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Confining Water in Ionic and Organic Solvents to Tune Its Adsorption and Reactivity at Electrified Interfaces

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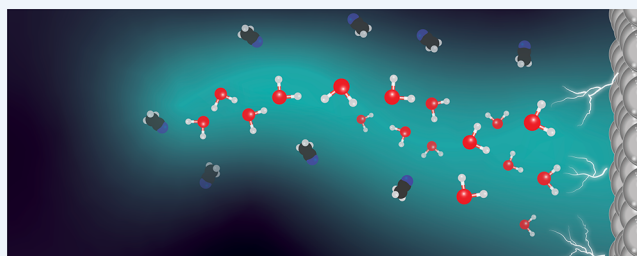
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CONSPECTUS: The recent discovery of “water-in-salt” electrolytes has spurred a rebirth of research on aqueous batteries. Most of the attention has been focused on the formulation of salts enabling the electrochemical window to be expanded as much as possible, well beyond the 1.23 V allowed by thermodynamics in water. This approach has led to critical successes, with devices operating at voltages of up to 4 V. These efforts were accompanied by fundamental studies aiming at understanding water speciation and its link with the bulk and interfacial properties of water-in-salt electrolytes. This speciation was found to differ markedly from that

in conventional aqueous solutions since most water molecules are involved in the solvation of the cationic species (in general Li^+) and thus cannot form their usual hydrogen-bonding network. Instead, it is the anions that tend to self-aggregate in nanodomains and dictate the interfacial and transport properties of the electrolyte. This particular speciation drastically alters the presence and reactivity of the water molecules at electrified interfaces, which enlarges the electrochemical windows of these aqueous electrolytes. Thanks to this fundamental understanding, a second very active lead was recently followed, which consists of using a scarce amount of water in nonaqueous electrolytes in order to control the interfacial properties. Following this path, it was proposed to use an organic solvent such as acetonitrile as a confinement matrix for water. Tuning the salt/water ratio in such systems leads to a whole family of systems that can be used to determine the reactivity of water and control the potential at which the hydrogen evolution reaction occurs. Put together, all of these efforts allow a shift of our view of the water molecule from a passive solvent to a reactant involved in many distinct fields ranging from electrochemical energy storage to (electro)catalysis.

Combining spectroscopic and electrochemical techniques with molecular dynamics simulations, we have observed very interesting chemical phenomena such as immiscibility between two aqueous phases, specific adsorption properties of water molecules that strongly affect their reactivity, and complex diffusive mechanisms due to the formation of anionic and aqueous nanodomains.



KEY REFERENCES

- Dubouis, N.; Lemaire, P.; Mirvaux, B.; Salager, E.; Deschamps, M.; Grimaud, A. The role of the hydrogen evolution reaction in the solid–electrolyte interphase formation mechanism for “Water-in-Salt” electrolytes. *Energy Environ. Sci.* **2018**, 11, 3491–3499.¹ *The hydroxides generated during the hydrogen evolution reaction were shown to react chemically with TFSI, thus catalyzing the formation of a solid–electrolyte interphase that prevents further water reduction.*
- Bouchal, R.; Li, Z.; Bongu, C.; Le Vot, S.; Berthelot, R.; Rotenberg, B.; Favier, F.; Freunberger, S. A.; Salanne, M.; Fontaine, O. Competitive salt precipitation/dissolution during free-water reduction in water-in-salt electrolyte. *Angew. Chem., Int. Ed.* **2020**, 59, 15913–15917.² *The impact of water speciation on the reduction potential of the LiTFSI-based water-in-salt and on the formation of the SEI was studied by combining experiments and molecular simulations.*

- Dubouis, N.; Serva, A.; Salager, E.; Deschamps, M.; Salanne, M.; Grimaud, A. The Fate of Water at the Electrochemical Interfaces: Electrochemical Behavior of Free Water vs Coordinating Water. *J. Phys. Chem. Lett.* **2018**, 9, 6683–6688.³ *The reactivity of water involved in the solvation shell of a series of cationic Lewis acids was shown to be greater than that of noncoordinating water molecules when dissolved in an organic solvent matrix.*
- Dubouis, N.; Serva, A.; Berthin, R.; Jeanmairret, G.; Porcheron, B.; Salager, E.; Salanne, M.; Grimaud, A. Tuning the water reduction through controlled nanoconfinement within an organic liquid matrix. *Nat. Catal.*

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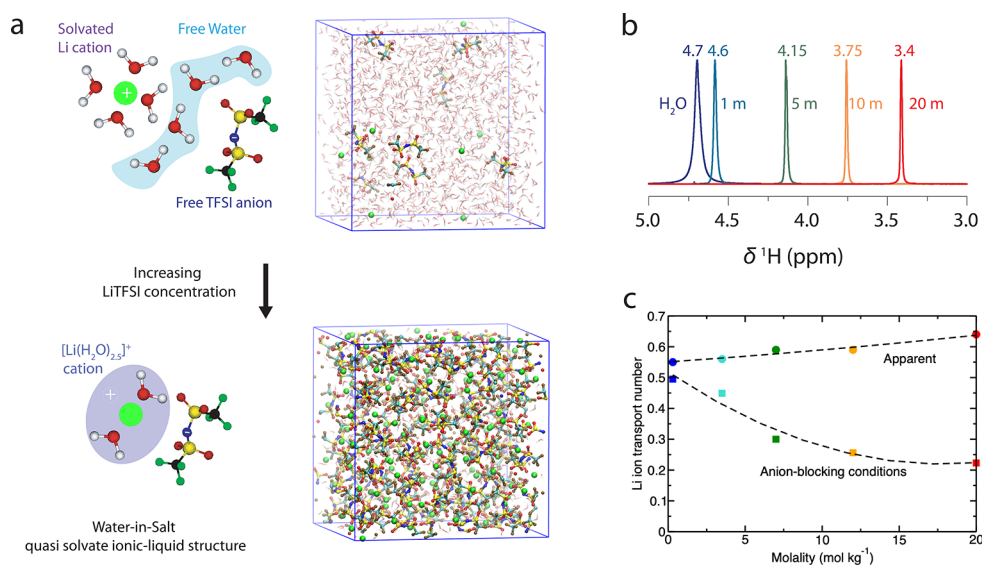


Figure 1. Physicochemical properties of water-in-salt electrolytes largely vary with concentration. (a) Typical structures and snapshots of (top) dilute and (bottom) highly concentrated systems. Reproduced with permission from ref 1. Copyright 2018 the Royal Society of Chemistry. (b) Normalized NMR spectra showing the ^1H chemical shift of water molecules in the presence of LiTFSI at several molalities (1 m, light blue; 5 m, green; 10 m, orange; 20 m, red) compared with that of pure water (dark blue). Adapted with permission from ref 1. Copyright 2018 Royal Society of Chemistry. (c) Apparent and anion-blocking conditions Li-ion transport numbers for varying salt molalities in LiTFSI water-in-salt electrolyte (data taken from ref 17).

