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Aqueous Solid Electrolyte Interphases in Water-in-Salt Electrolytes and Beyond

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The key issue with advancing aqueous batteries is the narrow electrochemical stability window (ESW) of the electrolyte; past efforts have focused on extending the water decomposition limits, principally using the highly concentrated water-in-salt electrolytes (WiSEs) with limited "free" water. However, the high salt content largely complicates practicability and long-term performance, necessitating alternative strategies to enhance ESWs without relying entirely on huge amounts of salt. Forming stable, functional interphases on electrode surfaces can help realize this vision by masking the electrode from water, thereby inducing high overpotentials for hydrolysis. Solid electrolyte interphase (SEI) formation on the negative electrode has been observed to be particularly tricky to navigate through, due to the faster kinetics of water reduction or the hydrogen evolution reaction (HER), something popularly termed the "cathodic challenge." We aim, through this concept review, to deliver a comprehensive overview of the mechanistic and electrochemical understandings that have been recognized over the years about the SEI formation in aqueous electrolytes. A broad analysis is drawn ranging from diluted to highly concentrated systems (WiSEs), while highlighting current challenges and limitations. The discussion is kept limited to Li-based batteries, which however, in most cases, could also be extrapolated to Na and K-based ones.

1. Introduction

The high costs and safety risks associated with the currently dominant organic electrolyte-based batteries have sparked renewed interest in aqueous chemistries among the battery community. Despite the numerous advantages that aqueous electrolytes offer—such as better safety, ease of storage and transport, and economic and environmental affability—their performance has been hugely limited by the narrow electrochemical stability window (ESW) which in turn reflect poor energy densities. They are, in theory, limited to operate below 1.23 V to prevent the water from decomposing to hydrogen (H_2) and OH^- on the negative side (hydrogen evolution reaction, HER) and to oxygen (O_2) and H^+ on the positive side (oxygen evolution reaction, OER). The hydrogen and oxygen evolution potentials, otherwise referred to as the cathodic and anodic "stability limits" respectively, are pH dependent.[1,2] However, the thermodynamic equilibrium maintains the gap between the stability limits constant at 1.23, as is evident from the Pourbaix diagram of water (**Figure 1**a).[3] This restricts the selection of suitable, high-energy electrochemical couples.

Most of the ESW enhancing strategies proposed so far were centered on limiting the amount of "free" water available to be adsorbed to electrode surfaces, thus inducing high kinetic overpotentials for hydrolysis. Some worth mentioning are: a) using high salt concentrations to introduce strong ionic interactions between water molecules, cations, and anions, thereby interrupting the hydrogen bonding of water (water-in-salt electrolytes, WiSEs); b) incorporating a highly water-soluble salt based on the same anion as the main salt to allow higher electrolyte concentrations (water-in-bi-salt electrolytes, WiBSs); and c) modifying the local chemical environment of "free" water through inorganic/organic cosolvents (bi-solvent and multisolvent electrolytes). Although proven successful, these strategies rely predominantly on additional salts and solvents, with many of them unfortunately being not the most environment-friendly.

Protecting electrode surfaces via interphases involves a redimensioning of the same concept (of making hydrolysis kinetically less viable) while not depending on high amounts of salts and cosolvents. Stable and functional solid electrolyte interphases (SEIs) on anodes and cathode electrolyte interphases (CEIs) on cathodes help suppress water decomposition by avoiding long-range electron conduction between electrode and water, while still allowing ion transport and so the cell reactions. To successfully apply this concept, a detailed understanding of aqueous interphase formation mechanisms is required, including differences with those formed in conventional organic electrolytes, and how chemical and electronic environments in different aqueous systems would influence the same. Considering that HER is typically the limiting parasitic reaction rather than OER in most aqueous media (since the kinetics of OER is relatively more

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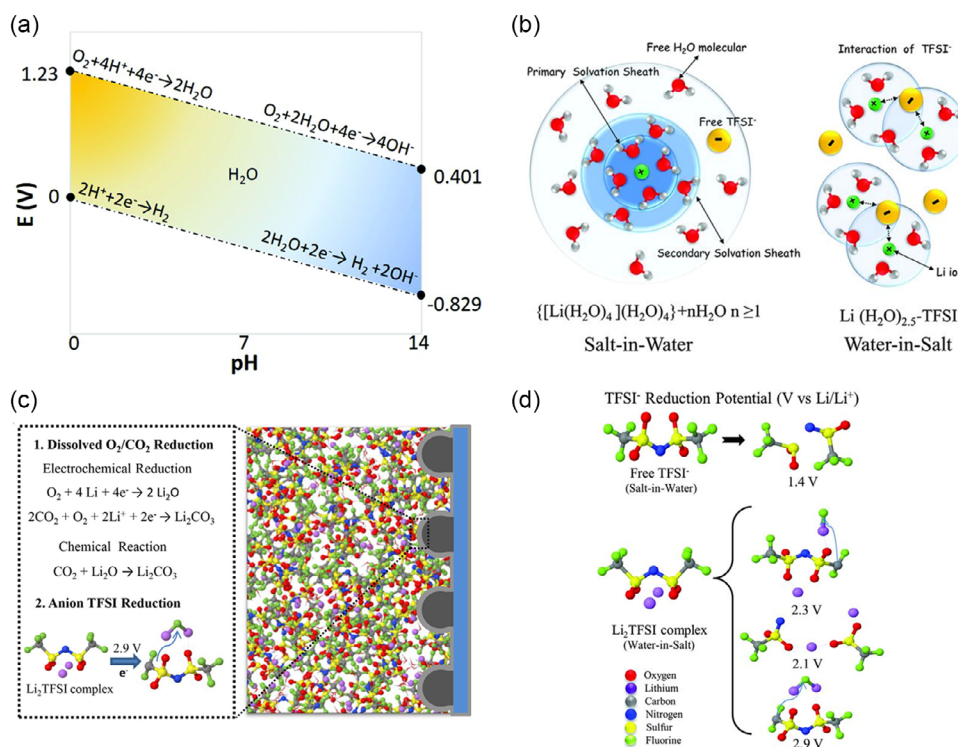
Figure 1. a) Pourbaix diagram of water, adapted with permission.[3] Copyright 2021, RSC. b) Altered solvation sheath of Li$^+$ in WiSEs, adapted with permission.[4] Copyright 2015, AAAS. c) Anion-derived SEI formation pathway in WiSEs, adapted with permission.[7] Copyright 2017, ACS. d) Upshifted TFSI$^-$ reduction potential in WiSEs, adapted with permission.[4] Copyright 2015, AAAS.

