands.

In summary, Figure 2, through multiple aspects such as ion aggregation, changes in effective permittivity, water activity, and transport properties, reveals how the physicochemical behavior of LiTFSI WIS electrolytes expands the electrochemical stability window by regulating the activity of free water and the interactions between ions. These results provide an important foundation for understanding the complex interfacial processes and transport phenomena in high-concentration electrolytes and lay the theoretical basis for optimizing electrochemical performance in superconcentrated electrolyte environments in the future. These findings suggest that further optimizing LiTFSI concentration and controlling ion aggregation behavior can achieve significant progress in expanding electrochemical stability and enhancing interfacial stability, thereby promoting

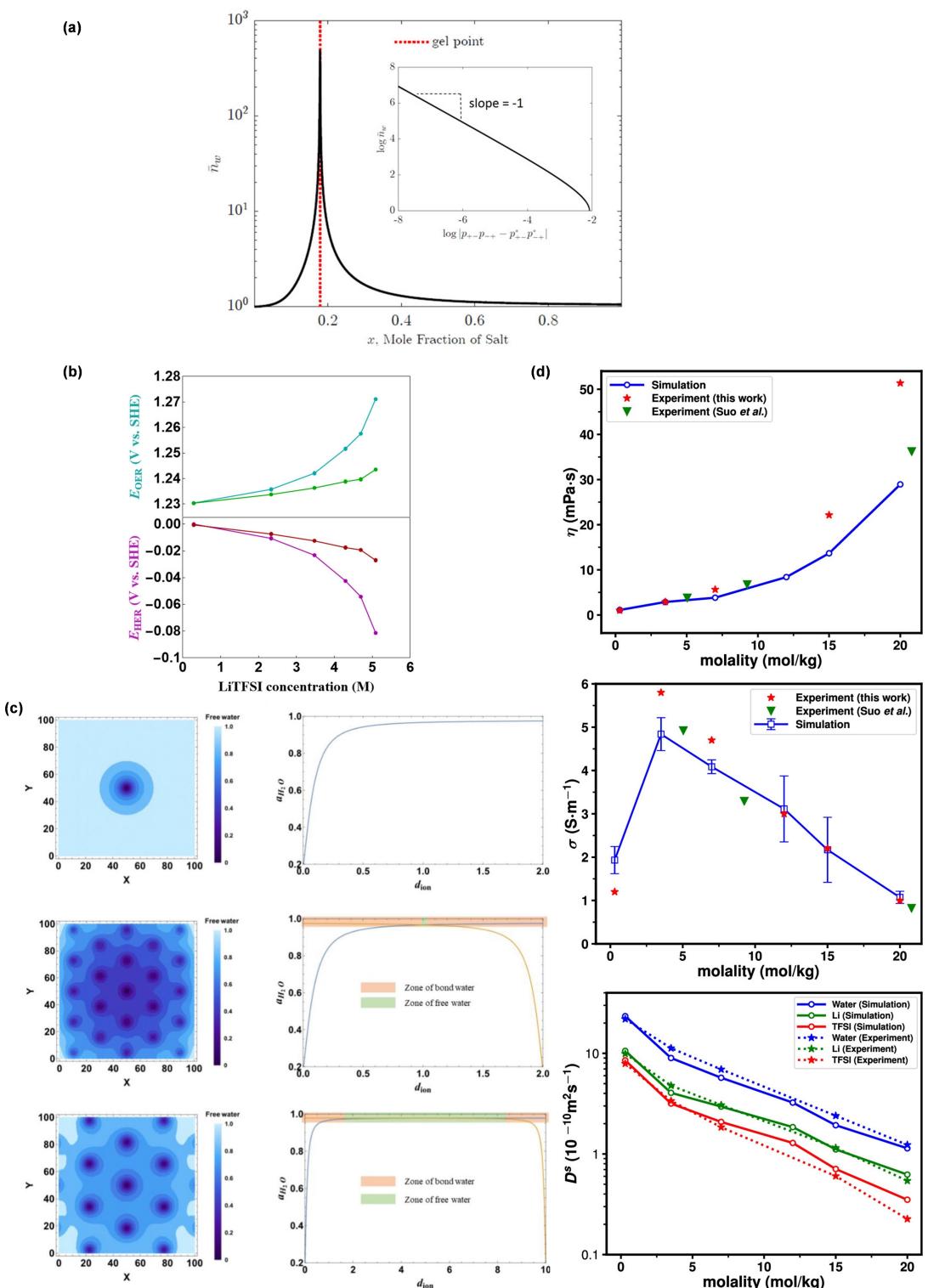


Figure 2. Physicochemical properties of LiTFSI water-in-salt electrolytes. (a) The degree of ion aggregation as a function of salt volume fraction, highlighting critical behavior near the gel point. (b) Effect of LiTFSI concentration on oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) potentials, calculated using effective permittivity models. Reproduced with permission: Copyright 2020, Angewandte Chemie International Edition.^[17] (c) 1D and 2D water activity distribution under different molalities, showing the balance between solvating and free water. Reproduced with permission: Copyright 2023, The Journal of Chemical Physics.^[20] (d) Comparison of simulated viscosity, electrical conductivity, and self-diffusion coefficients with experimental values, demonstrating the transport properties of LiTFSI-based water-in-salt electrolytes. Reproduced with permission: Copyright 2019, The Journal of Physical Chemistry B.^[23]

the application prospects of WIS electrolytes in high-energy-density batteries.

Furthermore, we concluded three important factors: the distance between ions, water activity, and solution permittivity. Three types of electrolyte structures were obtained: dilution, water content gradient, and aggregation. Two models were built to describe the effective dielectric constant: function of free water percentage and space distribution. It is found that most populations correspond to free water molecules in SIW electrolytes. In contrast, for the WIS electrolyte, the relative amount of water to salt greatly reduces. The consequence of high concentrations ($> 14 \text{ m LiTFSI}$) is the absence of free water molecules and the simultaneous incomplete solvation of the ions. We have shown that both the solvated ion radius and the distance between oppositely charged ions decrease. Additionally, it is practical to determine water activity. Two models were observed. In dilute aqueous electrolytes, the solvent activity is equal to 1. The water activity trend in WISE is zero. Consequently, the potentials of HER and OER link with water concentration and activity in dilute one, while this is not the same case in WISE. It was confirmed by the shifts of the OER and HER polarization potentials toward more positive and negative potentials, respectively, with increasing concentration. From 1 to 21 m LiTFSI, it theoretically obtains a larger voltage window of 0.12 V. Although this value is lower than the one obtained by the experimental result (around 0.4 V),^[20] it implies that the decreasing water activity is not the only factor responsible for the polarization potentials of OER and HER. However, it still demonstrates that the decrease of water activity or the concentration increase is beneficial to broadening the electrochemical window.

Yokoyama et al. investigated the influence of water activity on the electrochemical stability window (ESW) in highly concentrated electrolytes.^[25–26] They demonstrated that the potential for HER remains largely independent of water concentration, while the OER potential increases with decreased water activity. This asymmetry highlights the thermodynamic suppression of OER as a dominant factor in ESW expansion. In contrast, our study observed shifts in both HER and OER potentials, suggesting that kinetic factors may also contribute under certain conditions. Combining these findings provides a comprehensive understanding of the ongoing debate on whether ESW broadening is driven primarily by thermodynamic suppression or kinetic limitations. While thermodynamic suppression of the oxygen evolution reaction (OER) through reduced water activity clearly dominates the expansion of the ESW on the oxidative side, the role of kinetic factors, particularly for the hydrogen evolution reaction (HER), cannot be entirely dismissed. Khan et al. have convincingly shown that the HER potential remains relatively independent of water activity, suggesting that thermodynamic effects have limited influence on the reductive side. In contrast, our findings indicate observable shifts in both HER and OER potentials, which implies that kinetic effects, such as sluggish electron transfer and interfacial processes, play a supporting role in HER suppression.

This asymmetry highlights a critical conclusion: the broadening of ESW is predominantly governed by thermodynamic

suppression of OER, while the influence of kinetic factors on HER, although secondary, cannot be ignored. Therefore, under practical conditions, the thermodynamic stabilization of OER serves as the primary mechanism for ESW expansion in water-in-salt electrolytes (WISE), with kinetic limitations acting as supplementary contributors. This nuanced understanding reconciles previous conflicting observations and emphasizes that the oxidative limit is the primary driver for achieving a widened ESW, whereas the reductive limit remains more kinetically constrained.

Except for the critical physical structure, the transport properties are also captivating to study, which can largely influence the electrochemical performance. Some of us^[23] studied the transport properties of WIS electrolytes and how they evolve with rising concentration. The structure of WIS is reminiscent of ionic liquids, which are characterized by high concentrations of ionic species. Comparing simulated viscosity and self-diffusion coefficients with experimental measurements, a set of parameters was selected to reproduce well the transport properties. A detailed study of changes in the self- and collective diffusivity of all species and the transport number of lithium ions using selected force fields revealed that the correlation between ions and water plays an important role across the entire concentration range. Concentrating on the physicochemical properties of a prototype LiTFSI-based WIS, molecular dynamics (MD) simulations exhibited the transport properties using four different high-concentration force fields, such as viscosity, conductivity, and diffusion coefficient, comparing with reported work by Suo et al. (shown in Figure 2d).^[8] The simulated results are well consistent with the experimental results, suggesting that WIS electrolytes can be considered as an intermediate system between traditional solvent-based electrolytes and pure ionic liquids. The three transport properties described above can be reproduced well using classical molecular dynamics simulations and simple nonpolarizing force fields. Based on these analyses, LiTFSI-based WIS electrolytes are very similar to ionic liquids from a kinetic perspective. Therefore, the lithium transport number is larger than previously reported values for other representative electrolytes, which enhances the voltage window of WIS electrolytes for future battery applications.

The concentration dependence of ionic transport and solvation effects plays a crucial role in the electrochemical behavior of water-in-salt electrolytes (WISE). At low concentrations, cations are fully solvated by water molecules, forming solvent-separated ion pairs, which facilitate rapid ion transport. However, as the concentration increases, the number of free water molecules decreases, leading to the formation of contact ion pairs and ionic aggregates, which can limit ion mobility. Interestingly, at ultra-high concentrations, such as in water-in-polymer salt electrolytes, a unique hopping mechanism dominates ionic transport. Khan et al. demonstrated that hydrated cations migrate between polymer chain segments through localized hopping, which maintains relatively high ionic conductivity despite the limited availability of free water.^[27] This behavior deviates from the traditional Stokes-Einstein diffusion

mechanism and positions these systems as superionic conductors.