2020, 3, 656–663.⁴ *The composition and size of aqueous-rich nanodomains inside an organic matrix were tuned by changing the supporting electrolyte and water concentration. The reactivity of the system was shown to vary significantly with this nanostructure.*

1. INTRODUCTION

Liquid electrolytes are at the heart of many devices in energy storage and conversion applications. By variation of their composition, their reactivity can be tuned, both in the bulk with regard to their physical properties and at interfaces. There is an infinity of possible combinations, so they are generally classified according to their main features. Hence, while Li- and Na-ion batteries employ mixtures of carbonates as solvents,^{5,6} solvent-free ionic liquids also play an important role in the electrolyte portfolio.⁷ While being at center stage for decades for devices such as Pb–acid and Ni–Cd batteries, aqueous electrolytes have been quickly overshadowed by their aprotic counterparts because of the narrow electrochemical stability window of water (1.23 V according to the thermodynamics). Thus, strategies are being developed to extend the stability window of aqueous systems and make them competitive energywise by slowing down the kinetics of water splitting. Driven by this research necessity, a strong synergy now exists between the field of aqueous electrolytes for secondary batteries and that of water splitting.⁸ Indeed, controlling the kinetics of water oxidation and reduction at interfaces is the main challenge pertaining to the development of better catalysts for water electrolyzers. Numerous reports have shown that both the oxygen evolution reaction (OER) kinetics and the hydrogen evolution reaction (HER) kinetics are dependent on the electrolyte composition because it changes the water environment.^{9–11} For instance, alteration of the solvation environment of water molecules was proved to drastically tune the activation energy of the OER.¹¹ Also, the observed effects of pH on the HER kinetics were explained by

a modification of the rigidity of the hydrogen-bonding network in the vicinity of the electrodes,¹⁰ which demonstrates that the environment of water molecules at a larger scale may also impact their reactivity.

In the past few years, numerous experimental and theoretical studies have thus been devoted to understanding how the water environment in aqueous electrolytes would control their physical properties and the water reactivity. This trend has only been reinforced by the recent application of super-concentrated electrolytes¹² to aqueous systems, namely, water-in-salt electrolytes (WiSEs).^{13,14} Indeed, such systems were rapidly shown to largely overcome the usual thermodynamic limit of water, resulting in high-voltage aqueous Li-ion batteries (LIBs) and reinvigorating our thirst for developing an activity–property relationship for water and its solvation structure.¹⁵ Several studies have thus focused on understanding the physicochemical properties of WiSEs,^{16,17} in which concentrations as high as 21 m (mol/kg) of lithium bis-[(trifluoromethyl)sulfonyl]imide (LiTFSI) can be dissolved, as well as elucidating the mechanism responsible for the electrochemical window enlargement.^{1,2,18–20} Those findings revealed that in these exotic systems, the modification of the water environment at the short and long range is responsible for their physicochemical properties. Such systems set a precedent of fruitful collaboration among theoreticians, chemists, and electrochemists to solve a fundamental question of practical importance that will certainly sow the seeds of a lasting approach in the field of energy conversion and storage devices.

Altogether, these observations highlight the necessity for bringing a molecular picture to our understanding of water reactivity. Such a picture is the key for unlocking our ability to develop custom aqueous electrolytes with the desired reactivity for electrochemical energy storage and conversion devices. Starting from our early works on understanding the physical properties of water-in-salt electrolytes, this Account provides a perspective on recent efforts carried out toward that goal. First,

we will summarize the current status of knowledge on the microscopic aspects of water-in-salt electrolytes in the bulk and at interfaces. Realizing that such systems remain complex, we will discuss approaches that were then developed to bring a finer understanding of how the water structure at short and long range tunes its reactivity. For that, we describe systems in which water is dissolved in organic inert matrices, allowing for isolation of water molecules and creating nanoscale reactors with controlled environments. Finally, building upon our comprehension of the microscopic aspects of aqueous systems, we will discuss the opportunities created by such fine understanding. Hence, we will describe how macroscopic properties of aqueous electrolytes can be modulated with for instance the formation of aqueous biphasic systems, which show great promise for the development of novel intercalation compounds for battery applications. As well, we will describe the novel directions that can be taken using such systems, in which the roles of water as reactant and as solvent can be dissociated for selective electrochemical reactions.

2. UNDERSTANDING WATER-IN-SALT ELECTROLYTES FOR AQUEOUS LI-ION BATTERIES

2.1. Physicochemical Properties

A solvent-in-salt electrolyte is defined as a system in which either the weight or volume ratio of salt to solvent exceeds 1.²¹ If we restrict the discussion to the weight-based definition, in the case of LiTFSI in water, this ratio is reached when there are fewer than 16 water molecules per ion pair. However, most of the experimental results were obtained in a much more concentrated regime. For example, for a typical molality of 20 m which is just below the solubility limit, there are only 2.77 water molecules per ion pair. The lithium ion interacts strongly with water, and in the dilute regime its solvation shell contains at least four molecules,²² while the TFSI anion is hydrophobic. As a consequence, at high salt concentrations almost all of the water molecules are involved in relatively long-lived $\text{Li}(\text{H}_2\text{O})_n^+$ complexes while a few of them remain unbound, as schematized in Figure 1a.^{1,13}

The peculiar speciation of water molecules in LiTFSI-based systems shows signatures in various spectroscopies. For example, the O–H stretching mode of water molecules shifts toward larger wavenumbers because of the existence of new molecular environments.¹ NMR spectra show even more dramatic shifts for all of the nuclei (see Figure 1b for the ¹H chemical shift variation) that were attributed to the progressive disappearance of the water hydrogen-bonding network in the water-in-salt regime.¹ Molecular dynamics (MD) simulations provide a consistent view of the system,¹³ which may be simply described as a quasi-solvate ionic liquid made of $\text{Li}(\text{H}_2\text{O})_n^+$ cations that interact softly with the TFSI anions.