sluggish than HER due to multiple intermediate steps involved), the discussion in this review will be limited to SEI and SEI-like interphases in aqueous batteries' negative electrodes. Additionally, Li batteries will be preferentially discussed for the sake of brevity and literature availability, though, in most cases, similar concepts apply to Na and K-based systems.

2. SEI Formation in Aqueous Electrolytes

2.1. Mechanistic Role of Water Decomposition

The SEI formation mechanism in organic electrolytes is close to well-established already, where it's understood that reductions of both the electrolyte salt as well as the solvent contribute to the formation of an SEI. However, in aqueous electrolytes, the solvent decomposition cannot directly contribute towards the growth of a solid interphase. That said, studies have shown that water hydrolysis is not purely parasitic either.

Suo et al. in 2015, reported the first ever evidence of an "aqueous SEI" formed by a WiSE containing 21 m lithium bis(trifluoromethane sulfonyl)imide (LiTFSI), which restructured the Li$^+$ primary solvation sheath, creating an anion-containing shell due to insufficient water available to fully solvate Li$^+$ (Figure 1b).[4] Since the water molecules getting reduced during HER are by and large those solvating Li$^+$,[5] such an altered water-scarce solvation sheath lowers the amount of "reducible" water molecules. Furthermore, from a thermodynamic point of view, high salt concentrations reduce water activity and increase Li$^+$ activity, modulating redox processes to positive potentials following the Nernst equation. Although it should be noted here that the thermodynamic factors affect the slow OER more than the fast HER.[6] The HER was found to diminish with increasing LiTFSI concentrations (1 to 21 m), with an SEI forming at 21 m. The interphase was dense in LiF (dominant), Li$_2$CO$_3$, and Li$_2$O, and possessed a layered structure: LiF and Li$_2$O in the inner layers and Li$_2$CO$_3$ in the outer. The SEI's efficacy was demonstrated in a full lithium-ion battery, achieving a voltage of 2.3 V and nearly 100% Coulombic efficiency (CE) at both low and high C-rates.

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In a follow-up investigation on the SEI's formation mechanism,[7] it was further suggested that whether or not an SEI is formed in an aqueous electrolyte—and if yes, whether it will be stable enough—depends on three competitive reductive pathways: 1) reduction of the salt, 2) reduction of dissolved gases (O_2 and CO_2), and 3) decomposition of water (Figure 1c). In the case of a LiTFSI WiSE, the strong ionic aggregation upshifts the anion's reduction potential (Figure 1d) well above that of water reduction. Consequently, the anion reduction leads to the formation of halides (LiF) and the dissolved gases (CO_2 and O_2) of carbonates and oxides (Li_2CO_3 and Li_2O). The SEI's chemical composition was also found to be dependent on the relative potentials, with the Li_2CO_3 formation subsequent to that of LiF and Li_2O, consistent with its layered structure.

Clearly, in a diluted "salt-in-water" electrolyte—where "free" (weakly coordinated) water molecules outnumber cations and anions, and the anion's reduction potential lies below that of HER—it is probable that the water decomposition becomes limiting and ends up blocking any possibilities of forming a solid interphase, either by preventing anion reduction and/or by dissolving its products. In contrast, in a modified ionic environment such as that in a WiSE, water decomposition plays a more complex role. Further studies following Suo's work largely focused on tracing how anion reduction occurs in the presence of such strong ion pairs, and whether water influences it. Interestingly, Dubouis et al. found that the HER could in fact catalyze anion decomposition, thereby indirectly facilitating SEI formation.[8] The strong proximity of the salt anion (TFSI⁻) to the high amount of OH⁻ formed via water reduction $\{H_2O + e^- \rightarrow 1/2H_2 + OH^-\}$ and to the LiOH formed via reaction of the formed hydroxides with the cations $\{Li^+ + OH^- \rightarrow LiOH\}$ enables a nucleophilic attack by the OH⁻ at the electrophilic sulfur/carbon atom of TFSI⁻ (**Figure 2**). Li⁺ further reacts with the products of this attack (F⁻ and other organic compounds such as trifluoromethanol, CF_3OH)[9] and precipitates due to common cation effect, building the SEI. They also observed that TFSI⁻ reactivity is much higher when K⁺ (weak Lewis acid, low influence on OH⁻ nucleophilicity) is the carrier ion as opposed to Li⁺ (strong Lewis acid, diminishes OH⁻ nucleophilicity). Together, this could be translated to the hydroxide-anion proximity and the nucleophilic attack as having a huge influence in enabling an SEI in a WiSE.

2.2. Increasing the Chances of SEI Formation

By deciphering the SEI formation pathways, one could put the possible interactions between various electrolyte components to scrutiny in order to manipulate and optimize the aqueous interphasial chemistry.