Furthermore, the solvation structure is equally concentration-dependent. At low concentrations, water molecules maintain an extensive hydrogen-bond network, providing strong solvation to cations. As the concentration increases, the disruption of this network weakens solvation, particularly affecting the OER potential, which shifts significantly due to reduced water activity. In contrast, the HER potential remains largely unchanged, indicating its kinetic limitation. He et al. further confirmed that the reduction in free water molecules and solvation effects suppresses OER while having negligible influence on HER.^[28] This concentration-driven solvation disruption and the associated reduction in water activity are critical factors contributing to the broadened electrochemical stability window observed in WiSE systems.

Our findings align with these observations, suggesting that while OER suppression is predominantly thermodynamically driven, kinetic factors play a secondary role in HER behavior. The concentration-dependent ionic transport mechanisms further underscore the importance of solvation dynamics in achieving high ionic conductivity and extended ESW in water-in-salt and water-in-polymer salt electrolytes.

3. Interface Analysis

The above unique physical structure of WIS electrolytes can strongly impact the electrochemical behavior at the interface. As reported,^[8,16] the extended ESW corresponds to the possible electrochemical processes on both positive and negative electrode interfaces. The issue is that the studies of electrochemical processes on the positive side are rarely reported. And there is an intense debate^[8,16–18] on the forming mechanism of solid-electrolyte interphase (SEI) on the negative interface. So, it is necessary to spotlight these two significant processes, unveiling the true factors of obtaining the broadened ESW for aqueous systems.

On the positive side, some of us^[29] investigated the electrochemical and chemical processes at highly positive potentials using analytical electrochemistry tools such as cyclic voltammetry, rotating ring-disk electrode (RRDE), and online mass spectrometry (OEMS). They studied the effect of salt concentration on electrochemical stability (ESW) using both glassy carbon (GC) and Pt electrodes. The observations show that both electrodes expand the electrochemical stability window when the number of salts is higher which is related to the literature^[16] as shown in Figure 3a.

Furthermore, the study investigates the electrochemical behavior of GC and Pt electrodes at highly positive potentials in “water-in-salt” electrolytes as shown in Figure 3a. For Pt electrodes, oxidation waves between 0 and 2.8 V vs. Ag/AgCl and reduction waves between 1 and 0 V vs. Ag/AgCl are observed across all electrolytes, occurring during the reverse sweep after the OER. These processes are attributed to the oxidation of the Pt electrode and the reduction of the formed oxides, with oxidation potentials shifting to more positive values and

reduction potentials shifting to more negative values as the molality of LiTFSI increases. In contrast, GC electrodes do not show well-defined oxide formations but exhibit slight variations between 1–2 V vs. Ag/AgCl and 1.5–0 V vs. Ag/AgCl, which may correspond to the oxidation and reduction of the GC electrode and the intercalation/de-intercalation of TFSI anions. Prior research suggests that TFSI anions can insert between carbon sheets, leading to their separation at high positive potentials; this process may also occur in GC electrodes due to their microstructure of discrete fragments of curved carbon planes.

The study finds that the electrochemical OER contributes negligibly to the current, with most of the current involved in the formation of surface films resulting from carbon oxidation and the partial evolution of CO₂ and CO gases. Three potential mechanisms for the formation of these surface films are proposed: salt oxidation, salt precipitation, and salt decomposition. To conclude, these findings underscore the non-inert nature of GC and Pt electrodes at positive potentials in “water-in-salt” electrolytes, highlight the primary role of surface film formation in current contribution, and provide insights essential for the design and optimization of high-voltage aqueous batteries.

On the other hand, on the negative electrode, the composition and mechanism of SEI formation in WiSEs still remain in crisis debate. First, Suo et al.^[8] conducted the beginning study, according to the competitive reduction of water, dissolved O₂, CO₂, and TFSI⁻, concluding that TFSI⁻ in ionic clusters and water are reduced at the same potential, while hydrogen evolution is considered a parasitic reaction. They employed XPS, TEM, and EDX to characterize the SEI formed in aqueous electrolytes. They identified a dense and robust interphase predominantly composed of LiF, which originates from the electrochemical reduction of TFSI⁻. This LiF-rich interphase acts as an electron barrier, preventing water reduction while allowing lithium-ion migration. Furthermore, TEM imaging revealed a 10–15 nm crystalline LiF layer, chemically distinct from SEIs in non-aqueous systems due to the high salt concentration and reduction potential of TFSI⁻.

Second, Dubouis et al.,^[16] argued that water is reduced at a negative potential, leading to H₂ formation and release of OH⁻ on the electrode surface, precipitating LiOH. After, TFSI⁻ is decomposed on the presence of LiOH or OH⁻, reacting with the electrophilic sulfur atom to generate fluorinated species and organic compounds, eventually forming a fluorinated solid-electrolyte interphase. They used operando and ex situ XRD analyses complemented by EDX, highlighted LiOH as the dominant crystalline phase in the SEI formed during reduction processes in water-in-salt electrolytes (WiSEs). They noted that LiOH precipitation occurs at –0.7 V vs. SHE, with amorphous phases contributing to the SEI, a feature more characteristic of organic systems. The absence of other crystalline components underscores the distinct chemistry of WiSEs, emphasizing the role of potential in determining SEI composition.

However, some of us,^[17] two above conclusions were not observed and identified following various analyses. Interestingly, two reduction peaks, i.e. free water and bound water, were presented, both contributing to the formation of SEI. More

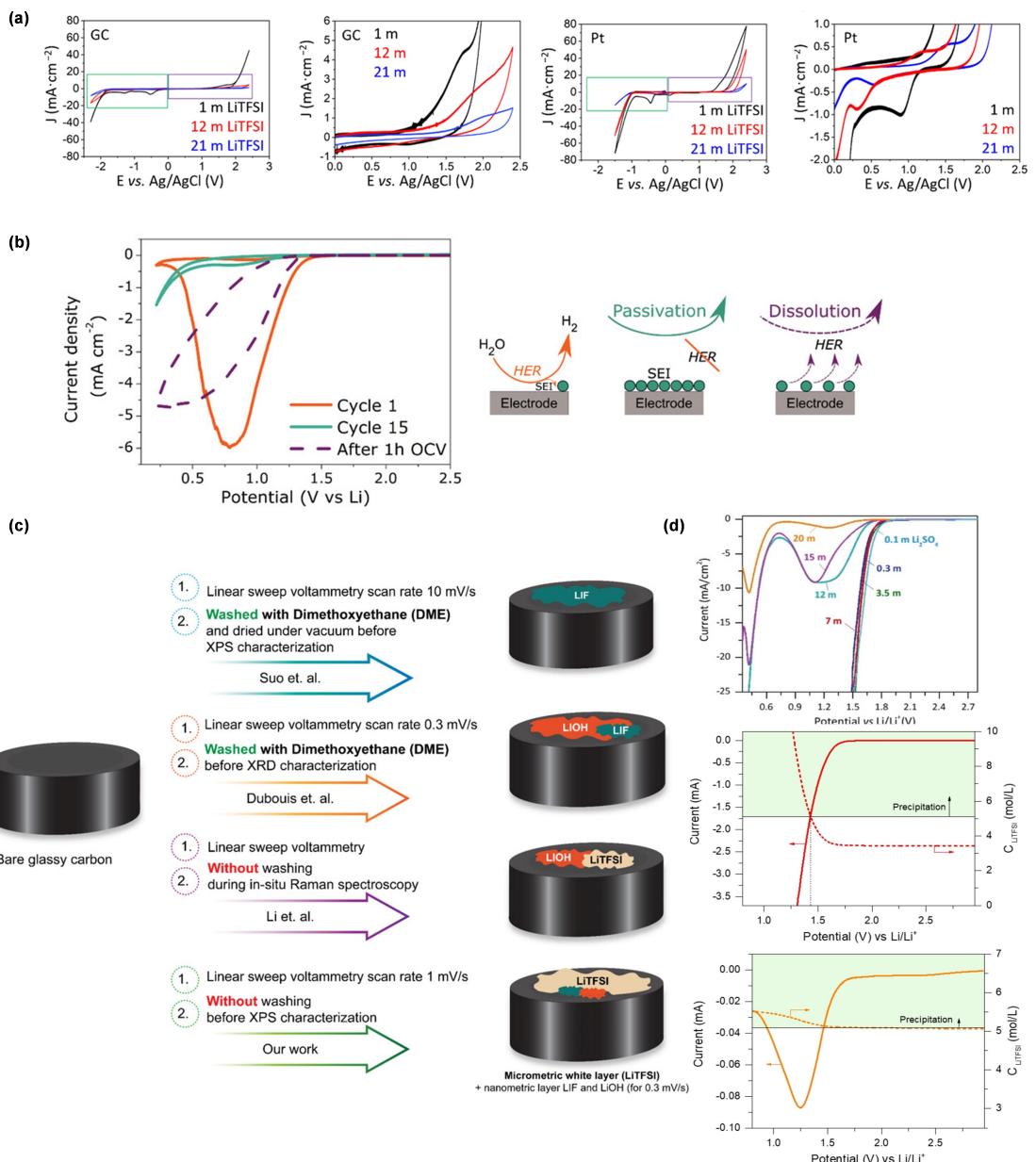


Figure 3. Electrochemical processes and SEI formation in water-in-salt electrolytes (WiSE). (a) Cyclic voltammograms of GC and Pt electrodes in LiTFSI solutions with varying concentrations, showing the expanded electrochemical stability window at positive potentials. Reproduced with permission: Copyright 2021, Journal of The Electrochemical Society.^[29] (b) Assessment of SEI stability over time on a glassy carbon electrode, demonstrating its dynamic behavior after open circuit voltage (OCV) resting. Reproduced with permission: Copyright 2020, Advanced Energy Materials.^[30] (c) Schematic representation of SEI composition and evolution, comparing literature findings with our work. Reproduced with permission: Copyright 2023, Small.^[18] (d) Linear polarization analysis showing the dynamic salt concentration profile at the interface during water reduction. Reproduced with permission: Copyright 2020, Angewandte Chemie International Edition.^[17]

significantly, at the negative interface, except for the reductions of two types of water, it also occurred simultaneous LiTFSI salt precipitation/dissolution, establishing a dynamic interface. Therefore, the ongoing water reductions and continuous precipitation-dissolution mechanism cause serious decay during charge-discharge cycling processes. From Figure 3d, under a concentration of 12 m, there is only one reduction slash caused by the serious decomposition of water. In comparison, at and above 12 m concentration, the process turns into a reduction wave with a distorted bell shape at about 1.2 V, corresponding

to the water reduction. We concluded that there are two different water populations (namely free water and bound water) in corresponding chemical environments, thereby interpreting two reducing peaks of water molecules at two potentials.