This similarity of water-in-salt electrolytes with ionic liquids called for further investigation of their medium- to long-range structure. Indeed, ionic liquids are known to form polar/apolar domains²³ that give rise to specific templating properties²⁴ and have been well-characterized by analysis of structure factors obtained by small-angle X-ray scattering (SAXS).²⁵ This is of prime interest since it has been established that at low concentration in ionic liquids, the water molecules are mostly present in a “free” state through the formation of hydrogen bonds with the anions,²⁶ thus creating water-rich anionic domains. Moreover, simulations have shown that those dissolved water molecules will tend to accumulate in the

vicinity of the electrodes.²⁷ Interestingly, this accumulation is exacerbated at the positive electrode for hydrophobic ionic liquids because strong water–anion correlations exist. Such observations are interesting since recent studies coupling molecular simulations and experiments highlighted that the accumulation of water at electrified interfaces has a detrimental effect on the electrochemical stability of these ionic liquids.²⁸ Inspired by the water-in-salt approach, Chen et al. thus proposed dissolving small amounts of lithium ions in wet ionic liquids in order to “trap” these water molecules and expand the voltage window of the liquid.²⁹ Using small-angle neutron scattering combined with molecular dynamics, Borodin et al. showed that water-in-salt electrolytes also display nano-heterogeneities with characteristic lengths of 1 to 2 nm.³⁰ However, instead of being formed of groups of different polarities, they are made of a 3D percolating lithium–water network dispersed inside a TFSI-rich matrix, as shown on Figure 1a.

From the dynamic point of view, this nanostructuring has an important impact. Indeed, unlike in ionic liquids, where it shows sluggish dynamics, the lithium cation exhibits a relatively large self-diffusion coefficient even at high LiTFSI molalities.³⁰ This result was expected to enhance the performance of LIBs at high rates, which is known to depend importantly on the lithium transference number. However, in such highly concentrated electrolytes, it is important to take the correlations between the ions into account, and the apparent transport number based on diffusion coefficients only cannot be taken as a proxy for the one measured under anion-blocking conditions, which is the important quantity to take into account.³¹ As shown in Figure 1c, as soon as the correlation effects are considered in the case of the LiTFSI water-in-salt electrolytes, much smaller transport numbers are obtained, so better performances should finally not be expected.¹⁷

2.2. Reactivity at the Interface

Although the transport numbers of water-in-salt electrolytes are probably not as optimal as initially expected, the main advantage of these systems is the possibility to operate lithium-ion cells at high voltages. This is particularly important at the anode, where the formation of a crystalline LiF-based solid–electrolyte interphase (SEI) was established.¹³ First studies attributed the formation of this protective layer to the reduction of the TFSI anion, but the mechanism at play is in fact more complex. As illustrated in Figure 2a, electrochemical studies using a rotating disk setup have shown that the onset potential for water reduction is hardly modified by the increase in LiTFSI concentration^{1,2} and, more importantly, that it is also similar to the potential at which water reduction occurs in other highly concentrated alkali salts (e.g., Li_2SO_4 , LiNO_3 , or LiCl). However, in the LiTFSI water-in-salt regime the reduction wave has a distorted bell shape that suggests the formation of a passivating layer, which was confirmed using an electrochemical quartz crystal microbalance.¹

Molecular dynamics simulations involving a constant applied potential between two carbon electrodes in contact with a water-in-salt electrolyte showed that the adsorption profiles of the water molecules (Figure 2b) are not affected by the concentration of ions. However, as in the bulk, water molecules are either “free” or involved in the solvation shell of the Li^+ ions at the interface. As shown in Figure 2c, in both regimes, numerous “bound” water molecules are present at the

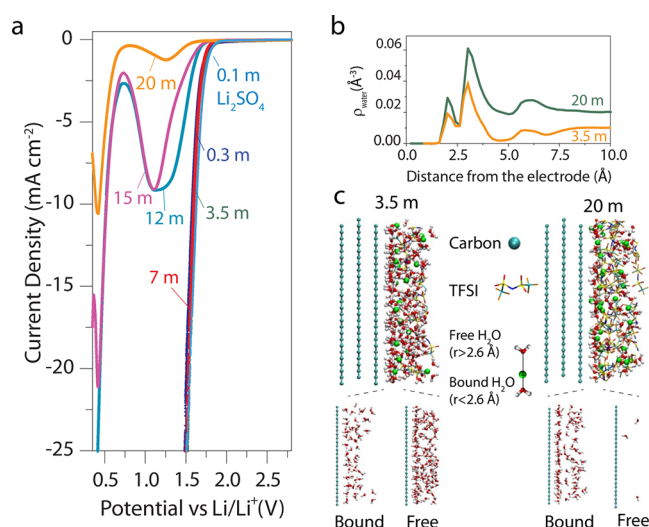


Figure 2. (a) Linear polarization at a rotating glassy carbon disk electrode with different salt molalities. (b) Water density profiles at the negative electrode from MD simulations with a 3 V potential difference between graphite electrodes at two molalities (3.5 and 20 m). (c) Representative snapshots of (top) the whole adsorbed layer and (bottom) only the bound and free water molecules at two molalities (3.5 and 20 m). From ref 2. CC BY 4.0 (<https://creativecommons.org/licenses/by/4.0/>).

electrochemical interface, which may explain the electrochemical behavior of the system.

On-line electrochemical mass spectrometry was used to analyze the products formed during the first reduction. It showed that a major product was H_2 , which confirms that the cathodic current is associated with the reduction of the water molecule since water molecules are the only source of protons in the electrolyte.^{1,2} The water reduction is accompanied by a basification of the liquid near the electrode, which leads to chemical decomposition of the TFSI anion and triggers the formation of a fluoride-rich SEI.¹ Also, the water reduction decreases the water concentration at the electrochemical

interface and thus increases the local concentration of LiTFSI, which can give birth to competitive salt precipitation/dissolution during formation of the SEI.²

The main conclusion arising from the understanding of these mechanisms is that although water-in-salt-based practical batteries may not yet be mature enough for practical applications,³² tuning the electrolyte composition to control the SEI structure is a very promising lead. Moreover, such high concentrations of organic salts lead to several complications, such as higher cost compared with traditional electrolytes, poor wetting of the porous electrodes due to the high viscosity of the electrolyte, or even electrolyte–separator compatibility.^{33,34} These studies on the WiSE system unravel that changing the water environment may drastically alter the physicochemical properties of aqueous electrolytes. Nevertheless, these systems remain complex, and it is not so easy to draw general conclusions about how the water environment may modify its reactivity at electrified interfaces.