2.2.1. Co-solvents, Co-Salts, and Additives

Co-solvents

Increasing electrolyte viscosity and/or tuning the cation's solvation structure through co-solvents may slow down the HER kinetically by affecting the ion diffusion behavior (reduced ion migration speed), allowing more room for salt decomposition. For instance, non-aqueous co-solvents like dimethyl carbonate (DMC)[10] and sulfolane[11] have been found to form/stabilize SEIs in LiTFSI-based aqueous electrolytes by modifying the cation solvation chemistry. DMC forms ionic solvates with cations (Li^+_2(DMC), **Figure 3**a) which are easily reduced to products with low water solubility, introducing stable secondary ingredients such as alkyl carbonates to the SEI.[10] Similarly, sulfolane, with its strong solvating ability, facilitates a water-scarce primary solvation sheath for Li⁺ (similar to that in WiSEs), by competing with the water molecules to coordinate with Li⁺.[11] The unique solvation structure as-formed, by replacing solvated water with the "electrochemically inert" sulfolane (Figure 3b), reduced the overall water fraction, which in turn reduced the solubility of anion reduction products, thereby stabilizing the SEI. These hybrid "bisolvent-in-salt" (BSiS) systems exhibited enhanced ESWs as well as functional SEIs at relatively low salt concentrations, owing to the organic co-solvents also acting as diluents.

A slightly different perspective involves using "crowding agents" to disrupt water's hydrogen-bonding network, effectively lowering water activity and enabling broader ESWs and SEIs at low salt concentrations. Drawing inspiration from the crowded intracellular environments within living cells, Y.-C. Lu and team utilized a water-miscible *liquid* polymer—poly(ethylene glycol) (PEG)—to introduce "molecular crowding" in a low-concentration (2 m) LiTFSI electrolyte.[12] Water–PEG interactions were found to strengthen the H—O covalent bonds in water, an effect attributed to PEG's alkyl groups increasing the negative charge density around its oxygen atoms, thereby reducing their electron-withdrawing tendency. This led to a substantially improved electrochemical stability of the electrolyte, while keeping it less toxic and non-inflammable. In later studies, the expanded ESW was further shown to support the formation of a LiF-rich SEI.[13]

Co-Salts

Moreover, incorporating co-salts that could potentially add to the solubility of the main salt (or vice-versa) enables higher electrolyte concentrations and prevents the main salt's precipitation/crystallization from competing with SEI formation. Suo et al.
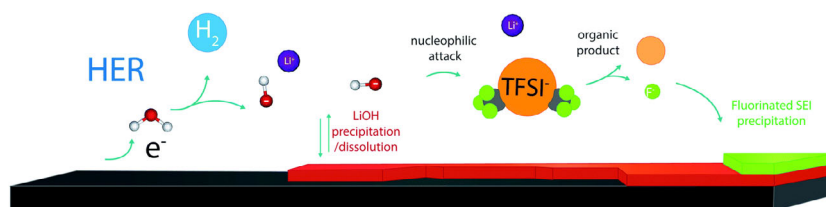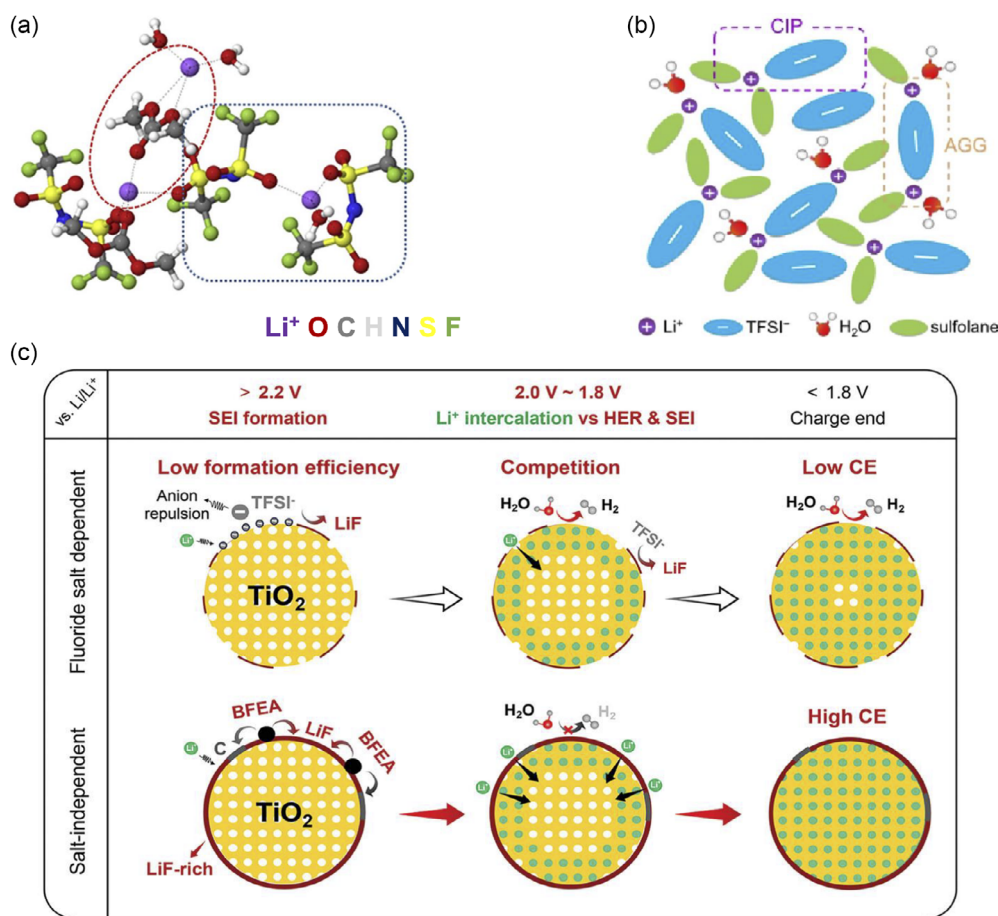
Figure 2. HER-catalyzed anion reduction in WiSEs. Reproduced with permission.[8] Copyright 2018, RSC.

