



“Water-in-salt” electrolyte for supercapacitors : a molecular dynamics study

Zhujie Li

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Sorbonne Université

École Doctorale 388 : Chimie Physique et Chimie Analytique de Paris Centre

Laboratoire Physicochimie des Électrolytes et des Nanosystèmes Interfaciaux

“Water-in-salt” electrolyte for supercapacitors: a molecular dynamics study

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Soutenue le 15 novembre 2018

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Contents

General introduction	9
Chapter 1: Introduction	11
1.1 Concentrated electrolytes	11
1.1.1 Solvent-in-salts	11
1.1.2 Water-in-salts	12
1.2 Application of water-in-salts in batteries	15
1.3 Application of water-in-salts in supercapacitors	18
1.4 Motivation and objective	21
Chapter 2: Methods	27
2.1 Molecular dynamics	27
2.1.1 General principle of molecular dynamics	27
2.1.2 Verlet algorithm	29
2.1.3 Ensembles	30
2.2 Interactions: the force field	32
2.2.1 Bonded interactions	32
2.2.2 Non-bonded interactions	33
2.3 Simulating constant potential electrodes	34
2.3.1 Fluctuating charges model and its implementation	34
2.3.2 Importance of polarizability of electrode	36

Chapter 3: Transport properties of water-in-salts: force field dependence	41
3.1 Simulation cell	41
3.2 Viscosity	43
3.2.1 Methods	43
3.2.2 Results	45
3.3 Diffusion coefficient	46
3.3.1 Methods	46
3.3.2 Results	47
3.4 Conductivity	48
3.4.1 Methods	48
3.4.2 Results	49
3.5 Comparison with other force fields	51
3.5.1 Type of force fields	51
3.5.2 Results	52
3.6 Conclusions	54
Chapter 4: Structural properties of water-in-salt electrolyte	57
4.1 Solvation shell of Lithium	57
4.1.1 Coordination number of Lithium	57
4.1.2 Residence time of water	60
4.1.3 Potential of mean force	62
4.1.4 Fraction of free water	64
4.1.5 Lithium-lithium dimer	65
4.2 Role of water	69
4.2.1 Coordination number of water	69
4.2.2 Competition between Li and TFSI	70
4.3 Conclusions	71
Chapter 5: Water-in-salt electrolyte at interface	73
5.1 Model and computational details	74

5.2	Number density and charge density	76
5.3	Calculation of integral capacitance from average surface charge	80
5.3.1	Average surface charge	80
5.3.2	Integral capacitance of full electrochemical cell	81
5.4	Calculation of differential capacitance of single electrode based on po- tential drop	81
5.4.1	Poisson potential	81
5.4.2	Differential capacitance of single electrode	82
5.5	Calculation of differential capacitance of full cell from fluctuation of surface charge	85
5.5.1	Fluctuation of surface charge	85
5.5.2	Distribution of surface charge and differential capacitance . . .	86
5.6	Effects of potential-driven structural changes on differential capacitance	88
5.7	Conclusions	92
General conclusions		93
Appendix A		97
Appendix B		99
Bibliography		108

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General introduction

Electrochemical storage and conversion devices are in urgent need nowadays for the exploitation of energy generated from alternative but fluctuating sources, like wind and sun, in particular for employing them in emerging electrified systems, such as transport vehicles or advanced technological devices. At the core of these energy materials, such as batteries or supercapacitors, is typically the electrode/electrolyte couple, which strongly impacts the performance of the devices. Super-concentrated aqueous solutions recently emerged as promising electrolytes for high-performance energy storage systems due to their unique physico-chemical properties. Indeed, they differ markedly from conventional aqueous electrolytes. By dissolving salt at high concentrations in water, in which either the weight or volume ratios of salt-to-water exceed 1, a new family of electrolytes is classified as “water-in-salt”. It was demonstrated that these water-in-salt electrolytes exhibit high electrochemical stability windows (3–4 V) far beyond that of pure water (1.23 V), making it possible to achieve high-voltage performance in batteries and supercapacitors. However, comprehensive studies aiming at understanding the microscopic mechanisms at play in water-in-salt electrolytes and their properties at the interface are needed to fully exploit their properties.