Our colleague, Droguet et.al.^[30] reveal the SEI stability test of WiSE by cycling a glassy carbon working electrode in a three-electrode cell, followed by a 1-hour resting period and another cyclic voltammetry (CV) measurement to assess the cathodic current linked to the hydrogen evolution reaction (HER) (Fig-

ure 3b). In the first CV scan, a peak appears at 0.75 V versus Li/Li⁺, indicating HER activity on the surface of the glassy carbon electrode. With subsequent cycling, the peak's intensity decreases and nearly disappears after 15 cycles (green line), likely due to the progressive passivation of the glassy carbon electrode from SEI formation, as illustrated in Figure 3b. However, after the 1-hour rest, the following CV scan (purple dashed line) shows that the passivation effect is reversed, as the peak intensity for HER returns to the initial level observed in the first cycle. Which mean that this SEI layer has a dynamic behavior.

More precisely, our group^[18] identified that the formed SEI is indeed a micrometric white layer, where there is a major part of LiTFSI precipitation but small reduced nanoscale components (LiF and LiOH) demonstrated by an operando high-resolution optical microscope. Again, the passivation interphase was proved to be a dynamic layer since it can be dissolved back into the electrolyte during open circuit voltage. As imaged in Figure 3b, it signifies that a micrometric white layer was formed during two water reductions (bubble desorption) on the electrode surface at around 0.76 V and 0.23 V. Through XPS and HRTEM analysis, the main component of this white layer was mainly LiTFSI precipitation, with secondary contributions from LiF and LiOH. Notably, LiOH appeared only at slower scan rates (0.3 mV/s) and was absent at higher rates (1 mV/s). Their analyses demonstrated that LiTFSI and its decomposition products, including CF₃, dominate the SEI, with crystallographic structures varying with scan rate. Figure 3b reveals that the concentration of LiTFSI was constant (about 3.8 m) prior to the first reduction peak. During cycling, water was continuously consuming near the electrode surface, gradually raising the concentration of LiTFSI until reaching the solubility limit point (≈ 4.71 m), then precipitating the white layer of LiTFSI. However, after open circuit voltage (OCV), the concentration of LiTFSI returned to equilibrium, indicating that LiTFSI dissolved back into the bulk solution.

To make clear the whole story of the SEI formation and its nature, we concluded the evolution of SEI in Figure 3c and the mechanism of SEI formation at the negative electrode as shown in Figure 4. We noted that in most studies, the electrode is washed with solvents such as dimethoxyethane (DME)^[8,16] or water^[17,30] before characterization, resulting in the observation of the nanometric layer associated with the SEI (which are LiF and LiOH). In contrast, our previous work^[18] investigated the electrode surface through the direct observation of the micrometric white layer, a thicker layer, using optical microscopy without washing the electrode with any solvent (Figure 3c). This approach enabled us to observe the micrometric white layer, originating from LiTFSI precipitation as part of the SEI layer, which was not reported by other authors. Additionally, our previous work also detected the nanometric layer (LiF), confirmed through XPS analysis. Then, Figure 4 illustrates the proposed mechanism for SEI layer formation at the negative electrode surface, as previously reported in the literature.^[8,16] Upon the application of a negative potential to the electrode surface, the hydrogen evolution reaction occurs, resulting in the generation of hydroxide anions (OH⁻) and the precipitation of LiTFSI due to water consumption. Consequently, the SEI layer predominantly forms from LiTFSI precipitation, with additional contributions from LiOH under lower scan rates (Figure 4c), as identified in our previous studied.^[18] Furthermore, LiF is formed as a byproduct of TFSI reduction, as depicted in Figure 4e. We also found that the SEI layer is dynamic as mentioned before.

Simulation techniques have also become indispensable tools for understanding the formation mechanisms of the SEI, offering insights at atomic and molecular levels that are difficult to achieve through experimental approaches alone.^[31] These methods provide a theoretical framework to analyze complex interfacial processes, elucidate reaction pathways, and predict the structural and chemical properties of SEI layers under various conditions. By bridging gaps in experimental data,

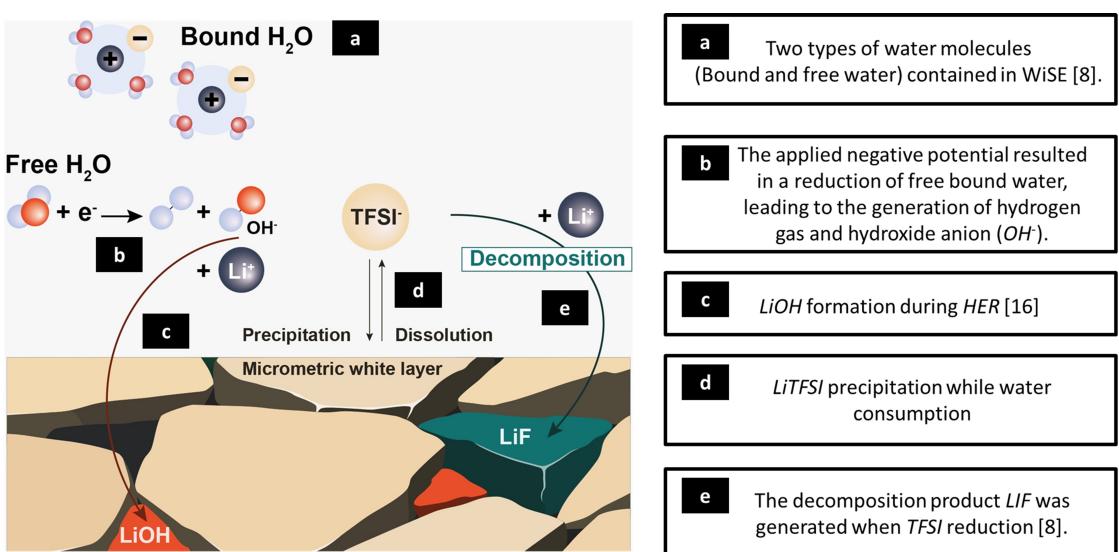


Figure 4. Schematic represent the mechanism of the solid-electrolyte interphase (SEI) formation on the negative electrode in water-in-salt electrolytes. Reproduced with permission: Copyright 2023, Small.^[18]

simulation studies allow for a more comprehensive understanding of the dynamic nature of SEI formation.

Molecular dynamics simulation, also called MD simulation, is particularly effective in capturing the dynamic behavior of ions and solvent molecules at the electrode-electrolyte interface. They enable researchers to observe the real-time evolution of solvation structures, ion transport mechanisms, and the initial nucleation of SEI layers.^[32] MD simulations reveal how specific electrolyte components, such as salts and solvents, influence the distribution and mobility of ionic species near the electrode surface. This approach also provides insights into the role of concentration, temperature, and electric field effects on the stability and growth of SEI layers.^[33] Through MD simulations, it is possible to determine how the local ionic environment affects the reduction of electrolyte species, leading to the formation of key SEI components.

Density functional theory (DFT) calculations complement MD simulations by providing a quantum mechanical perspective on the reaction mechanisms involved in SEI formation.^[34] DFT enables the identification of thermodynamically stable reaction intermediates and the evaluation of their formation energies. This method also elucidates the electronic structure changes that occur during the reduction and decomposition of electrolyte molecules, providing a deeper understanding of how specific species contribute to the composition and functionality of the SEI.^[35] Furthermore, DFT calculations allow for the prediction of reaction pathways and kinetic barriers, helping to identify the rate-limiting steps in SEI formation. These insights are crucial for designing electrolytes that favor the formation of stable and protective SEI layers.^[36]

Beyond individual methods, multiscale simulation approaches have been developed to integrate atomic-scale and mesoscale phenomena. For example, using COMSOL Multiphysics allows researchers to investigate the interplay between chemical reactivity and ion diffusion within the SEI.^[37] COMSOL Multiphysics plays a critical role in understanding the formation and characteristics of the SEI by integrating electrochemical, thermal, and mechanical modeling.^[38] Its multi-physics approach enables the simulation of ionic transport and interfacial reactions using coupled Nernst-Planck^[39] and Butler-Volmer^[40] equations, providing insights into the growth dynamics and chemical composition of the SEI. For example, simulations reveal how electric fields and ionic concentration gradients drive the preferential deposition of components such as LiF and Li₂CO₃, and how competitive reduction pathways influence SEI formation under different conditions.

Beyond chemical processes, COMSOL's structural mechanics capabilities allow for the evaluation of mechanical stresses within the SEI during electrode expansion and contraction.^[41] These simulations identify regions prone to cracking or delamination, helping to design more robust SEI layers. Additionally, thermal-electrochemical coupled models highlight how temperature affects SEI stability, from accelerated decomposition at elevated temperatures to ionic blockages at lower ones.^[42] By incorporating reaction kinetics for additives, COMSOL also predicts their impact on SEI growth and stability, guiding electrolyte optimization for improved battery

performance.^[43] This holistic modeling framework bridges the gap between experimental observations and theoretical insights, enabling a deeper understanding of SEI behavior and its implications for energy storage systems.

Simulations address several critical challenges in SEI research that are difficult to resolve experimentally. They provide atomic-level clarity on the competition between different reduction pathways, elucidating why certain species dominate SEI formation under specific conditions.^[44] Moreover, simulations help quantify the effects of impurities and electrolyte additives on SEI composition and stability, offering predictive insights into how these factors modify interfacial reactions. Another key contribution of simulations is their ability to model the mechanical properties of the SEI, such as its elasticity and fracture resistance, which are essential for maintaining electrode integrity during cycling.

Simulation techniques offer a powerful platform for dissecting the complex processes underlying SEI formation. They not only complement experimental findings but also extend the scope of understanding by revealing atomistic details and predicting behaviors that are challenging to observe directly. These capabilities make simulations an essential tool for the rational design of next-generation electrolytes and electrode materials, enabling the optimization of SEI properties to enhance battery performance and longevity.