Figure 3. a) Liquid structure of LiTFSI/H_2O+DMC BSiS, adapted with permission.[10] Copyright 2018, Cell Press. b) Solvation structure of LiTFSI/H_2O+sulfolane BSiS, adapted with permission.[11] Copyright 2022, ACS. c) Comparison between BFEA- and anion-dependent SEI formation, adapted with permission.[15] Copyright 2024, Wiley.

incorporated a second Li salt lithium trifluoromethanesulfonate (LiOTf) into the LiTFSI WiSE, creating a "water-in-bisalt" electrolyte with an ultra-high concentration of 28 m.[14] The high Li^+ content combined with reductions of both the anions (TFSI$^-$ and OTf$^-$) suppressed the water activity and formed a denser SEI than the one formed in the parent WiSE. That said, contrarily, this approach may not be ideal in terms of keeping costs and toxicity in check, whilst the added viscosity further complicating the electrolyte's storage and long-term operation. A recent study by Liu et al. addresses this issue and proposed using an electrode additive (bifunctional fluorocarbon electrode additive, BFEA) instead of an electrolyte additive, which gets "pre-reduced" instead of anions to form a salt-independent SEI (Figure 3c).[15] By choosing an electrode additive with a reduction potential higher than that of both anode lithiation and HER, SEI formation bypasses the traditional anion-derived pathway, eliminating its reliance on electrolyte salt types as well as concentrations.

Additives

Additives offer an effective way to facilitate SEI formation, without the practical hassles typically encountered when using additional salts or solvents. Zhu et al. recently employed aminopolycarboxylic

EDTA **(ethylenediaminetetraacetic acid)** as a "multi-functional" additive, acting both as a solvation modulator as well as an SEI promoter in high-concentration LiTFSI electrolytes.[16] Interestingly, they noticed that EDTA has low solubility at low concentrations (7 m) and much higher solubility at high concentrations (21 m). This was attributed to EDTA's chelating behavior, where its solubility is heavily influenced by the surrounding ion number density, necessitating a sufficient supply of Li^+ ions to efficiently dissolve EDTA. The additive was further found to alter the solvation structure, establishing a unique EDTA-Li^+-(H_2O/TFSI$^-$) arrangement, with Li^+ serving as a bridge connecting EDTA and TFSI$^-$-H_2O. Additionally, EDTA was found to get reduced while also downshifting the (bound) water reduction potential, thereby contributing to the formation of a fluorine–oxygen–sulfur-based SEI.

In addition to the aforementioned, we also suggest leveraging Dubouis' findings—on anion reduction being mediated by hydrolysis—to identify suitable additives capable of triggering SEI formation.[8] Tuning the anion electrophilicity, for instance using halogen substitutions, may accelerate the OH$^-$ nucleophilic attack and henceforth the anion reduction. Above all, adding such suitably substituted salts (based on the same anion as the main salt) as additives can help maintain the system near to nontoxic. The major preconditions to be met while selecting

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such an electrophilic additive as an SEI-inducing precursor are: 1) The anion counterpart of it should get reduced easily in alkaline environments, meaning the anion should have charge localized electrophilic centers, rendering it a high polarity that can attract the OH^-. 2) Its reduction potential should lie well above the reductive stability limit of water, ensuring minimal interference from the highly corrosive H_2 evolution.

2.2.2. Dissolved Gas Saturation

The halide component of aqueous SEIs (LiF for Li-based WiSEs) is conditional to the presence of a fluorinated salt, while the other components (Li_2O, Li_2CO_3) are expected to originate from the dissolved gases (O_2, CO_2) in the electrolyte. Therefore, saturating the electrolyte with suitable gases could be another effective approach to induce SEI formation in aqueous electrolytes. As with anions, the reduction potentials of most dissolved gases are also upshifted at high salt concentrations, allowing their reduction products to deposit as stable solids.[7] The same is unlikely in diluted electrolytes, where the gas reduction products would quickly hydrolyze and dissolve in water.[7]

A notable example of such gas-induced SEI formation was reported by Yue et al., who discovered that $TFSI^-$ ions have a strong affinity for CO_2, which is not easily removed by simple gas purging.[17] A constant CO_2 pumping in the electrolyte was found to accelerate the anion reduction besides stabilizing the SEI components (**Figure 4**a–c). They found, using FTIR, NMR, and MD simulations, that a concentration-dependent complexation between CO_2 and $TFSI^-$ affects the charge density around the anion's F center and that the interaction peaked at a TFSI concentration of 5 m. Hence, this strategy even allowed them to stay within the "salt-in-water" (diluted) regime, by significantly lowering the cross-dependence between SEI characteristics and the electrolyte's bulk properties (like ionic conductivity and concentration). It is, however, important to acknowledge that CO_2 may not have such strong bonding capabilities with all kinds of anions; demanding individual investigations of gas-anion interactions for different anion chemistries.