In this thesis, we have performed molecular dynamics simulations to systemically investigate the transport and structural properties of lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) salt/water mixtures ranging from the dilute solution to the water-in-salt regime and the interfacial properties of a water-in-salt electrolyte at an extremely high concentration in supercapacitors. The thesis is divided into 5 chapters:

Chapter 1 starts with a brief introduction of the state-of-the-art concentrated elec-

trolytes, in particular, water-in-salts and their applications in batteries and supercapacitors. As a complement of experiments, molecular dynamics simulation studies of water-in-salt electrolytes are emphasized in the last part and the current research status is summarized, along with the presentation of the motivation and objective of this thesis at the end of this chapter.

Chapter 2 recalls the general principle of molecular dynamics, the basic algorithm and the common ensembles used in molecular dynamics simulations. The constant potential electrode model and its implementation in our simulations are briefly introduced, and the importance of accounting for the surface polarization is illustrated.

Chapter 3 is dedicated to the study of i) the transport properties of LiTFSI and water mixtures in a wide range of salt concentrations; and ii) the force field dependence of the transport properties at high concentrations. The viscosity, diffusion coefficients, and conductivity are computed and analyzed for various concentrations. Different parameterizations of force field are compared, which allows us to select the best parameters for further studies of highly concentrated water-in-salt.

Chapter 4 focuses on the structural properties of the water-in-salt electrolyte. The solvation property of lithium cations, such as the coordination number, the residence time of water in lithium's hydration shell, the potential of mean force for water molecules or TFSI anions escaping solvation shell of lithium, and the fraction of free water not bound to any lithium are computed and analyzed. The role of water in the water-in-salt electrolyte is analyzed based on the molecules local structural environments.

Chapter 5 presents the study of a super-concentrated water-in-salt electrolyte at the planar interface. The capacitive performance of a supercapacitor consisting of planar graphite electrodes separated by water-in-salt electrolyte is investigated. The evolutions of the interfacial structure at various applied potentials are analyzed to account for the non-trivial features of differential capacitance.

The last section summarizes all aforementioned aspects of this thesis and proposes some perspectives of future work.

Chapter 1

Introduction

1.1 Concentrated electrolytes

1.1.1 Solvent-in-salts

Liquid electrolytes can be classified according to their ionic concentrations. Two main families are generally used in electrochemical devices. In conventional electrolytes, the major species is a neutral solvent and a few, highly solvated ions are present; seawater is an archetypal example. On the contrary, ionic liquids are solvent-free electrolytes that have gained more and more attraction for energy storage applications over the past decade [1]. However, they suffer from a rather large viscosity, which hinders their use at relatively low temperatures.

Recently, a third class of liquid electrolytes was proposed, in which the ionic species are dissolved in large amounts inside the solvent [2], these are called “solvent-in-salts”. As shown in [Figure 1-1](#), the weight and volume ratios of salt-to-solvent are used to classify liquid electrolytes. The region C (both the weight and volume ratio are less than 1) covers most of the studied non-aqueous organic-based electrolytes, in which the salt concentration is generally limited in a range of 1–2 mol/L due to the solubility of the salt and optimal balance between viscosity and ionic conductivity. The increase of the salt concentration by choosing proper salt/solvent couple moves an electrolyte into the region A, B, and D in [Figure 1-1](#), in which the concept of