3. CONFINING WATER TO STUDY ITS ELECTROCHEMICAL REACTIVITY

3.1. Impact of the Nature of the Salt on the Reactivity of Water

Thus, the recent development of water-in-salt electrolytes shines a light on the importance of controlling both short- and long-range interactions in aqueous electrolytes in order to tune the reactivity of water at electrochemical interfaces. Toward that goal, we therefore explored systems that are comparatively less studied and in which water is confined in an organic matrix, acetonitrile in our case. First focusing on short-range interactions, systems were prepared by dissolving a very scarce amount of water in acetonitrile in the presence of perchlorate salts at a concentration of 100 mM, varying the nature of the cation.³ Doing so, we demonstrated that depending on the hydrophilicity/hydrophobicity of the cation, a difference in the reactivity of water upon reduction conditions is observed: in the cyclic voltammogram in Figure 3a, a large cathodic current is measured for Li^+ and Na^+ , while almost no cathodic current

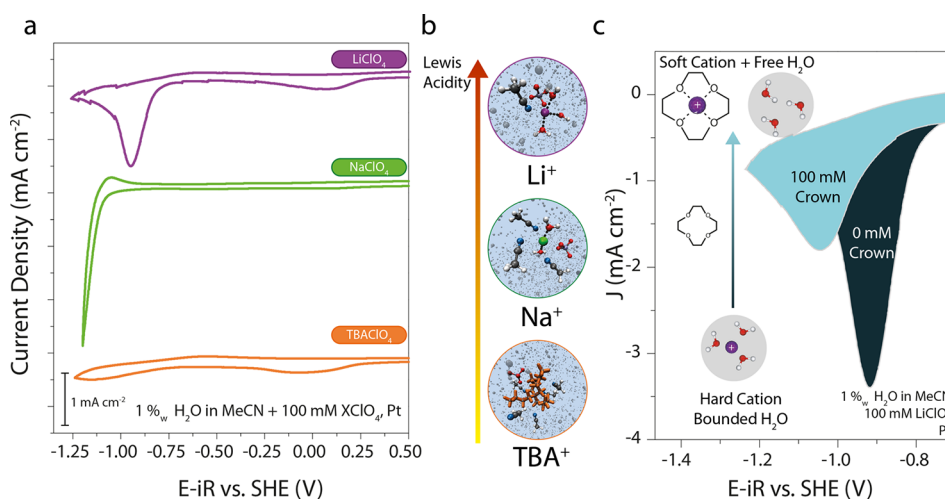


Figure 3. Hydrophilicity/hydrophobicity of the cation in the electrochemical double layer dictates the reactivity of water. (a) Cyclic voltammograms recorded over a platinum electrode in acetonitrile electrolytes containing 10 000 ppm of water in the presence of LiClO_4 (purple), NaClO_4 (green), or TBAClO_4 (orange). Potentials are compensated for the ohmic drop (iR) and reported vs the SHE. (b) Typical snapshots extracted from MD simulations illustrating the cations' first solvation shells. (c) Evolution of the water reduction electrochemistry in the presence/absence of a crown ether that coordinates the lithium ion. Adapted from ref 3. Copyright 2018 American Chemical Society.

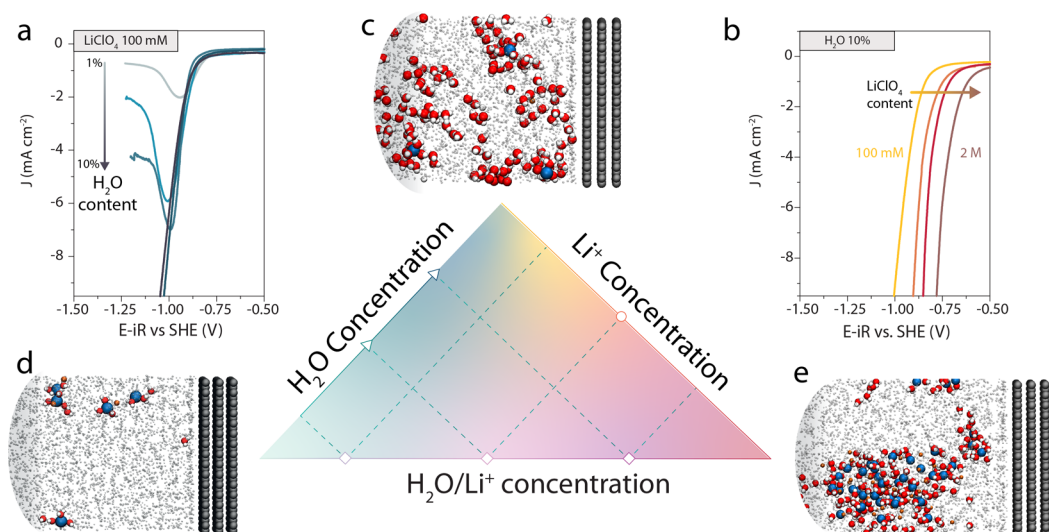


Figure 4. Playing independently or concomitantly with the salt and water concentrations is a strategy for fine-tuning the reactivity of water. (a, b) Evolution of the linear sweep voltammograms recorded in acetonitrile with increasing H₂O or LiClO₄ content, respectively. (c–e) Typical snapshots of electrified interfaces at the corresponding H₂O and Li⁺ concentrations. Reproduced with permission from ref 4. Copyright 2020 Springer Nature.

is recorded in the case of tetrabutylammonium (TBA⁺). Accompanying molecular dynamics simulations of the bulk electrolyte showed that the number of water molecules in the solvation shell of the cation is large for Li⁺ and, to a lesser extent, for Na⁺, while it is almost zero for TBA⁺ (see Figure 3b), with a consequent increase of free (noncoordinating) water molecules. These results together with NMR measurements led to the conclusion that upon negative polarization, cations move to the interface with their solvation shell, and their hydrophilicity dictates the water reactivity. Water molecules coordinating hydrophilic cations, such as Li⁺, are more reactive than free water molecules. Such a conclusion was further confirmed by using chelating molecules (i.e., crown ethers) to trap Li⁺ and suppress the Li⁺–water interactions, thus freeing all water molecules from the Li⁺ solvation sheath. Comparing the electrochemical responses recorded with or without added crown ether molecules, we once again found that free water molecules are less reactive than the ones solvating Li⁺ (see Figure 3c). Here, a first analogy with the WiSEs system can be drawn. Indeed, in both systems the water molecules are strongly coordinated to Li⁺ cations. Since this population of water is found to be the most reactive for water in the acetonitrile system, these observations corroborate the poor cathodic stability of WiSEs.