2.2.3. Hydrophobic Anode Coatings

Hydrophobic, water-immiscible molecules pre-coated on the anode can act both as means of mitigating the HER (by phase-separating the anode from the electrolyte before it decomposes) and as an artificial SEI precursor. Yang et al. could reach an enormous ESW of 4.0 V for a WiBS and even employ metallic Li and graphite as anodes, by applying an "inhomogeneous additive" (a mixture of LiTFSI and a highly fluorinated ether,
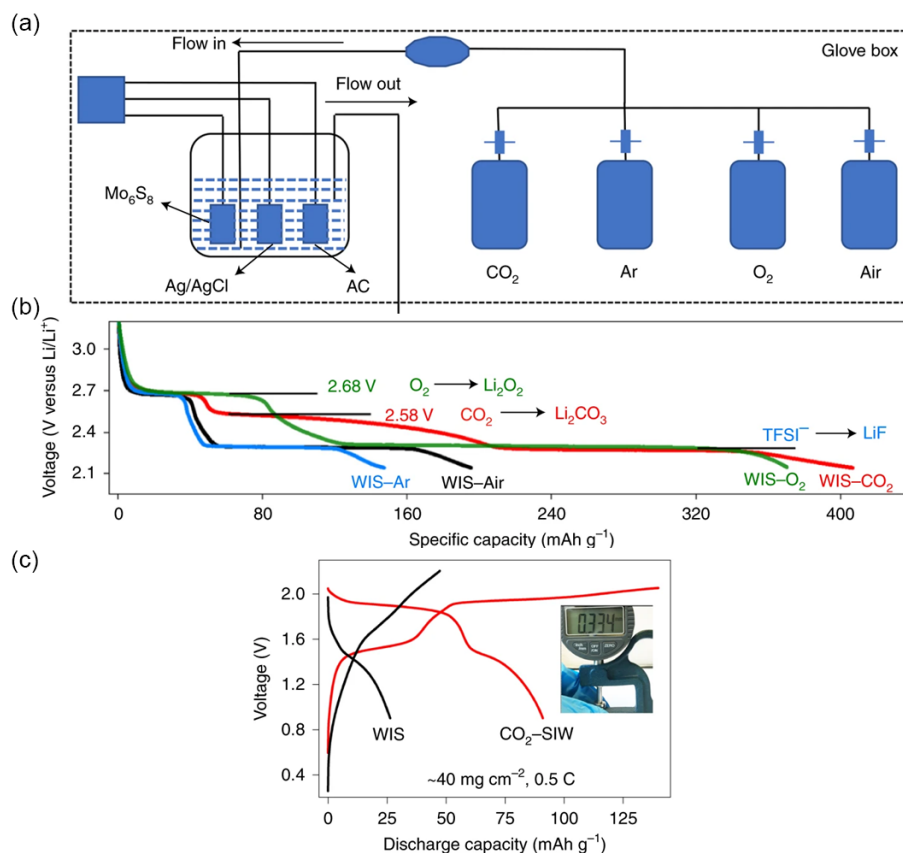
Figure 4. a) Set-up for quantitative analysis of TFSI-CO_2 association. b,c) Influence of gas saturation on SEI formation in WiSEs [b: half-cell, c: full cell], all adapted with permission.[17] Copyright 2021, Nature.

HFE) as a precursor coating on the anode surface. The additive in itself undergoes a reductive decomposition upon lithiation of the anode to form a fluorinated SEI.[18]

Previous research using MD simulations suggests that the severity of HER on the anode surface is heavily influenced by the spatial distribution of water molecules and salt anions at the inner–Helmholtz layer.[18–20] At high potentials (low negative polarization), the inner Helmholtz region is dominated by salt anions, preventing direct contact between the electrode surface and water, and favouring SEI formation. However, towards low potentials (high negative polarization), the anions experience increased repulsion from the now negatively charged electrode surface, leading to preferential adsorption of water molecules, thereby triggering HER. Since a hydrophobic coating can effectively exclude water molecules from the electrode regardless of its polarization state, this approach is particularly beneficial for accommodating energy-dense anode materials with very low insertion potentials (<0.5 V versus Li), hugely boosting the resulting energy density (**Figure 5**a,b).

The as-formed SEI was also found to be amorphous, in contrast to the crystalline ones typically observed in WiSEs/WiBSs and in close resemblance to those formed in non-aqueous electrolytes. Similar attempts were also made by Zhu et al. who explored modifying the electrode surface via artificial diazonium grafting (Figure 5c,d).[21] However, they also commented that while this method of electrode protection via polymer grafting may help in eliminating the "free" water reaching the electrode surface, it can only downshift the decomposition potentials of "bound" water (those coupled with Li$^+$).

3. Challenges and Practical Perspective

3.1. SEI Stability and Self-Discharge

Regardless of the various strategies that have been hypothesized and successfully tested in the past to foster the formation of an aqueous SEI, improving its long-term stability is still a work in progress. As could be imagined, water being a powerful solvent, the SEI components derived via reduction of highly water-soluble salts could as well be water soluble and hence would not realistically be stable enough to hold the SEI intact. Nor does it help that the SEI formation in a WiSE is much slower than in organic electrolytes, meaning, that it could take 10–20 cycles after the initial charging until the rate of SEI formation surpasses the rate of its dissolution.[7,14,15,20,21] Combined, these lead to both compromised mechanical integrity as well as chemical dissolution. This was demonstrated by Suo et al. as a continual water decomposition observed in the first several cycles, together with an increase in the K-edge sXAS signal intensities of some of the SEI components (Li$_2$CO$_3$, Li$_2$O).[7] For the same reasons, many of the studies reported so far have identified high rates of self-discharge after the formation step (representative reaction for self-discharge: $2\text{Li}_x(\text{Host}) + 2x\text{H}_2\text{O} \rightarrow 2\text{Host} + 2x\text{LiOH} + \text{H}_2$).[7,14,22,23]

A well-thought-out work by Droguet and colleagues marks the same, by using operando gas monitoring, cyclic voltammetry (CV), and self-discharge studies to evaluate the growth and stability of WiSE SEIs as a function of varying temperatures and concentrations (5 M, 10 M, 20 M).[22] They reinstated that aqueous SEIs are incapable of fully protecting the electrode surface from water decomposition, both during cycling as well as storage.
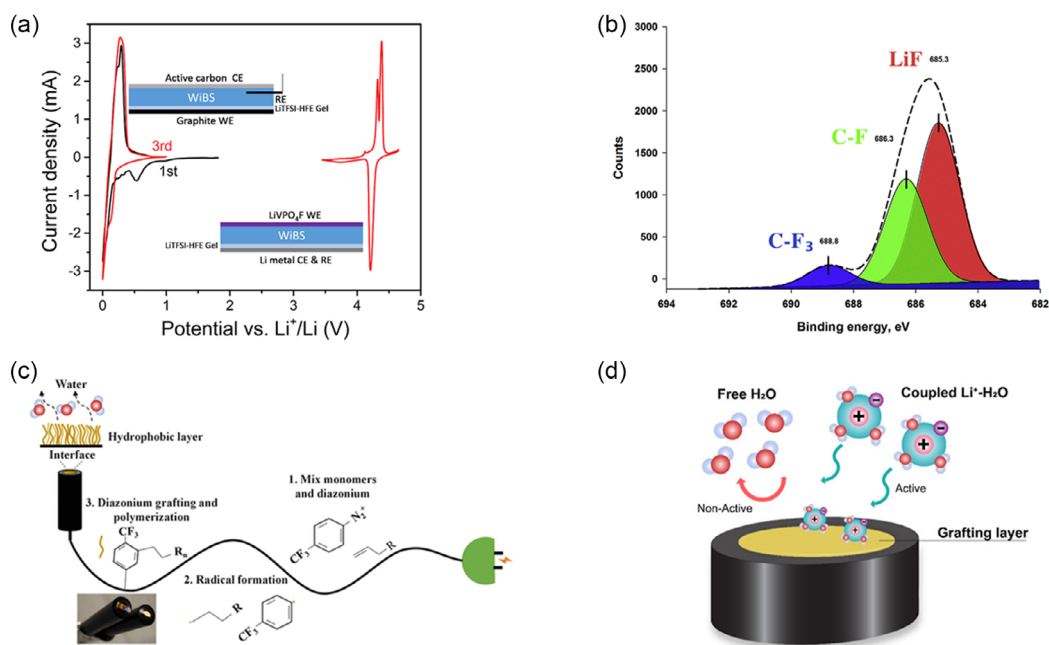