Figure 5 demonstrates the application of computational simulations, including molecular dynamics,^[45–46] density functional theory,^[47] and COMSOL Multiphysics,^[48] in the study of SEI. These simulations highlight the potential of computational methods to explore structural evolution, mechanical properties, and interfacial dynamics, showcasing their utility in advancing the understanding of SEI formation and behavior.

4. Additives Contribution

Physical chemistry provides a clear understanding of water-in-salt essence. The study of interface processes gives an insight into comprehending the origin of extending ESW. As proved above, the anode interface is still countering water molecules because of the ununiform SEI layer, resulting in unsatisfactory ESW and unexpected parasitic reactions. And the interphase is also suffering from precipitation/dissolution phenomenon due to the dynamic LiTFSI layer, leading to cell drying until failure. Therefore, it is urgent to develop a robust interphase to ensure the long-term cycling stability of aqueous systems. One of the most efficient ways is introducing additives, such as polymer additives,^[49] diazonium additives,^[19,21] and the redox mediator.^[50] In addition, the accessible specific area is limited in carbon electrode materials, especially involving a highly concentrated electrolyte (i.e. WIS electrolyte). It would be more complicated in porous materials due to extreme aggregated ions on the interface in WIS electrolytes.^[51–52]

The dynamic SEI is not functional enough to protect the electrode interface from parasitic reactions. Here, we crafted an artificial interphase of diazonium-based layers at the electrode surface by a grafting method (Figure 6a).^[21] The aim was to

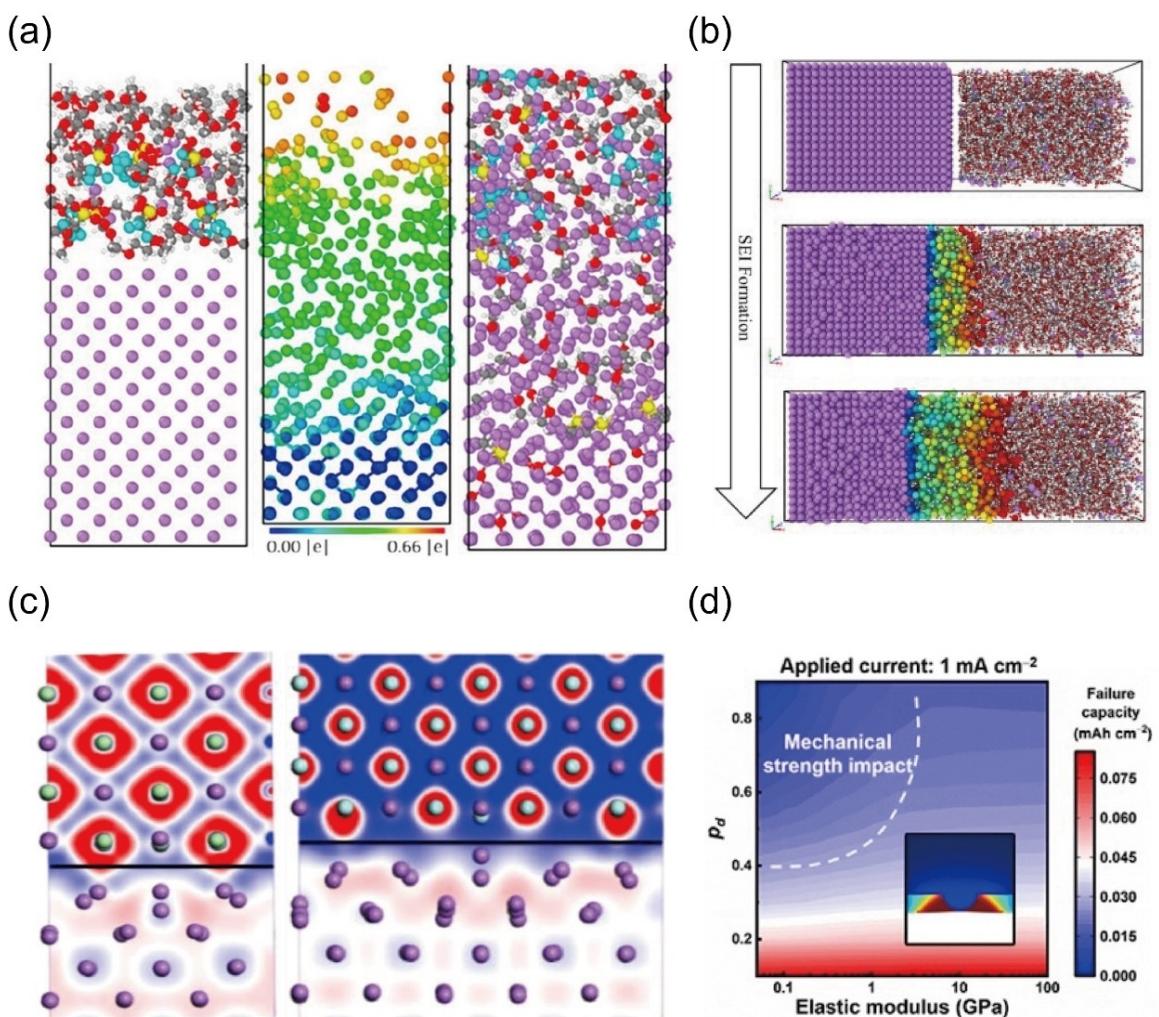


Figure 5. Application of computational simulations in SEI research. (a) and (b): the calculation of molecular dynamics.^[45–46] Reproduced with permission: Copyright 2020, Journal of Materials Chemistry A,^[45] copyright 2025, Journal of Energy Storage.^[46] (c): the calculation of density functional theory.^[47] Reproduced with permission: Copyright 2020, Journal of Materials Chemistry A.^[47] (d): COMSOL Multiphysics simulations.^[48] Reproduced with permission: Copyright 2019, COMSOL.^[48]

efficiently suppress the reduction of free water on the electrode without affecting the ionic conductivity of lithium ions. Some monomers [such as poly(ethylene glycol), α -methoxy, ω -allyloxy (PEG), and allyl glycidyl cyclocarbonate (AGC)] were used, experiencing radical formation of diazonium, diazonium grafting, and polymerization. Contact angle and Cyclic voltammetry (CV) measurements demonstrated the hydrophobic property of the grafted electrode surface. As a result, in the 20 m LiTFSI electrolyte, the free water reduction process was not observed with grafted layers, compared with a prominent free water reduction peak on a bare glassy carbon electrode. Also, a larger potential was needed to trigger the bound water reduction after grafting. More significantly, after applying the 1 h open-circuit voltage (OCV) procedure, the artificially grafting layer was stable, in contrast to the dynamic SEI in our previous work.

Besides, we applied a portable optical microscope to observe the electrode surface to give visual proof of the suppressed water after grafting the diazonium-based layer, as displayed in Figure 6a. A close snapshot was captured at

applied potentials (i, ii, and iii), and the intensity of generating bubbles could directly reflect the strength of water reduction. Strong bubbles were developed on the bare electrode surface over the first reduction (i.e., free-water reduction) at the corresponding potential. In contrast, few bubbles were observed with the grafting hydrophobic layer. The bubbles were dramatically rising on the bare electrode surface over the second reduction, while limited bubbles appeared on the grafting electrode surface.

The hydrophobic grafting layer prevented the free water molecules from approaching the electrode surface but the bound water coupling with Li^+ can still access the interface as shown in Figure 6a. We first directly visualized the water reduction process on the electrode by the bubble evaluation. It directed a novel way to grasp the status of water reduction on the electrode surface and understand the microscopic surface with optical images.

Moreover, polymer additives^[19] are another alternative that can be used to advance the SEI layer. Our colleague used the