3.2. Formation of Water-Rich Domains

Once the hydrophilic Li⁺ cations were identified as the species that promote the HER the most when the water content is low, we decided to investigate the effect of interactions taking place at long range on the HER.⁴ In a first step, fixing the LiClO₄ concentration at 100 mM while increasing the water content from 1% to 10% by mass was found not to modify the onset potential at which the water reduction occurs, as shown in the linear sweep voltammogram in Figure 4a. Molecular dynamics simulations of the electrolyte between two carbon electrodes held at a constant applied voltage showed that water is mostly coordinated to Li⁺ cations at both 1% and 10% by mass (see Figure 4c,d). Increasing the amount of water in the system leads only to the formation of some small clusters of free water surrounding the Li⁺–(H₂O)_x adducts (Figure 4c). A different

picture was drawn when the LiClO₄ concentration was increased from about 100 mM to 2 M in the 10 mass % H₂O (water-rich) system. Water was found to be more easily reduced, as shown by the shift of the onset potential toward less negative values in the linear voltammogram in Figure 4b. Molecular dynamics simulations combined with SAXS measurements revealed that larger water clusters are formed with increasing salt concentration, with aqueous-rich channels connecting the bulk to the interface (see Figure 4e). We could ascribe the easiest water reduction observed in this case because the OH[−] ions formed during Volmer step of the water reduction can shuttle from the electrified interface into the bulk of the electrolyte, which stabilizes the system.^{10,35,36}

Such findings are in line with our first hypothesis regarding the cathodic stability of the WiSEs when looking at the short-range environment of the water molecules. Indeed, the long-range ordering of the water molecules in these electrolytes is somehow similar to the one observed in WiSEs, with the formation of Li⁺/H₂O-rich domains at the electrode–electrolyte interface, a phenomenon that is exacerbated upon negative polarization.^{2,37} Such fundamental insights probably rationalize previous observations suggesting that the kinetics of water reduction in WiSEs is not drastically diminished on platinum or glassy carbon electrodes.^{1,2}

4. PERSPECTIVES

The framework developed during our investigations, in which electrochemistry is coupled to bulk characterizations and molecular dynamics simulations at the interface, allowed us to reach a deep understanding about the complex behavior of highly concentrated aqueous electrolytes. However, this fundamental understanding of the water molecule environments at short and long ranges and how they alter the reactivity of the electrolytes extends far beyond aqueous batteries. The knowledge acquired is directly transferable to practical devices such as LIBs, multivalent batteries, supercapacitors, or even electrolyzers. Indeed, we have demonstrated that the reactivity of water molecules at the negative electrode is exacerbated in the presence of acidic cations such

as lithium. Such a conclusion finds direct application in understanding the parasitic reactions due to water contamination in carbonate-based LIBs. Indeed, the “perfect” water content for organic-based LIBs was long debated, as water contamination may modify the SEI composition on anode materials and thus enhance or deteriorate their performances.^{38–40} The approach we deployed to understand how water speciation may impact its reactivity at electrified electrodes may thus help to rationalize these experimental observations. For instance, it was recently suggested that because water and Li^+ are strongly bonded, they can coadsorb on a metallic surface upon negative polarization, leading to the formation of oxide species and the evolution of molecular hydrogen, both of which are detrimental for battery cycling.⁴¹ Water is also used as an additive in organic electrolytes for divalent ion batteries to boost the kinetics for the intercalation of divalent anions into oxides.⁴² However, divalent cations such as Mg^{2+} are strong Lewis acids and strongly bind water molecules, which facilitates their electrochemical reduction and drastically limits the tolerable amount of water in these systems. Moreover, this strong cation–water affinity may also lead to cointercalation of water molecules in the bulk of the electrode, limiting the effective capacity. Interestingly, similar phenomena have also been observed in aqueous electrolytes. For instance, proton-based pseudocapacitors have been demonstrated to cointercalate water molecules with protons.⁴³ Such phenomena may also find applications in developing efficient and stable heterogeneous catalysts for water splitting. Indeed, hydrated cation intercalation was recently demonstrated to take part in the mechanism of water electro-oxidation.⁴⁴ Water–cation cointercalation is also known to impact catalysts for the HER, such as MoS_2 , which can intercalate hydrated cations with a number of water molecules depending on their acidity.⁴⁵ Hence, applying the previously described methodology to these systems could be pivotal to understanding the complex water–cation–material interactions that are at play in these systems and improve the overall rate of hydrogen production.

While the short-range environment of water molecules drastically influences their chemical reactivity, we have also highlighted the possibility to master their long-range ordering. By this means, it is now possible to prepare organic electrolytes that contain aqueous nanoreactors with tunable sizes that could prove very useful for a wide variety of applications. For instance, such aqueous–organic mixtures have already been employed in CO_2 reduction.^{46,47} Indeed, apolar small molecules such as CO_2 and N_2 have poor affinities for water molecules and thus low solubilities in aqueous phases, which drastically hampers the reaction rates for CO_2 or N_2 reduction. Nevertheless, a proton source is required to achieve the transformation of CO_2 into high-added-value compounds such as methane, methanol, ethanol, ethylene, etc. Thus, one could seize the opportunity of tuning the size of aqueous domains that form in aprotic solvents to enhance the selectivity rate toward high-value-added products while sustaining a sufficient CO_2 solubility. This stratagem could even be pushed toward more complex processes, such as synthetic electrochemistry. Indeed, changing the size and composition of the aqueous and/or organic nanodomains formed in the electrolytes could allow polar and apolar reactants to be brought together at the electrochemical interface and thus increase the molecular complexity of products that could be formed.