Figure 5. Hydrophobic anode coatings as artificial SEI precursors: a) Electrochemical performance of graphite anodes with hydrophobic coatings (LiTFSI-HFE gel) in WiSEs; b) F1s spectra of SEI formed by the hydrophobic coating (LiTFSI-HFE gel) in WiSEs, both adapted with permission.[18] Copyright 2017, Cell Press. c,d) diazonium grafting method, adapted with permission.[21] Copyright 2023, ACS.

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It was observed that the HER does not stop occurring after the formation step and that it persists through cycling even at the highest concentration (20 M LiTFSI), as seen by a direct increase in the cell pressure and H_2 production in online electrochemical mass spectrometry (OEMS) and pressure cells (**Figure 6**a,b). Even though the cycling performance improved at higher salt concentrations, the cycling rates demonstrated a bigger role, with faster rates ($\geq$1C) delivering higher Coulombic efficiencies. However, interestingly, faster rates were not beneficial for maintaining the integrity of the SEI (and hence for long-term storage), since the time taken for self-discharge was found to be proportional to the time taken to form the SEI. The higher the time spent building the SEI (low C-rates during charge), the higher the time it was required for a full discharge (end of delithiation plateau) during rest (Figure 6c,d). This evidently highlights the importance of SEI formation protocols, and of ensuring realistic cycling conditions, as discussed shortly below.

An SEI stability test based on mimicking its formation on an inert glassy carbon electrode further revealed the dynamic behavior of aqueous SEIs—the reduction wave (commonly attributed to HER[8,24]) diminished with cycling due to SEI formation; however, it reappeared after a 1 h hold at open-circuit voltage (OCV) indicating that the formed SEI had dissolved (Figure 6e,f). Additionally, the SEI stability worsens with increasing temperature due to enhanced HER kinetics (downshifted onsets) and accelerated dissolution. In consequence, there is a continuous consumption of water that eventually dries out the cell.

What's more, as the water keeps getting depleted during the formation cycles, the relative local ion concentration of the salt keeps increasing, potentially leading to its precipitation,[24] the same of which could also be contributing to the SEI layer as was observed in real time by Bouchal et al. using operando high-resolution optical microscopy.[25] If the SEI stability is disrupted, such "water consumption induced salt precipitation" gets reversed with the salt dissolving back into the electrolyte, evidently compromising a decent long-term operation of the cell (**Figure 7**a,b). Nevertheless, we believe one way to make full use of this anomaly (where the cell drying indirectly helps in protecting the electrode) would be to use a co-salt with a solubility limit lower than that of the main salt and pushing it to precipitate
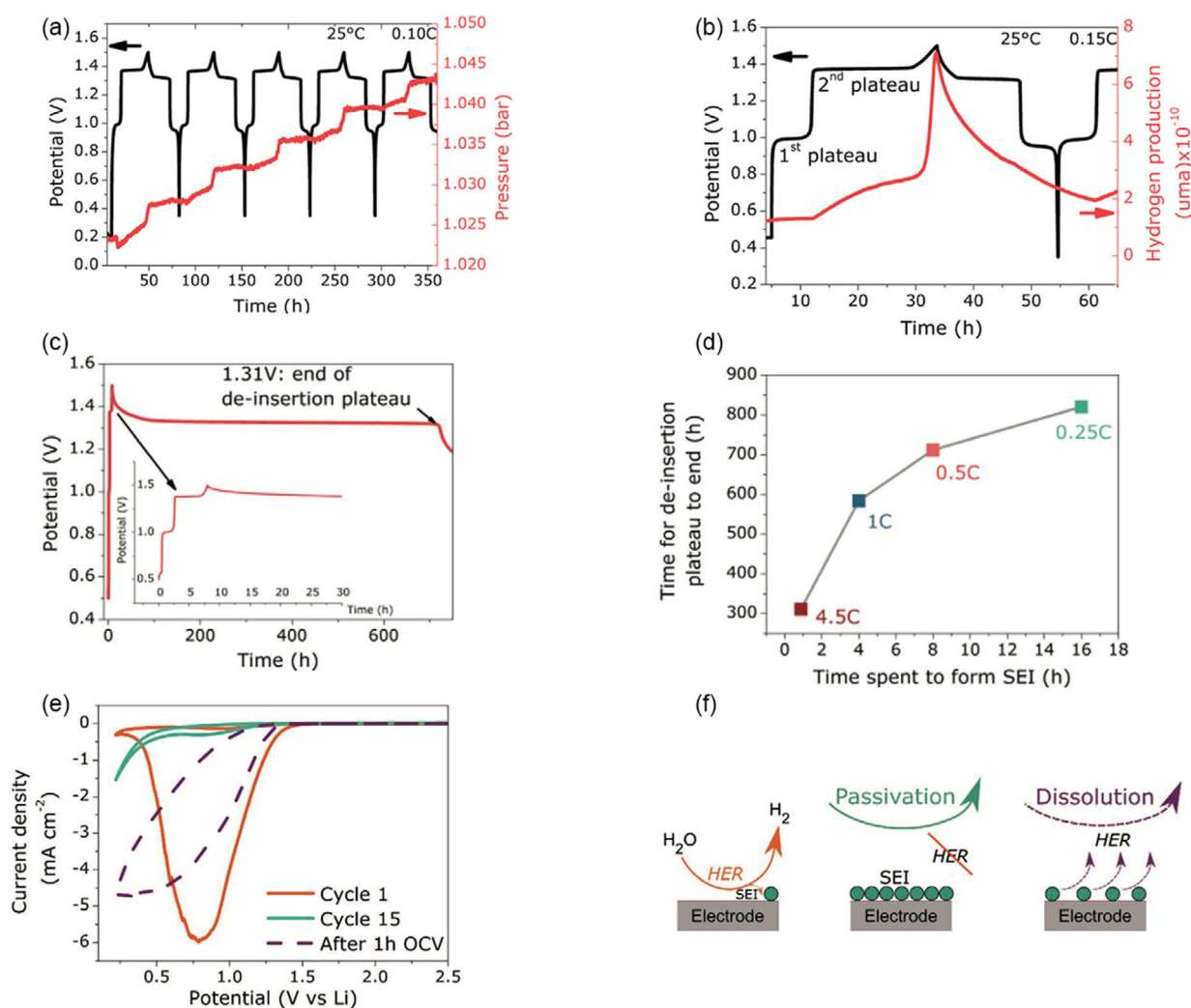
Figure 6. a,b) Potential, pressure, and H_2 evolution as a function of time in WiSEs. c,d) Effect of C-rates on self-discharge in WiSEs. e,f) SEI dissolution in WiSEs; all adapted with permission.[22] Copyright 2020, Wiley.