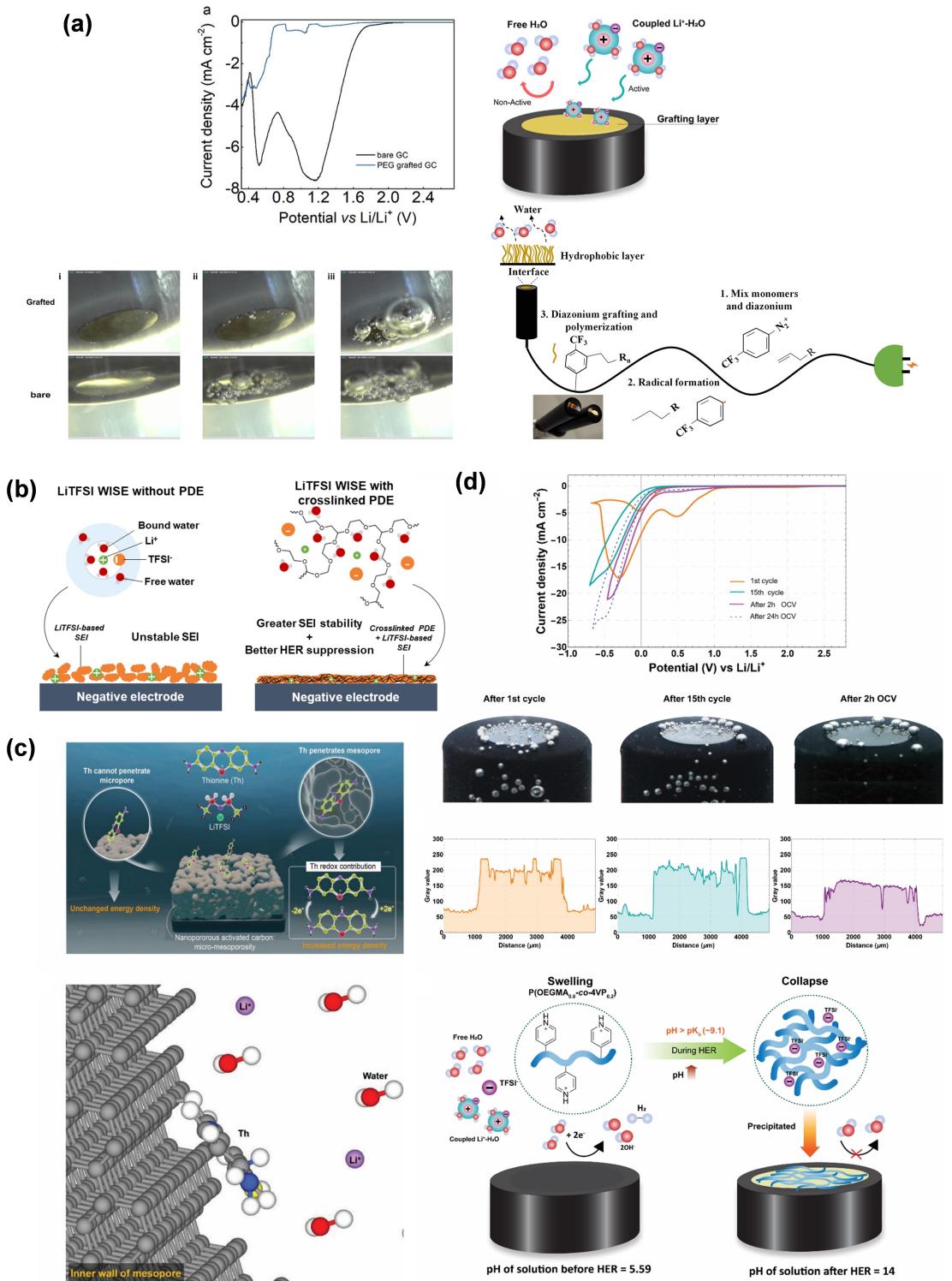


Figure 6. Strategies to stabilize the SEI layer using additives in water-in-salt electrolytes. (a) Visualization of water reduction on glassy carbon electrodes with and without diazonium-grafted layers, highlighting the suppression of free water reduction. Reproduced with permission: Copyright 2023, ACS Applied Materials & Interfaces.^[21] (b) Schematic representation of LiTFSI-based SEI layers with and without PDE polymer additives, showing improved SEI stability. Reproduced with permission: Copyright 2022, Journal of The Electrochemical Society.^[19] (c) Schematic illustration of Thionine (Th) redox species within mesoporous carbon, enhancing pseudo-capacitive contributions in WISE. Reproduced with permission: Copyright 2023, Energy Storage Materials.^[53] (d) SEI stability assessment with pH-responsive polymer additives, demonstrating improved SEI robustness over extended cycling. Reproduced with permission: Copyright 2024, ACS Materials Letters.^[49]

poly(ethylene glycol) diglycidyl ether (PDE) as a polymer additive that was added to 21 m LiTFSI WiSE to further reduce free water content. They found that novel networks with crosslinking PDE, LiTFSI, and water were constructed by taking advantage of LiTFSI's catalytic properties to initiate the epoxide ring-opening polymerization of the PDE end-groups. The cross-linked network increased the solubility of LiTFSI in water, thereby solving the issue of salt precipitation/dissolution as shown in Figure 6b. In PDE-free 21 m LiTFSI WiSEs, passivating SEI layers covering all the electrode surfaces can be produced via multiple CV cycles; however, these passivation layers were not stable following a 1 h open circuit voltage (OCV) resting period as identified in our previous work. Indeed, during the water decomposition, the ion concentration increases at the electrode surface leading to the precipitation. Water migrated towards the electrode surface, leading to an increase in local ion concentration, which eventually induced SEI dissolution. This dynamic precipitation/dissolution process is consistent with observations reported in the literature.^[17] For example, water activity near the electrode surface significantly affects SEI stability and can induce reversible dissolution and re-precipitation of salt species under cycling conditions.^[54] Furthermore, the competition between water reduction and salt precipitation at the electrode interface plays a crucial role in determining the dynamic nature of SEI formation.^[31] The above results demonstrate that water-in-salt crosslinked electrolytes based on epoxide-terminated poly(ethylene glycol) are an efficient way to avoid the precipitation/dissolution process.

In highly concentrated water-in-salt electrolytes, the movement of water molecules towards the electrode surface is a dynamic process driven by localized electrochemical reactions. The reduction of water molecules at the interface consumes free water, creating a concentration gradient that facilitates the migration of additional water from the bulk solution to the electrode. This migration not only replenishes the consumed water but also alters the local ionic environment, significantly increasing the concentration of LiTFSI near the electrode. The elevated ionic concentration can surpass the solubility limit, resulting in the precipitation of LiTFSI and the concurrent formation of a transient SEI. During cycling, this interphase demonstrates dynamic behavior, as the dissolution of LiTFSI occurs when the system returns to equilibrium at open circuit voltage, reversing the precipitation process. This reversible transition is further influenced by the competition between water reduction and ion reorganization at the interface, highlighting the interplay between electrochemical activity and solvation dynamics. Such phenomena underscore the inherent instability of SEI layers in these electrolytes, where continuous shifts in ion concentration and water activity dictate the evolution of the interphase structure. Understanding this dynamic behavior is pivotal for optimizing SEI stability and enhancing the longevity of aqueous energy storage systems.^[55–58]

Furthermore, we synthesized a pH-responsive copolymer of P(OEGMA-co-4VP) as an additive in the electrolyte.^[49] The rationale for the macromolecular design was to introduce oligo(ethylene glycol) methacrylate moieties to allow the

polymer to be solubilized in the WiSE. Indeed, poly(ethylene glycol) and its derivatives are known to be soluble in WiSE and have been extensively used in lithium batteries because they are able to inhibit dendrite growth. A pH-responsive property in polymers can be introduced either by incorporating ionizable units or cleavable bonds. 4-vinyl pyridine (4VP) moieties in the polymer, on the other hand, provide the copolymer with a pH-responsive property due to its pK_b of ~9.5. Thus, the polymer is protonated and swollen in acidic and neutral conditions whereas it is deprotonated and precipitated in basic conditions. It is anticipated that the polymer precipitates in the vicinity of the anode, where hydroxide ions are generated. Furthermore, the ligand properties of the pyridine group in the polymer favor intimate co-precipitation with LiTFSI salt (see Figure 6d).

One important reason for the capacity decay in batteries is the instability of the passivation layer at the electrode surface. Therefore, we examined the SEI layer after cyclically operating a glassy carbon working electrode in a three-electrode cell using a previously reported methodology. A resting period of 2 h and 24 h was implemented before conducting another cyclic voltammetry (CV) measurement to quantify the cathodic current associated with HER. The impact of the polymer additives on the dynamics of SEI was examined by high-resolution optical microscopy and cyclic voltammetry as shown in Figure 6d. The experimental configuration involved a scan rate of 50 mV/s and 15 cycles. During the first cycle, peaks associated with the reduction reaction of free and bound water were observed, respectively. Subsequent cycles led to the development of an increasingly thicker white layer on the electrode surface, as shown in Figure 6d. The presence of this white layer was associated with its ability to impede water activity on the electrode surface, ultimately leading to the disappearance of the reduction.^[18]

To gain further insights into the stability and structure of the white layer, we immersed it in a solution at open circuit voltage for 2 h before reapplying a potential to WiSE. Interestingly, the reduction peak did not reemerge while the white layer persisted on the electrode surface. In comparison, we showed previously that the reduction peak appears again after OCV because of the instability of the white layer on the electrode surface in the absence of polymer.^[18] Additionally, the same phenomena occurred when we added 1 wt% P(OEGMA_{0.8}-co-4VP_{0.2}) into WiSE, and the reduction peak reappeared (refer to Figure 6d, blue). This result was attributed to the insufficient amount of the polymer additive (1 wt%), which proved to be inadequate for sustaining the SEI layer over an extended period.

Redox mediators have emerged as another class of impactful additives, capable of directly participating in charge transfer processes to mitigate parasitic reactions such as hydrogen evolution.^[59] Quinones and similar organic molecules have been shown to improve the stability of WiS electrolytes by creating intermediate redox-active species that reduce overpotentials and balance the oxidative and reductive processes.^[60] For example, high-purity LiTFSI salts, combined with such mediators, not only suppress hydrogen evolution but also enhance ionic conductivity by modulating the local solvation environment.^[61] Thermodynamic studies have revealed that the

presence of these mediators shifts the hydrogen evolution reaction (HER) equilibrium potential by approximately 70 mV due to changes in proton activity, significantly enhancing the Coulombic efficiency of aqueous batteries.^[62]

In the realm of interface engineering, functional coatings and in situ-generated SEI layers have played a pivotal role in enhancing the compatibility between electrodes and WiS electrolytes.^[63] Advanced strategies, such as the deposition of LiF, Li₂O, and Li₂CO₃-based layers during electrolyte cycling, have been shown to suppress HER and oxygen evolution reaction (OER) kinetics.^[64] These protective layers reduce ionic migration barriers and enhance the mechanical integrity of the SEI. Additionally, the use of hydrophobic polymer films or fluorinated coatings on electrode surfaces has effectively minimized water decomposition at the interface, thereby reducing gas evolution and extending cycle life.^[65]

Novel electrolyte formulations, such as acidic WiS systems or mixed-salt matrices, have demonstrated synergistic benefits by combining the advantages of ionic conductivity with interfacial stability. For instance, acidic water-in-salt electrolytes composed of sulfuric acid and saturated lithium halides have doubled the energy density of MXene-based symmetric supercapacitors, achieving high capacitance retention over 10,000 cycles. The presence of proton redox in such systems contributes to enhanced charge storage mechanisms, expanding the operational voltage window to 1.1 V. X-ray diffraction (XRD) studies further confirm the structural integrity of electrodes in these systems, highlighting the compatibility of acidic environments with highly concentrated salts.^[66]

Moreover, insights from thermodynamic and kinetic analyses have elucidated the suppression of HER and OER by reducing free water activity through molecular crowding effects and high salt concentrations.^[67] For example, in concentrated LiTFSI solutions, the decreased water activity leads to a thermodynamically widened ESW, while kinetic barriers for water decomposition are elevated due to the high ionic strength and modified solvation structure.^[68] Electrochemical impedance spectroscopy (EIS) and rotating disk electrode (RDE) studies provide quantitative evidence of reduced exchange current densities for HER, demonstrating the critical role of impurities and concentration in modulating interfacial reactions.^[69]

In conclusion, the strategic integration of tailored additives into WiS electrolytes has led to transformative advancements in their performance and stability. By combining polymer networks, redox mediators, interface engineering, and advanced electrolyte formulations, these approaches have addressed fundamental limitations of aqueous systems, paving the way for the next generation of high-energy, durable, and safe energy storage technologies. These findings underscore the importance of continued innovation in additive design, emphasizing the interplay of chemistry, materials science, and electrochemical engineering in advancing practical applications.