Furthermore, multiphase electrolytes could also prove useful for electrochemical synthesis. Indeed, in a classical electrochemical reactor, a metallic electrode is needed to bring/remove electrons, and an electrolyte is required to solvate the reactants and products of the reaction, while cosolvents are often used to extract the products and improve the yield of the electrochemical reaction. There, multiphase electrolytes (made, e.g., by emulsion) have been investigated as a way to unlock new synthesis paths because of their ability to tune the reaction processes at the triple phase boundary.⁴⁸ Usually, these biphasic systems are obtained by combining two liquids with very different physicochemical properties such as water and an apolar solvent. Aiming at understanding the role of the anion in WiSEs, our groups recently discovered that such biphasic systems can also be obtained simply by mixing two alkali salts at high concentration with water. Those aqueous biphasic systems (ABSs) do not contain any organic solvent and can thus be envisaged to develop even greener organic electrosynthesis processes. Besides, we could demonstrate that ions shuttling between two aqueous phases is possible, which paves the way to membraneless electrolyzers or batteries using nonmiscible catholytes and anolytes. Indeed, the concept of membraneless anolyte/catholyte systems was recently implemented to assemble promising high-energy-density batteries based on a new insertion chemistry for the positive electrode, namely, the insertion of chloride and bromide into graphite.⁶ Altogether, such findings highlight that mastering the water environment at the atomic, nanoscopic, or macroscopic scale is a key to unlock new electrochemical technologies for electricity storage, electrocatalysis, or electrosynthesis, as illustrated in Figure 5.

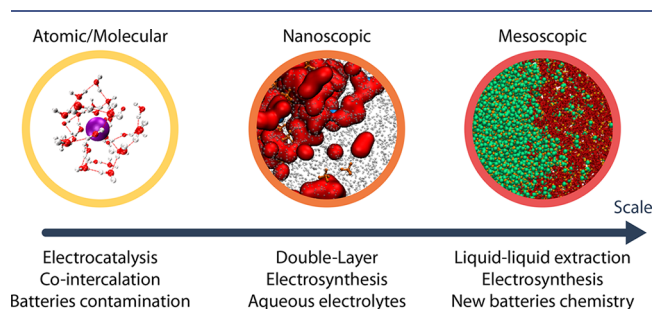


Figure 5. Tuning the water environment at the atomic, nanoscopic, or macroscopic scale is a promising strategy to unlock new electrochemical technologies.

From a fundamental perspective, these systems raise numerous interrogations. For instance it is known that increasing the ionic strength of an electrolyte drastically alters the activity coefficients of ionic species and solvents in an opposite way.³⁷ However, it is not so clear how this can correlate with electrochemical reactions such as water splitting, which involve both ions and solvents as reactants/products. Establishing such links between the electrolytes’ physicochemical properties and reactivity would certainly lead to more rational design of new (aqueous) electrolytes for LIBs and catalysis. Evidently, this will rely on the development of numerical tools that avoid the pitfalls currently encountered by classical MD simulations (i.e., no reactivity) and by density functional theory (i.e., the large computational cost that prevents computation of events on long time scales). Similarly, our understanding of such fine phenomena occurring at solid–

liquid interfaces will also rely on the development of adapted characterization techniques that can capture rare, complex, and quick chemical events confined in a thin interfacial layer. With regard to the electrolyte structures, we suggested that a large size asymmetry between the anions could trigger the formation of aqueous biphasic systems because of packing constraints at the molecular scale.⁴⁹ From this, a simple question emerges: how can we define the size of an ion into these solutions and how can it be captured? Moreover, it has been demonstrated that the anion size also modifies the nanostructuring of the electrolytes. Indeed, it was recently suggested that the growth of aqueous-rich/poor domains in WiSEs is strongly influenced by the nature (and thus the size) of the organic anion.⁵⁰ The investigation of the influence of the nanostructuring of these electrolytes on the formation of ABSs could prove useful to better glimpse the rationale behind the formation of these complex systems.

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REFERENCES

- (1) Dubouis, N.; Lemaire, P.; Mirvaux, B.; Salager, E.; Deschamps, M.; Grimaud, A. The Role of the Hydrogen Evolution Reaction in the Solid-Electrolyte Interphase Formation Mechanism for "Water-in-Salt" Electrolytes. *Energy Environ. Sci.* **2018**, *11*, 3491–3499.
- (2) Bouchal, R.; Li, Z.; Bongu, C.; Le Vot, S.; Berthelot, R.; Rotenberg, B.; Favier, F.; Freunberger, S.; Salanne, M.; Fontaine, O. Competitive Salt Precipitation/Dissolution During Free-Water Reduction in Water-in-Salt Electrolyte. *Angew. Chem., Int. Ed.* **2020**, *59*, 15913–15917.
- (3) Dubouis, N.; Serva, A.; Salager, E.; Deschamps, M.; Salanne, M.; Grimaud, A. The Fate of Water at the Electrochemical Interfaces: Electrochemical Behavior of Free Water Versus Coordinating Water. *J. Phys. Chem. Lett.* **2018**, *9*, 6683–6688.
- (4) Dubouis, N.; Serva, A.; Berthin, R.; Jeanmairat, G.; Porcheron, B.; Salager, E.; Salanne, M.; Grimaud, A. Tuning Water Reduction through Controlled Nanoconfinement within an Organic Liquid Matrix. *Nat. Catal.* **2020**, *3*, 656–663.
- (5) Xu, K. Electrolytes and Interphases in Li-Ion Batteries and Beyond. *Chem. Rev.* **2014**, *114*, 11503.
- (6) Yang, C.; Chen, J.; Ji, X.; Pollard, T. P.; Lü, X.; Sun, C.-J.; Hou, S.; Liu, Q.; Liu, C.; Qing, T.; Wang, Y.; Borodin, O.; Ren, Y.; Xu, K.; Wang, C. Aqueous Li-ion Battery Enabled by Halogen Conversion–Intercalation Chemistry in Graphite. *Nature* **2019**, *569*, 245–253.
- (7) Armand, M.; Endres, F.; MacFarlane, D. R.; Ohno, H.; Scrosati, B. Ionic-Liquid Materials for the Electrochemical Challenges of the Future. *Nat. Mater.* **2009**, *8*, 621–629.
- (8) Dubouis, N.; Grimaud, A. The Hydrogen Evolution Reaction: From Material to Interfacial Descriptors. *Chem. Sci.* **2019**, *10*, 9165–9181.
- (9) Subbaraman, R.; Tripkovic, D.; Strmcnik, D.; Chang, K.-C.; Uchimura, M.; Paulikas, A. P.; Stamenkovic, V.; Markovic, N. M.