before the water is consumed to a large extent. This way, one could still force-evolve a protective layer while not fully drying out the cell.

3.2. pH Fluctuations

Another critical and timely concern recently emphasized by Hou et al. is the impact of local pH fluctuations—driven by variable proton activity during cycling—on the stability of aqueous SEIs.[26] *Operando* studies on the interfacial behavior of V_2O_5 model electrodes in dilute LiTFSI-based aqueous electrolytes revealed that pH changes, arising from V_2O_5 dissolution and related polyvanadate redox reactions (occurring both at rest and during cycling), significantly influence the interphase

formation and dissolution. Though pH swings helped trigger SEI formation (namely via the alkalinity developed during the initial charge promoting TFSI⁻ reduction), the SEI dissolved completely at the end of the final discharge as pH dropped and amount of H⁺ increased ($LiF + H^+ \rightarrow Li^+ + HF$, $Li_2CO_3 + 2H^+ \rightarrow CO_2 + H_2O + 2Li^+$). As Zhang et al. highlighted further,[27] regulating proton activity is hence crucial in realizing stable aqueous SEIs.

While pH buffering could help, its implementation in full cells remains challenging due to practical difficulties in ensuring a continuous supply of the buffering agent. Therefore, minimizing local pH fluctuations—for instance, by mitigating active material dissolution—should be a design priority. Potential strategies include electrode surface modification with protective,
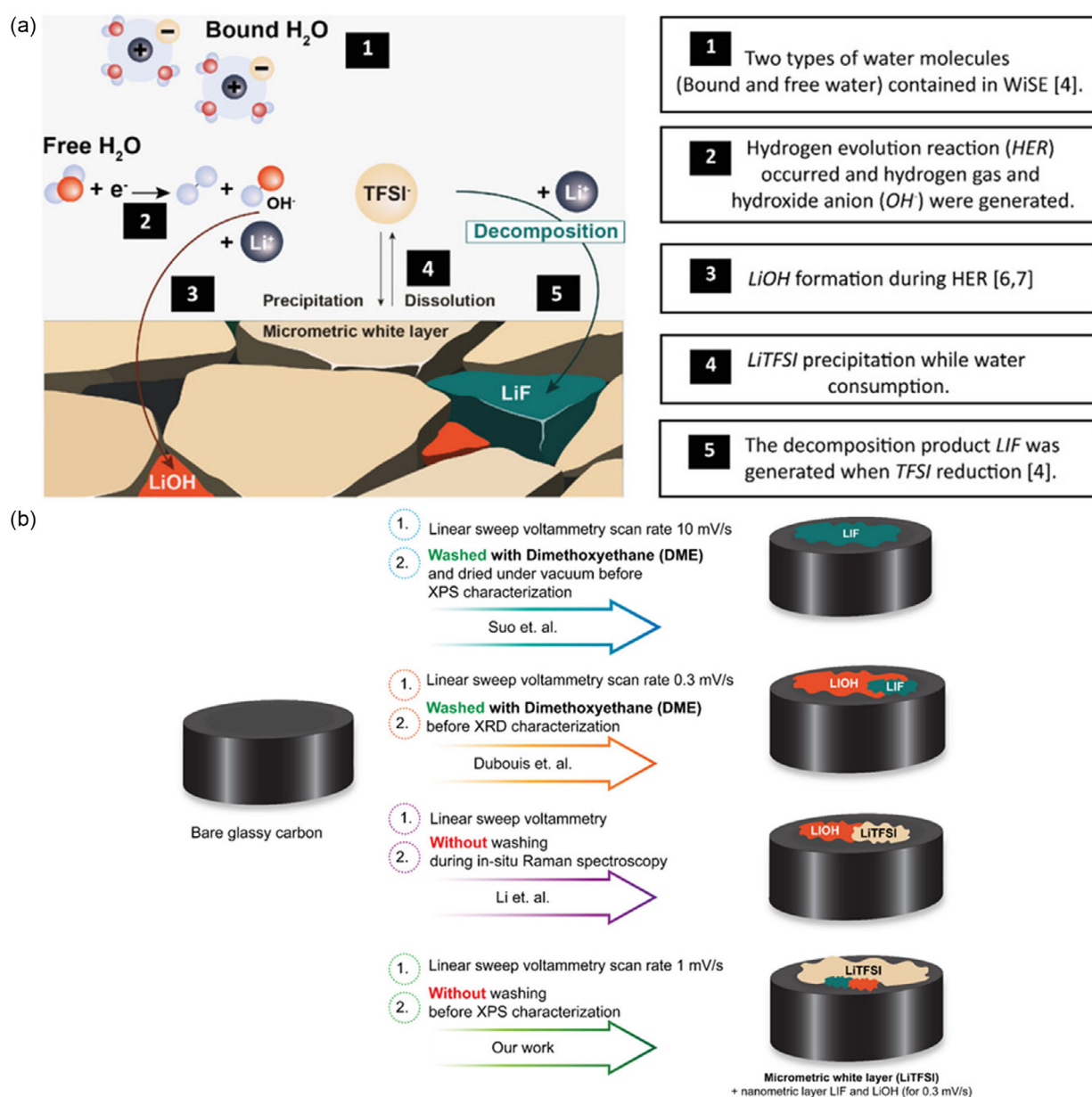
Figure 7. a) Contribution of salt precipitation to aqueous SEIs. b) Different SEI formation pathways in WiSEs, all adapted with permission.[25] Copyright 2024, Wiley.