5. Devices

After figuring out the mystery physical structure and establishing the mechanism of SEI, it would be easier to use WiS electrolytes in devices, such as supercapacitors and batteries. For aqueous supercapacitors, the working voltage window is limited to 1.6 V in a symmetric device. Lannelongue et al. prepared a 31 m WiS electrolyte using two identical porous carbon electrodes, possessing a high cell voltage of 2.4 V.^[70] This wide voltage window therefore endowed a high energy density of 30.4 Wh kg⁻¹, surpassing classic aqueous device and even comparable to redox devices. However, it is still unsatisfactory regarding capacitance/capacity, resulting from the limited available specific area surface of carbon electrodes. To raise the performance of carbon-based electrodes, some of us^[21] introduced the redox mechanism in carbon porous materials by adding the Thionine (Th) molecule in LiTFSI electrolytes. It was found that adding the Th molecule can enter mesoporous carbon but not microporous one as shown in Figure 6c. During the charging-discharging process, Th redox molecules comfortably pass through mesopores but not micropores, where they are blocked from further contribution to the system. The entered Th molecules continually interact with the inner wall of mesopores, forming an interaction between Th and the inner carbon wall (Figure 6c). The redox molecules can then dangle on the inner wall in mesopores, thereby contributing to the system with extra pseudo capacitance in the mesopores system.

Droguet et al.^[30] defined the practical conditions for WiS devices, such as current collectors, electrode materials, etc. Besides, the influences from electrolyte concentrations and cycling rate were investigated thoroughly. More importantly, the origin of performance decay was disclosed by a gas monitoring technique, largely resulting from H₂ release (namely water decomposition). The gap was detailed between WiS devices and commercial aqueous batteries, especially focusing on the working temperature, stability, and self-discharge. The decay from water decomposition is worse when the device is working at a high temperature (for example, 55 °C). Therefore, it is still questionable that if the WISE-based device is able to compete with the current commercial system before solving the issue of HER eroding.

Another application direction is pouch cells. Figure 7 shows the schematic illustration of pouch cell^[71] and different electrochemical performance.^[72–74] The application of pouch cells, as a battery configuration closer to practical systems, has garnered significant attention in recent studies utilizing WiS electrolytes.^[75] Unlike conventional coin cells used in laboratory settings, pouch cells offer more representative insights into the real-world performance of WiS electrolytes due to their larger size, flexible structure, and commercial relevance.^[76] Research has demonstrated that WiS electrolytes can effectively extend the electrochemical stability window in pouch cells, enabling higher operating voltages and improving energy density.^[77] This characteristic highlights the potential of WiS electrolytes in developing high-energy-density aqueous batteries.

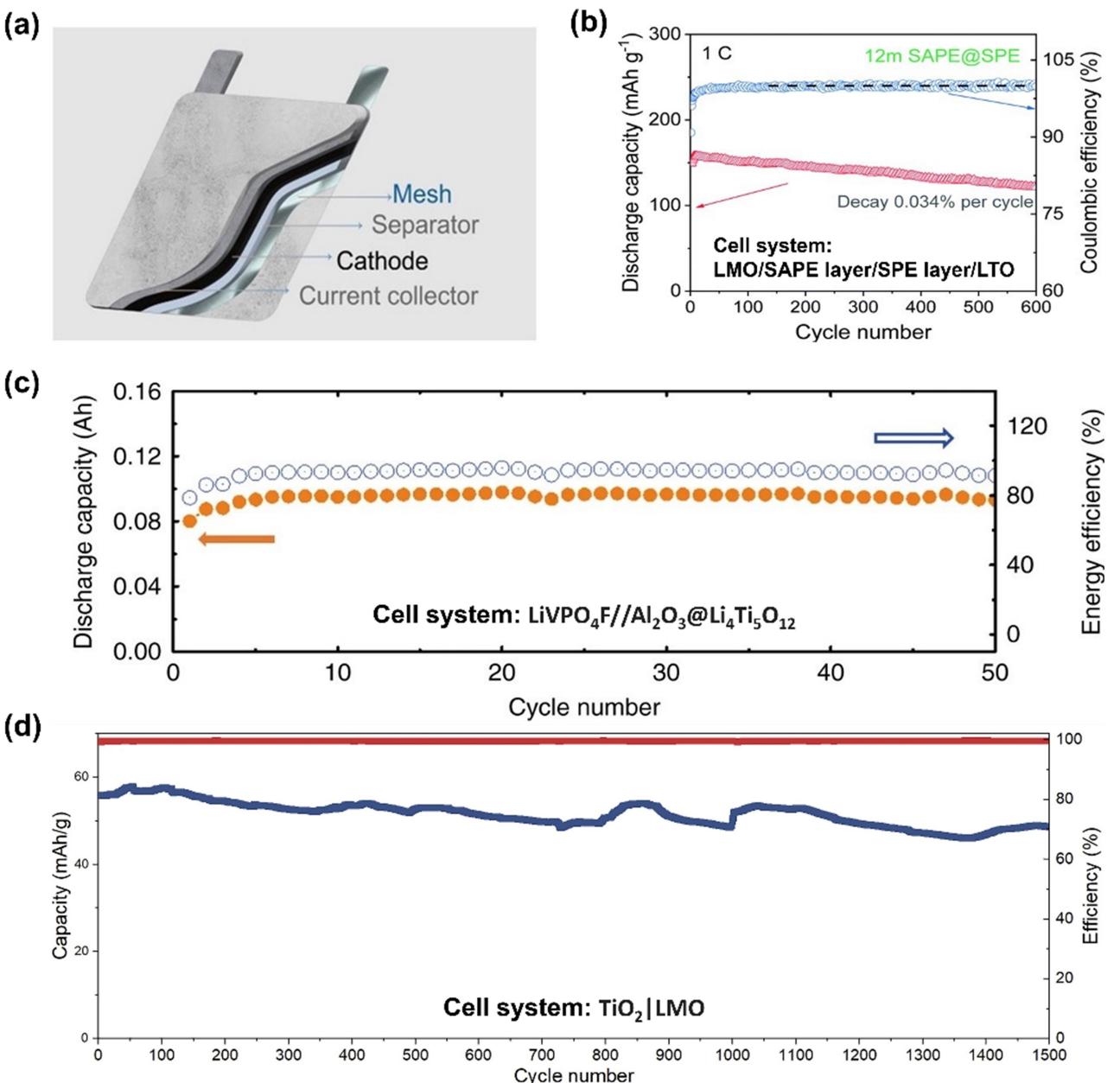


Figure 7. Pouch cell and electrochemical performance of WIS electrolytes application. (a) Schematic illustration of pouch cell. Reproduced with permission.^[71] Copyright 2024, Rare Metals. (b) Electrochemical performance of the LMO/LTO full cell in 12 m SAPE@SPE electrolyte. Reproduced with permission.^[72] Copyright 2020, Energy & Environmental Science. (c) Electrochemical performance of LiVPO₄F//Al₂O₃@Li₄Ti₅O₁₂ open pouch cell with the 63 m WIS electrolyte. Reproduced with permission.^[73] Copyright 2020, Nature Communications. (d) Electrochemical performance of TiO₂|LMO cell in the mixed Li-Cs electrolyte solution (14 m LiCl + 4 m CsCl). Reproduced with permission.^[74] Copyright 2022, Cell Reports Physical Science.

However, challenges remain in the practical implementation of WIS electrolytes in pouch cells. One of the primary issues is gas evolution caused by water decomposition, which becomes more pronounced at elevated voltages, high temperatures, or rapid charge-discharge cycling. This gas generation can lead to increased internal pressure, compromising cycling stability and safety.^[78] Additionally, the high concentration and cost of WIS electrolytes pose limitations for their scalability and commercial viability.^[79] Addressing these challenges requires innovative solutions, such as incorporating advanced additives to stabilize the electrolyte interface and mitigate side reactions, as well as

developing electrode materials optimized for compatibility with WIS electrolytes.^[80]

In recent years, the research on pouch cells using WIS electrolytes demonstrates the potential of these systems to revolutionize aqueous battery technology by improving safety, extending electrochemical stability, and enhancing longevity. A study of 12 m UV-curable WIS polymer electrolyte was employed to assemble LiMn₂O₄ | Li₄Ti₅O₁₂ pouch cells. This configuration achieved an extended electrochemical stability window of approximately 3.86 V, enabling the cells to deliver an energy density of 151 Wh/kg at 0.5 C. Over 600 cycles, the

cells exhibited a Coulombic efficiency of 99.97%, showcasing the polymer electrolyte's ability to suppress water activity and promote the formation of a robust SEI layer. These advancements significantly reduced parasitic reactions, enhancing cycling stability.^[72]

The application of 28 m and 63 m WIS electrolytes in open and sealed pouch cells shows that the 28 m electrolyte, composed of 21 m LiTFSI and 8 m LiOTf, enabled stable operation of $\text{LiMn}_2\text{O}_4 \parallel \text{Al}_2\text{O}_3@\text{LiTi}_2(\text{PO}_4)_3$ cells for over 1000 cycles with an energy density of 62.4 Wh/kg. Meanwhile, the 63 m electrolyte (42 m LiTFSI + 21 m Pyr13-TFSI) was employed in $\text{LiVPO}_4\text{F} \parallel \text{Al}_2\text{O}_3@\text{Li}_4\text{Ti}_5\text{O}_{12}$ pouch cells, achieving a higher energy density of 170 Wh/kg and maintaining 92.8% energy efficiency over 50 cycles. The super-concentrated WiS electrolytes suppressed oxygen reduction reactions and reduced water activity, ensuring exceptional thermal and cycling stability.^[73]

Another notable work investigated the use of a mixed aqueous electrolyte of 14 M LiCl and 4 M CsCl in $\text{TiO}_2 \parallel \text{LiMn}_2\text{O}_4$ pouch cells. The addition of Cs^+ ions improved stability by forming an electrical double layer on the anode interface, effectively suppressing hydrogen evolution. The cells operated stably at 2.15 V, with high efficiency and capacity retention over extended cycles. The use of a cost-effective electrolyte also highlighted the practicality of adopting mixed chloride systems for aqueous batteries.^[74]

These works illustrate that WIS electrolytes provide a significant impact for pouch cell applications. By expanding the electrochemical stability window, reducing parasitic reactions, and enhancing thermal and cycling performance, WIS electrolytes hold great promise for advancing safe and efficient energy storage systems. The use of concentrated and mixed WIS electrolytes, particularly in conjunction with advanced electrode modifications, is a critical enabler for achieving high energy density and long-term durability in aqueous lithium-ion batteries.