Enhancing Hydrogen Evolution Activity in Water Splitting by Tailoring $\text{Li}^+\text{-Ni(OH)}_2\text{-Pt}$ Interfaces. *Science* **2011**, *334*, 1256–1260.

(10) Ledezma-Yanez, I.; Wallace, W. D. Z.; Sebastián-Pascual, P.; Climent, V.; Feliu, J. M.; Koper, M. T. M. Interfacial Water Reorganization as a pH-Dependent Descriptor of the Hydrogen Evolution Rate on Platinum Electrodes. *Nat. Energy* **2017**, *2*, 17031.

(11) Duan, Y.; Dubouis, N.; Huang, J.; Dalla Corte, D. A.; Pimenta, V.; Xu, Z. J.; Grimaud, A. Revealing the Impact of Electrolyte Composition for Co-Based Water Oxidation Catalysts by the Study of Reaction Kinetics Parameters. *ACS Catal.* **2020**, *10*, 4160–4170.

(12) Yamada, Y.; Yaegashi, M.; Abe, T.; Yamada, A. A Super-concentrated Ether Electrolyte for Fast-Charging Li-ion Batteries. *Chem. Commun.* **2013**, *49*, 11194–11196.

(13) Suo, L.; Borodin, O.; Gao, T.; Olguin, M.; Ho, J.; Fan, X.; Luo, C.; Wang, C.; Xu, K. Water-in-SaltTM Electrolyte Enables High-voltage Aqueous Lithium-ion Chemistries. *Science* **2015**, *350*, 938–943.

(14) Yamada, Y.; Usui, K.; Sodeyama, K.; Ko, S.; Tateyama, Y.; Yamada, A. Hydrate-melt Electrolytes for High-Energy-Density Aqueous Batteries. *Nat. Energy* **2016**, *1*, 16129.

(15) Borodin, O.; Self, J.; Persson, K. A.; Wang, C.; Xu, K. Uncharted Waters: Super-Concentrated Electrolytes. *Joule* **2020**, *4*, 69–100.

(16) Bordin, J. R.; Podgornik, R.; Holm, C. Static Polarizability Effects on Counterion Distributions Near Charged Dielectric Surfaces: A Coarse-Grained Molecular Dynamics Study Employing the Drude Model. *Eur. Phys. J.: Spec. Top.* **2016**, *225*, 1693–1705.

(17) Li, Z.; Bouchal, R.; Mendez-Morales, T.; Rollet, A.-L.; Rizzi, C.; Le Vot, S.; Favier, F.; Rotenberg, B.; Borodin, O.; Fontaine, O.; Salanne, M. Transport Properties of Li-TFSI Water-in-Salt Electrolytes. *J. Phys. Chem. B* **2019**, *123*, 10514–10521.

(18) Coustan, L.; Shul, G.; Bélanger, D. Electrochemical Behavior of Platinum, Gold and Glassy Carbon Electrodes in Water-in-Salt Electrolyte. *Electrochem. Commun.* **2017**, *77*, 89–92.

(19) Suo, L.; Oh, D.; Lin, Y.; Zhuo, Z.; Borodin, O.; Gao, T.; Wang, F.; Kushima, A.; Wang, Z.; Kim, H.-C.; Qi, Y.; Yang, W.; Pan, F.; Li, J.; Xu, K.; Wang, C. How Solid-Electrolyte Interphase Forms in Aqueous Electrolytes. *J. Am. Chem. Soc.* **2017**, *139*, 18670–18680.

(20) Steinrück, H.-G.; Cao, C.; Lukatskaya, M.; Takacs, C.; Wan, G.; Mackanic, D.; Tsao, Y.; Zhao, J.; Helms, B.; Xu, K.; Borodin, O.; Wishart, J. F.; Toney, M. Interfacial Speciation Determines Interfacial Chemistry: X-ray-Induced Lithium Fluoride Formation from Water-in-salt Electrolytes on Solid Surfaces. *Angew. Chem., Int. Ed.* **2020**, *59*, 23180–23187.

(21) Suo, L.; Hu, Y.-S.; Li, H.; Armand, M.; Chen, L. A New Class of Solvent-in-Salt Electrolyte for High-Energy Rechargeable Metallic Lithium Batteries. *Nat. Commun.* **2013**, *4*, 1481.

(22) Chandrasekhar, J.; Spellmeyer, D. C.; Jorgensen, W. L. Energy Component Analysis for Dilute Aqueous Solutions of Lithium(1+), Sodium(1+), Fluoride(1-), and Chloride(1-) Ions. *J. Am. Chem. Soc.* **1984**, *106*, 903–910.

(23) Canongia Lopes, J. N. A.; Pádua, A. A. H. Nanostructural Organization in Ionic Liquids. *J. Phys. Chem. B* **2006**, *110*, 3330–3335.

(24) Elfgen, R.; Hollóczki, O.; Kirchner, B. A Molecular Level Understanding of Template Effects in Ionic Liquids. *Acc. Chem. Res.* **2017**, *50*, 2949–2957.

(25) Kashyap, H. K.; Hettige, J. J.; Annapureddy, H. V. R.; Margulis, C. J. SAXS Anti-Peaks Reveal the Length-Scales of Dual Positive–Negative and Polar–Apolar Ordering in Room-Temperature Ionic Liquids. *Chem. Commun.* **2012**, *48*, 5103–5105.

(26) Cammarata, L.; Kazarian, S. G.; Salter, P. A.; Welton, T. Molecular States of Water in Room Temperature Ionic Liquids. *Phys. Chem. Chem. Phys.* **2001**, *3*, 5192–5200.

(27) Feng, G.; Jiang, X.; Qiao, R.; Kornyshev, A. A. Water in Ionic Liquids at Electrified Interfaces: The Anatomy of Electrosorption. *ACS Nano* **2014**, *8*, 11685–11694.

(28) Bi, S.; Wang, R.; Liu, S.; Yan, J.; Mao, B.; Kornyshev, A. A.; Feng, G. Minimizing the Electrosorption of Water from Humid Ionic Liquids on Electrodes. *Nat. Commun.* **2018**, *9*, 5222.

(29) Chen, M.; Wu, J.; Ye, T.; Ye, J.; Zhao, C.; Bi, S.; Yan, J.; Mao, B.; Feng, G. Adding Salt to Expand Voltage Window of Humid Ionic Liquids. *Nat. Commun.* **2020**, *11*, 5809.