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ion-conductive coatings (such as thin oxide layers) and/or pH-buffering layers. Hydrophobic coatings that induce electrolyte-electrode phase separation can be especially effective, since they fully limit direct contact of the active material with water.[18] Additionally, as previously demonstrated in non-aqueous LIBs,[28] pulsed or asymmetric charging protocols—such as applying intermittent pauses during insertion (lithiation) to allow ion equilibration—may enhance SEI longevity. However, this approach may compromise charging rates and will require material- and system-specific optimization, given that reaction mechanisms of active materials can differ significantly with differing electrolyte concentrations.[26] High salt concentrations (like in WiSEs) can indeed limit active material dissolution, at least partially, by reducing free water; however, it's key to remember that they still cannot prevent local pH shifts caused by HER (protons get used up, alkalinity increases), if not those caused by active material dissolution and/or proton assisted insertion/de-insertion.

3.3. Standardized Formation and Testing Protocols

While opinions differ on self-discharge rates and compositions of aqueous SEIs, including whether it is the anion reduction products or the precipitated main salt that is contributing primarily to the SEI, it is safely agreed that their formation, thickness, density, component distribution, and robustness are highly sensitive to the polarization period applied both during and after the formation step. Additionally, since different cell configurations (half-cell/full-cell, 2-electrode/3-electrode) use different electrolyte-active material ratios, careful setting of the formatting conditions/protocol is substantial in avoiding an overestimation or even underestimation of the SEI's dissolution time.

Monitoring how the OCV changes at a fully charged state (100% state of charge/SOC, in the context of a full cell) at low C-rates/scan rates (at least below $1C/0.5$ mV s^{-1}) as well as after prolonged cycling of at least 10–20 cycles (both ensuring sufficient exposure time at the formation potentials) can tell to an extent how stable the formed aqueous SEI is. While tests using only CV and at fast C-rates may help "get past" the corrosive HER; comparison to "real" battery environments necessitates potentio/galvano static conditions + low charging rates, which will only reveal if the SEI formed on the working electrode can withstand extreme potentials and HER. Exposure to thermal fluctuations (up to 30–40 °C for consumer storage) combined with operando monitoring of pH swings will also bring us closer to a realistic evaluation of the SEI's stability over cycling and storage. Proper defining and selection of (non-passivating) current collectors, active materials, and reference/counter electrodes will further help rule out any discrepancies and avoid false claims.

4. Summary and Outlook

Despite the significant progress made in the world of WiSEs, all of which have been instrumental in shaping the understanding of aqueous SEIs; it cannot be overlooked that aqueous batteries based on WiSEs, at the moment, are not at par with other commercially successful aqueous storage systems such as lead-acid or Ni-Cd, neither electrochemically nor economically. While a few reported formulations have shown reasonable performance, for example, ≈80%–90% capacity retention after 100–200 cycles in lab-scale cells, this is still short of commercial targets and leaves us a long way from scaling up let alone commercialization. With one of the biggest hurdles being the cathodic stability of water, ways to form a stable aqueous SEI and, more importantly, to prevent or "delay" its dissolution (and the consequent self-discharge and cell drying) are the call of the hour. As commented by Droguet, recombining the evolved gases via catalysts and/or compartment regulation may help prevent the drying out of the cell (if at all that's possible due to the unbalanced H_2 and O_2 generation in WiSEs).[22] However, this will only ensure a "re"-formation of the broken SEI followed by many cycles of dissolution-reformation. This will still drain the carrier ion (besides posing additional challenges with regulating the C-rate and limiting potentials) and lead to low efficiency in the long term. The recent work by Zhu et al. seems to have made substantial progress in addressing the issue of self-discharge through the use of EDTA additives.[16] Notably, the SEI remained stable even after 1 h of OCV following 10 cycles—a clear improvement over most prior studies. The system also exhibited good cycling stability at low C-rates (0.5 C), although not to forget that this was achieved at high salt concentrations (21 m). At least as of now, approaches balancing the electrochemical processes with the solvation dynamics of the bulk electrolyte—such as interface engineering via incorporating hydrophobic additives as functional anode coatings and in situ additive generated SEIs—seem to be the most promising ways forward to realize stable interphases at low electrolyte concentrations. Additionally, targeted approaches to suppress pH fluctuations—through material engineering and system-level design—are imperative to unlocking the long-term viability of these systems. The science behind aqueous SEIs has seen significant progress over the past decade. As the field continues to be explored, a few more leaps on bettering their chemical durability will open up new possibilities for large-scale stationary applications.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

Radhika Krishna Hema: conceptualization (lead); writing—original draft (lead). **Alberto Varzi**: funding acquisition (lead); supervision (lead); writing—review and editing (lead).

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