6. Conclusions and Perspectives

In summary, the prevailing WIS electrolytes were clarified following their merits, as well as their defects, particularly the unclear SEI formation mechanism and unblocked water reduction. Before unraveling the real story of SEI formation, we first elaborated on the physical properties of WIS electrolytes, offering insight into the reasons to grant them the possibility of substituting commercial organic electrolytes. As well, we provided a comprehensive understanding of SEI formation to disclose the main concern of unstable origins-dynamic mechanism, further directing the potential path to likely tackle the issues. Following the protocol, we offered significant strategies to address the instability issue of the interphase by using the additives as numerous reports in lithium-metal batteries, identifying our right directions to fix the issues instead of importing second or more types of salt as mainly reported in current articles. The experimental devices with WIS electrolytes disclosed the complexity of future applications, such as insufficient capacitance/capacity, unknown mechanisms (in a

porous environment), low working temperature, and self-discharge, showing the gap to catch the current commercial system. The WIS system needs to be more advanced to narrow the gap compared to the commercial one. Finally, we listed the challenges and future works that are needed to aim at. We hope that the way is not too far to have the first practical application of an aqueous energy storage device.

Water-in-salt (WIS) electrolytes offer a promising route to enabling aqueous energy storage systems due to their expanded electrochemical stability window (ESW), which surpasses that of traditional aqueous electrolytes. However, several challenges must be overcome before WIS electrolytes can achieve practical applications in commercial systems.

To further improve WIS electrolytes, future research should explore alternative approaches such as modifying salt concentration or introducing new salts or additives to enhance electrolyte performance, similar to strategies used in lithium metal batteries. One critical challenge is the development of a uniform and robust solid-electrolyte interphase (SEI) to prevent unwanted side reactions and water decomposition. Extending the ESW, particularly for graphite anodes, remains a key area of focus to resolve cathodic limitations and expand the range of electrode materials.

Cost reduction is another important consideration, as the current use of expensive salts like LiTFSI poses a barrier to widespread adoption. Identifying cheaper alternatives that maintain the performance benefits of WIS electrolytes is essential. Additionally, there is a need to find ways to reduce the salt concentration in these systems, potentially transitioning back to a salt-in-water regime while retaining the advantages of WIS electrolytes.

Further studies should delve into the mechanisms underlying SEI formation, focusing on its composition, stability, and performance under different conditions. Investigations into how lithium ions pass through the SEI while preventing electron transfer will provide insights into optimizing this layer. The influence of SEI thickness on performance, as well as the role of different components like LiF and Li_2CO_3 , should be explored to determine which are essential and which may be redundant.

In parallel, research should focus on the development of new electrode materials, as well as confinement studies in porous or layered materials, to enhance electrolyte performance. Physical studies of models, including solvation structure and basic electrolyte properties, will also play a key role in advancing the understanding of WIS electrolytes.

Finally, more studies involving optical measurements are needed to observe SEI formation and water activity in real time, providing valuable insights into the dynamics of these systems. With these advancements, WIS electrolytes may move closer to practical applications, offering a safer, more cost-effective alternative to current non-aqueous systems.

In conclusion, while WIS electrolytes hold significant promise, addressing the remaining challenges will be crucial to achieving their full potential in energy storage applications.

Author Contributions

X.W. and R.J. contributed equally to this work. J.D. and K.L. helped on formal analysis and data collection. J.Q., Y.Z. and O.F. supported on methodology, supervision and validation.

Acknowledgements

This research was supported by Vidyasirimedhi Institute of Science and Technology (VISTEC). This project was funded by National Research Council of Thailand (NRCT) (no. N42A650255), Wuhan University, and Institute Charles Gerhardt Montpellier (ICGM). Furthermore, the authors thank Ms. Siraprapha Deebansok for her helping on solving technique issue as the research assistant in VISTEC.

Conflict of Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Keywords: Water-in-Salt Electrolytes • Electrochemical Stability Window • Solid Electrolyte Interphase • Aqueous Energy Storage • Additives in Electrolytes

- [1] Z. Jia, S. Hou, J. Peng, X. Wu, W. Tang, W. Sun, S. Lv, X. Yuan, L. Liu, Y. Wu, *J. Mater. Chem. A* **2024**, *12*, 17835–17895.
- [2] X. Zheng, C. Han, C.-S. Lee, W. Yao, C. Zhi, Y. Tang, *Prog. Mater. Sci.* **2024**, *143*, 101253.
- [3] X. Chang, Z. Yang, Y. Liu, J. Chen, M. Wu, L. Li, S. Chou, Y. Qiao, *Energy Storage Mater.* **2024**, *69*, 103407.
- [4] H. Cheng, Z. Ma, P. Kumar, H. Liang, Z. Cao, H. Xie, L. Cavallo, Q. Li, J. Ming, *ACS Energy Lett.* **2024**, *9*, 1604–1616.
- [5] J. Xie, D. Lin, H. Lei, S. Wu, J. Li, W. Mai, P. Wang, G. Hong, W. Zhang, *Adv. Mater.* **2024**, *36*, 2306508.
- [6] Y. Wang, T. Ou, Y. Dong, L. Chen, Y. Huang, D. Sun, W. Qiang, X. Pei, Y. Li, Y. Tan, *Adv. Mater.* **2024**, *36*, 2311009.
- [7] S. Li, L. Huang, Q. Zhang, H. Lin, R. Wang, C. Feng, Y. Xu, Y. Jiao, L. You, J. Chen, *Int. J. Hydrogen Energy* **2024**, *49*, 103–115.
- [8] L. Suo, O. Borodin, T. Gao, M. Olguin, J. Ho, X. Fan, C. Luo, C. Wang, K. Xu, *Science* **2015**, *350*, 938–943.
- [9] M. A. González, H. Akiba, O. Borodin, G. J. Cuello, L. Hennet, S. Kohara, E. J. Maginn, L. Mangin-Thro, O. Yamamuro, Y. Zhang, D. L. Price, M.-L. Saboungi, *Phys. Chem. Chem. Phys.* **2022**, *24*, 10727–10736.
- [10] L. Suo, O. Borodin, W. Sun, X. Fan, C. Yang, F. Wang, T. Gao, Z. Ma, M. Schroeder, A. von Cresce, S. M. Russell, M. Armand, A. Angell, K. Xu, C. Wang, *Angew. Chem. Int. Ed.* **2016**, *55*, 7136–7141.
- [11] K.-Y. Yeh, M. J. Janik, J. K. Maranas, *Electrochim. Acta* **2013**, *101*, 308–325.
- [12] P. Clabaut, B. Schweitzer, A. W. Götz, C. Michel, S. N. Steinmann, *J. Chem. Theory Comput.* **2020**, *16*, 6539–6549.
- [13] J. Kim, F. Zhao, L. K. S. Bonagiri, Q. Ai, Y. Zhang, *Chem. Mater.* **2024**.
- [14] A. Wang, S. Kadam, H. Li, S. Shi, Y. Qi, *npj Comput Mater* **2018**, *4*, 15.
- [15] L. Suo, D. Oh, Y. Lin, Z. Zhuo, O. Borodin, T. Gao, F. Wang, A. Kushima, Z. Wang, H.-C. Kim, Y. Qi, W. Yang, F. Pan, J. Li, K. Xu, C. Wang, *J. Am. Chem. Soc.* **2017**, *139*, 18670–18680.
- [16] N. Dubouis, P. Lemaire, B. Mirvaux, E. Salager, M. Deschamps, A. Grimaud, *Energy Environ. Sci.* **2018**, *11*, 3491–3499.
- [17] R. Bouchal, Z. Li, C. Bongu, S. Le Vot, R. Berthelot, B. Rotenberg, F. Favier, S. A. Freunberger, M. Salanne, O. Fontaine, *Angew. Chem. Int. Ed.* **2020**, *59*, 15913–15917.
- [18] R. Jommongkol, S. Deebansok, J. Deng, Y. Zhu, R. Bouchal, O. Fontaine, *Small* **2024**, *20*, 2303945.
- [19] T. F. Burton, Y. Zhu, L. Droguet, R. Jommongkol, D. Zigah, A. Grimaud, J.-M. Tarascon, O. Fontaine, *J. Electrochem. Soc.* **2022**, *169*, 070533.
- [20] M. Maffre, X. Wang, J. Deng, S. Deebansok, Y. Zhu, F. Favier, D. Bélanger, O. Fontaine, *J. Chem. Phys.* **2023**, *159*.
- [21] Y. Zhu, L. Droguet, J. Deng, X. Wang, L. Li, Y. Dufil, M. Deschannels, R. Jommongkol, C. Pareseecharoen, A. Grimaud, J.-M. Tarascon, O. Fontaine, *ACS Appl. Mater. Interfaces* **2023**, *15*, 23899–23907.
- [22] G. M. Kontogeorgis, B. Maribo-Mogensen, K. Thomsen, *Fluid Phase Equilib.* **2018**, *462*, 130–152.
- [23] Z. Li, R. Bouchal, T. Mendez-Morales, A. L. Rollet, C. Rizzi, S. Le Vot, F. Favier, B. Rotenberg, O. Borodin, O. Fontaine, M. Salanne, *J. Phys. Chem. B* **2019**, *123*, 10514–10521.
- [24] A. Kornyshev, *Electrochim. Acta* **1981**, *26*, 1–20.
- [25] Z. Khan, D. Kumar, X. Crispin, *Adv. Mater.* **2023**, *35*, 2300369.
- [26] Y. Yokoyama, T. Fukutsuka, K. Miyazaki, T. Abe, *J. Electrochem. Soc.* **2018**, *165*, A3299.
- [27] Z. Khan, A. Martinelli, L. R. Franco, D. Kumar, A. Idström, L. Evenäs, C. M. Araujo, X. Crispin, *Chem. Mater.* **2023**, *35*, 6382–6395.
- [28] X. He, B. Yan, X. Zhang, Z. Liu, D. Bresser, J. Wang, R. Wang, X. Cao, Y. Su, H. Jia, C. P. Grey, H. Frielinghaus, D. G. Truhlar, M. Winter, J. Li, E. Paillard, *Nat. Commun.* **2018**, *9*, 5320.
- [29] M. Maffre, R. Bouchal, S. A. Freunberger, N. Lindahl, P. Johansson, F. Favier, O. Fontaine, D. Bélanger, *J. Electrochem. Soc.* **2021**, *168*, 050550.
- [30] L. Droguet, A. Grimaud, O. Fontaine, J.-M. Tarascon, *Adv. Energy Mater.* **2020**, *10*, 2002440.
- [31] H. Adenusi, G. A. Chass, S. Passerini, K. V. Tian, G. Chen, *Adv. Energy Mater.* **2023**, *13*, 2203307.
- [32] H. M. You, Y. Yoon, J. Ko, J. Back, H. Kwon, J. W. Han, K. Kim, *Langmuir* **2024**, *40*, 1961–1970.
- [33] F. Wang, J. Cheng, *Chin. J. Struct. Chem.* **2023**, *42*, 100061.
- [34] M. Bin Jassar, C. Michel, S. Abada, T. De Bruin, S. Tant, C. Nieto-Draghi, S. N. Steinmann, *Adv. Funct. Mater.* **2024**, *34*, 2313188.
- [35] X. Qin, A. Bhowmik, T. Vegge, I. E. Castelli, *ACS Appl. Mater. Interfaces* **2024**, *16*, 29347–29354.
- [36] S. Perez-Beltran, D. Kuai, P. B. Balbuena, *ACS Energy Lett.* **2024**, *9*, 5268–5278.
- [37] Y. Shi, X. Hu, Z. Zhang, Y. Sun, S. Xu, B. Zhao, Y. Xu, Y. He, J. Zhang, Y. Jiang, *Chem. Eng. J.* **2024**, *500*, 157202.
- [38] T. Wickramanayake, M. Javadipour, K. Mehran, *Batteries* **2024**, *10*, 126.
- [39] R. Li, X. Zou, T. Xu, H. Wang, B. Li, F. Jiao, F. Chen, C. Ma, *J. Energy Storage* **2024**, *88*, 111664.
- [40] K. Manmi, M. Tuchel, E. Kendrick, F. Brosa Planella, *J. Electrochem. Soc.* **2024**, *171*, 100530.
- [41] P. Lall, H. Jang, *J. Electron. Packag.* **2024**, *1*–9.
- [42] D. Chakraborty, R. Gupta, A. Gupta, *J. Electrochem. Soc.* **2024**, *171*, 080525.
- [43] A. J. Crawford, D. Choi, P. J. Balducci, V. R. Subramanian, V. V. Viswathan, *J. Power Sources* **2021**, *501*, 230032.
- [44] J. Pu, C. Zhong, J. Liu, Z. Wang, D. Chao, *Energy Environ. Sci.* **2021**, *14*, 3872–3911.
- [45] F. Ospina-Acevedo, N. Guo, P. B. Balbuena, *J. Mater. Chem. A* **2020**, *8*, 17036–17055.
- [46] J. Gao, R. He, P. Wu, K. H. Luo, *J. Energy Storage* **2025**, *106*, 114919.
- [47] Y. Xu, Y. Sun, Y. Sun, H. Fang, Y. Jiang, B. Zhao, *Surface. Interfac.* **2024**, *44*, 103768.
- [48] Q. Zhang, X. Shen, <https://www.comsol.com/paper/stress-modeling-of-solid-electrolyte-interface-on-lithium-metal-anode-77573>, 2019.
- [49] R. Jommongkol, N. Kaekratoke, Y. Zhu, T. Burton, D. Crespy, O. Fontaine, *ACS Materials Lett.* **2024**, *6*, 5402–5408.
- [50] S. A. Thomas, J. Vigneshwaran, S. Abinaya, D. N. Rajendran, S. P. Jose, J. Cherusseri, in *Supercapacitors* (Eds.: S. G. Krishnan, H. D. Pham, D. P. Dubal), Elsevier, **2024**, pp. 289–315.
- [51] J. Xu, T. Liu, X. Dong, X. Dong, W. Zhou, X. Li, D. Chao, Z. Zhou, R. Zhao, *Natl. Sci. Rev.* **2024**, nwae433.
- [52] J. Wei, P. Zhang, J. Sun, Y. Liu, F. Li, H. Xu, R. Ye, Z. Tie, L. Sun, Z. Jin, *Chem. Soc. Rev.* **2024**, *53*, 10335–10369.
- [53] Y. Zhu, G. Yang, X. Wan, J. Deng, T. F. Burton, S. Deebansok, D. Zigah, H. Zhou, Y. Guo, O. Fontaine, *Energy Storage Mater.* **2023**, *55*, 808–815.
- [54] X. Hou, R. Wang, X. He, T. P. Pollard, X. Ju, L. Du, E. Paillard, H. Frielinghaus, L. C. Barnsley, O. Borodin, K. Xu, M. Winter, J. Li, *Angew. Chem. Int. Ed.* **2021**, *60*, 22812–22817.
- [55] S. Angarita-Gomez, P. B. Balbuena, *J. Solid State Electrochem.* **2022**, *26*, 1931–1939.