(30) Borodin, O.; Suo, L.; Gobet, M.; Ren, X.; Wang, F.; Faraone, A.; Peng, J.; Olguin, M.; Schroeder, M.; Ding, M. S.; Gobrogge, E.; von Wald Cresce, A.; Munoz, S.; Dura, J. A.; Greenbaum, S.; Wang, C.; Xu, K. Liquid Structure with Nano-Heterogeneity Promotes Cationic Transport in Concentrated Electrolytes. *ACS Nano* **2017**, *11*, 10462–10471.

(31) Dong, D.; Sälzer, F.; Roling, B.; Bedrov, D. How Efficient is Li^+ Ion Transport in Solvate Ionic Liquids under Anion-Blocking Conditions in a Battery? *Phys. Chem. Chem. Phys.* **2018**, *20*, 29174–29183.

(32) Drognet, L.; Grimaud, A.; Fontaine, O.; Tarascon, J.-M. Water-in-Salt Electrolyte (WiSE) for Aqueous Batteries: A Long Way to Practicality. *Adv. Energy Mater.* **2020**, *10*, 2002440.

(33) Yamada, Y.; Wang, J.; Ko, S.; Watanabe, E.; Yamada, A. Advances and Issues in Developing Salt-Concentrated Battery Electrolytes. *Nat. Ener.* **2019**, *4*, 269–280.

(34) Kühnel, R.-S.; Reber, D.; Battaglia, C. Perspective—Electrochemical Stability of Water-in-Salt Electrolytes. *J. Electrochem. Soc.* **2020**, *167*, 070544.

(35) Marx, D.; Tuckerman, M. E.; Hutter, J.; Parrinello, M. The Nature of the Hydrated Excess Proton in Water. *Nature* **1999**, *397*, 601–604.

(36) Tuckerman, M. E.; Marx, D.; Parrinello, M. The Nature and Transport Mechanism of Hydrated Hydroxide Ions in Aqueous Solution. *Nature* **2002**, *417*, 925–929.

(37) McEldrew, M.; Goodwin, Z. A. H.; Kornyshev, A. A.; Bazant, M. Z. Theory of the Double Layer in Water-in-Salt Electrolytes. *J. Phys. Chem. Lett.* **2018**, *9*, 5840–5846.

(38) Aurbach, D.; Daroux, M.; Faguy, P.; Yeager, E. The Electrochemistry of Noble Metal Electrodes in Aprotic Organic Solvents Containing Lithium Salts. *J. Electroanal. Chem. Interfacial Electrochem.* **1991**, *297*, 225–244.

(39) Kitz, P. G.; Novák, P.; Berg, E. J. Influence of Water Contamination on the SEI Formation in Li-Ion Cells: An Operando EQCM-D Study. *ACS Appl. Mater. Interfaces* **2020**, *12*, 15934–15942.

(40) Xiong, D. J.; Petibon, R.; Madec, L.; Hall, D. S.; Dahn, J. R. Some Effects of Intentionally Added Water on LiCoO_2 /Graphite Pouch Cells. *J. Electrochem. Soc.* **2016**, *163*, A1678–A1685.

(41) Castelli, I. E.; Zorko, M.; Østergaard, T. M.; Martins, P. F. B. D.; Lopes, P. P.; Antonopoulos, B. K.; Maglia, F.; Markovic, N. M.; Strmcnik, D.; Rossmeisl, J. The Role of an Interface in Stabilizing Reaction Intermediates for Hydrogen Evolution in Aprotic Electrolytes. *Chem. Sci.* **2020**, *11*, 3914–3922.

(42) Wang, R.; Boyd, S.; Bonnesen, P. V.; Augustyn, V. Effect of Water in a Non-Aqueous Electrolyte on Electrochemical Mg^{2+} Insertion into WO_3 . *J. Power Sources* **2020**, *477*, 229015.

(43) Lemaire, P.; Sel, O.; Alves Dalla Corte, D.; Iadecola, A.; Perrot, H.; Tarascon, J.-M. Elucidating the Origin of the Electrochemical Capacity in a Proton-Based Battery H_2IrO_4 via Advanced Electrogravimetry. *ACS Appl. Mater. Interfaces* **2020**, *12*, 4510–4519.

(44) Yang, C.; Rousse, G.; Svane, K. L.; Pearce, P. E.; Abakumov, A. M.; Deschamps, M.; Cibir, G.; Chadwick, A. V.; Dalla Corte, D. A.; Hansen, H. A.; Vegge, T.; Tarascon, J.-M.; Grimaud, A. Cation Insertion to Break the Activity/Stability Relationship for Highly Active Oxygen Evolution Reaction Catalyst. *Nat. Commun.* **2020**, *11*, 1378.

(45) Alexiev, V.; Meyer zu Altenschildesche, H.; Prins, R.; Weber, T. Solid-State NMR Study of Hydrated Intercalation Compounds of Molybdenum Disulfide. *Chem. Mater.* **1999**, *11*, 1742–1746.

(46) Díaz-Duque, A.; Sandoval-Rojas, A. P.; Molina-Osorio, A. F.; Feliu, J. M.; Suárez-Herrera, M. F. Electrochemical Reduction of CO_2 in Water-Acetonitrile Mixtures on Nanostructured Cu Electrode. *Electrochem. Commun.* **2015**, *61*, 74–77.

(47) Figueiredo, M. C.; Ledezma-Yanez, I.; Koper, M. T. M. In Situ Spectroscopic Study of CO_2 Electroreduction at Copper Electrodes in Acetonitrile. *ACS Catal.* **2016**, *6*, 2382–2392.

(48) Marken, F.; Wadhawan, J. D. Multiphase Methods in Organic Electrosynthesis. *Acc. Chem. Res.* **2019**, *52*, 3325–3338.

(49) Dubouis, N.; Park, C.; Deschamps, M.; Abdelghani-Idrissi, S.; Kanduc, M.; Colin, A.; Salanne, M.; Dzubiella, J.; Grimaud, A.; Rotenberg, B. Chasing Aqueous Biphasic Systems from Simple Salts by Exploring the LiTFSI/LiCl/H₂O Phase Diagram. *ACS Cent. Sci.* **2019**, *5*, 640–643.

(50) Mendez-Morales, T.; Li, Z.; Salanne, M. Computational Screening of the Physical Properties of Water-in-Salt Electrolytes. *Batteries Supercaps* **2020**, DOI: [10.1002/batt.202000237](https://doi.org/10.1002/batt.202000237).