- [56] 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.
- [57] J. Yue, L. Lin, L. Jiang, Q. Zhang, Y. Tong, L. Suo, Y.-s. Hu, H. Li, X. Huang, L. Chen, *Adv. Energy Mater.* **2020**, *10*, 2000665.
- [58] M. R. Krumov, S. Lang, L. Johnson, H. D. Abruña, *ACS Appl. Mater. Interfaces* **2023**, *15*, 47692–47703.
- [59] Y.-Y. Hsieh, H.-Y. Tuan, *Energy Storage Mater.* **2024**, *68*, 103361.
- [60] N. Kim, A. Aguda, C. Kim, X. Su, *ACS Energy Lett.* **2024**, *9*, 3887–3912.
- [61] J. Gu, Z. Li, B. Hong, M. Wang, Z. Zhang, Y. Lai, J. Li, L. Zhang, *ACS Appl. Mater. Interfaces* **2024**, *16*, 61934–61945.
- [62] V. Muralidharan, S. Jayasubramanyan, H.-W. Lee, *EES. Catal.* **2024**, *2*, 522–544.
- [63] B. B. Upreti, N. Kamboj, R. S. Dey, *Small* **2024**, *n/a*, 2408138.
- [64] S. Wan, W. Ma, Y. Wang, Y. Xiao, S. Chen, *Adv. Mater.* **2024**, *36*, 2311912.
- [65] D. Lei, W. Shang, L. Cheng, Poonam, W. Kaiser, P. Banerjee, S. Tu, O. Henrotte, J. Zhang, A. Gagliardi, J. Jinschek, E. Cortés, P. Müller-Buschbaum, A. S. Bandarenka, M. Z. Hussain, R. A. Fischer, *Advanced Energy Materials* **2024**, *n/a*, 2403030.
- [66] C. Yuan, C. Chen, Z. Yang, J. Cheng, J. Weng, S. Tan, R. Hou, T. Cao, Z. Tang, W. Chen, B. Xu, X. Wang, J. Tang, *ACS Appl. Mater. Interfaces* **2024**, *16*, 55189–55197.
- [67] S. Sayah, A. Ghosh, M. Baazizi, R. Amine, M. Dahbi, Y. Amine, F. Ghamouss, K. Amine, *Nano Energy* **2022**, *98*, 107336.
- [68] Y. Zhigalenok, S. Abdumomyn, M. Levi, N. Shpigel, M. Ryabicheva, M. Lepikhin, A. Galeysheva, F. Malchik, *J. Mater. Chem. A* **2024**, *12*, 33855–33869.
- [69] Y. Zhao, X. Hu, G. D. Stucky, S. W. Boettcher, *J. Am. Chem. Soc.* **2024**, *146*, 3438–3448.
- [70] P. Lannelongue, R. Bouchal, E. Mourad, C. Bodin, M. Olarte, S. le Vot, F. Favier, O. Fontaine, *J. Electrochem. Soc.* **2018**, *165*, A657.
- [71] K.-X. Liu, R. Tan, Z. Zheng, R.-R. Zhao, B. Ülgüt, X.-P. Ai, J.-F. Qian, *Rare Met.* **2025**, *44*, 81–94.
- [72] J. Zhang, C. Cui, P.-F. Wang, Q. Li, L. Chen, F. Han, T. Jin, S. Liu, H. Choudhary, S. R. Raghavan, N. Eidson, A. von Cresce, L. Ma, J. Uddin, D. Addison, C. Yang, C. Wang, *Energy Environ. Sci.* **2020**, *13*, 2878–2887.
- [73] L. Chen, L. Cao, X. Ji, S. Hou, Q. Li, J. Chen, C. Yang, N. Eidson, C. Wang, *Nat. Commun.* **2020**, *11*, 2638.
- [74] M. Turgeman, V. Wineman-Fisher, F. Malchik, A. Saha, G. Bergman, B. Gavriel, T. R. Penki, A. Nimkar, V. Baranauskaite, H. Aviv, M. D. Levi, M. Noked, D. T. Major, N. Shpigel, D. Aurbach, *Cell Rep Phys Sci* **2022**, *3*, 100688.
- [75] Y. Jie, C. Tang, Y. Xu, Y. Guo, W. Li, Y. Chen, H. Jia, J. Zhang, M. Yang, R. Cao, Y. Lu, J. Cho, S. Jiao, *Angew. Chem. Int. Ed.* **2024**, *63*, e202307802.
- [76] L. Shi, S.-M. Bak, Z. Shadike, C. Wang, C. Niu, P. Northrup, H. Lee, A. Y. Baranovskiy, C. S. Anderson, J. Qin, S. Feng, X. Ren, D. Liu, X.-Q. Yang, F. Gao, D. Lu, J. Xiao, J. Liu, *Energy Environ. Sci.* **2020**, *13*, 3620–3632.
- [77] D. Peng, R. Sun, J. Han, T. Zhao, R. Tian, A. Zhang, Y. Zhang, Y. You, *ACS Energy Lett.* **2024**, 6215–6224.
- [78] F. Schomburg, B. Heidrich, S. Wennemar, R. Drees, T. Roth, M. Kurrat, H. Heimes, A. Jossen, M. Winter, J. Y. Cheong, F. Röder, *Energy Environ. Sci.* **2024**, *17*, 2686–2733.
- [79] D. Xiao, L. Zhang, Z. Li, H. Dou, X. Zhang, *Energy Storage Mater.* **2022**, *44*, 10–28.
- [80] Y. Liu, L. Hong, R. Jiang, Y. Wang, S. V. Patel, X. Feng, H. Xiang, *ACS Appl. Mater. Interfaces* **2021**, *13*, 57430–57441.

Manuscript received: November 11, 2024

Revised manuscript received: January 4, 2025

Accepted manuscript online: January 27, 2025

Version of record online: February 5, 2025