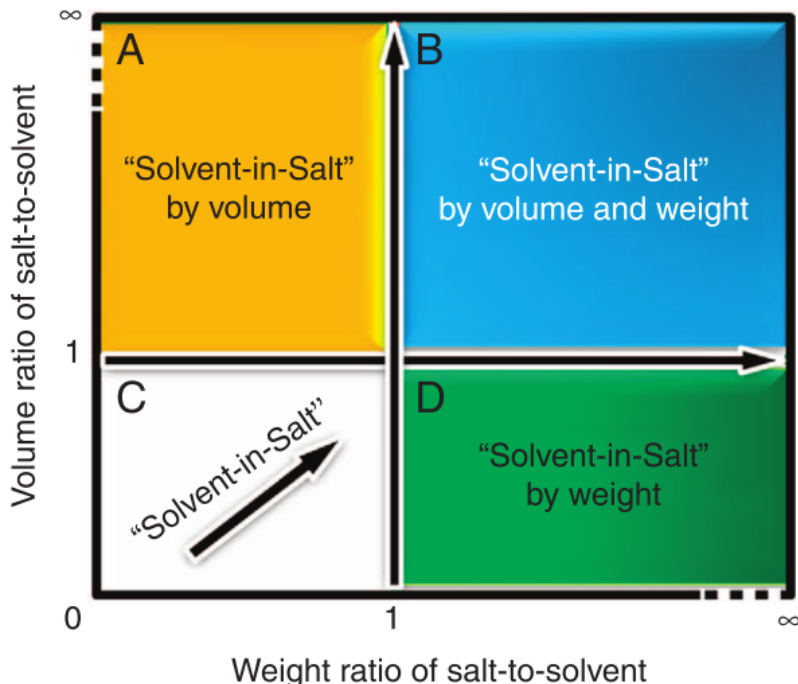


Figure 1-1: Distribution map of liquid electrolytes with weight and volume ratio of salt-to-solvent [2].

“solvent-in-salts” (SIS) is proposed and to denote highly concentrated electrolytes. Moreover, when the ratio is infinite (i.e., absence of the solvent), it is in the region of the above mentioned ionic liquids.

The synthesis of SIS electrolytes requires to find salts with a good solubility, which is generally the case when they are made of organic ions. However, Suo *et al.* showed that such concentrated electrolytes could also involve inorganic cations by using $\text{Li}[(\text{CF}_3\text{SO}_2)_2\text{N}]$ (LiTFSI). Due to the very low lattice energy of this salt, it can be mixed up to very large amounts with organic solvents. This work was extended to a series of other salts and solvents [3–26], which opens the way to explore new electrolytes for energy storage systems.

1.1.2 Water-in-salts

Among the potential solvents, water can be an attractive one due to its various advantages, such as non-toxic, high dielectric constant, and non-flammability, however, it is often discarded in electrochemical energy storage applications because of its narrow

electrochemical stability window (ESW) of 1.23 V, which allows neither high voltages nor high energies to be reached. Recently, this limitation was overcome through the introduction of a “water-in-salt” (WiS) electrolyte [27], for which the window could be extended to ≈ 4.0 V [28]. Such an important breakthrough leads to the development of aqueous-based electrolytes for energy storage systems.

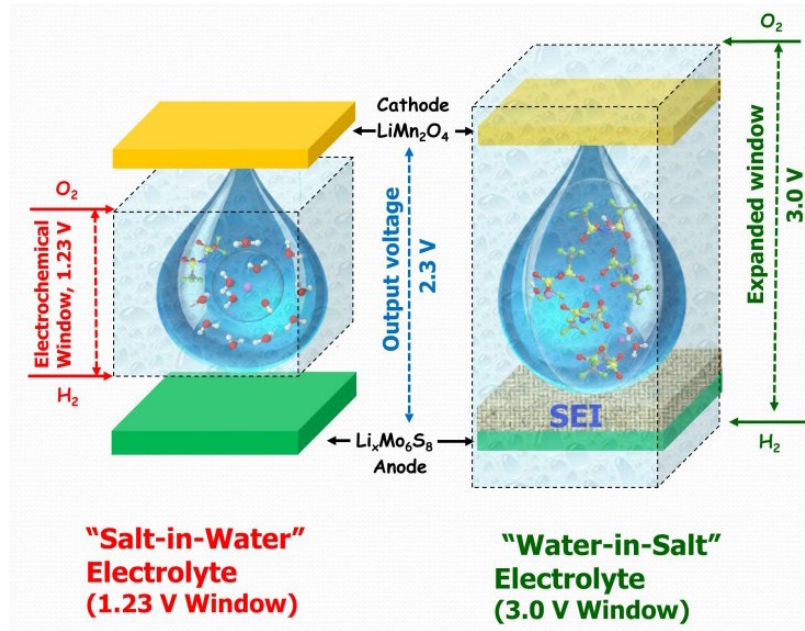


Figure 1-2: Illustration of enhanced electrochemical stability window (ESW) when switching from “salt-in-water” to “water-in-salt”. Adapted from *chargedevs.com*

Specifically, the first “water-in-salt” electrolyte was reported by Suo *et al.* in 2015, where LiTFSI is dissolved in water at extremely high salt concentration of 21 m (m = mol/kg) [27]. A high-voltage aqueous lithium-ion battery was enabled through the formation of the solid-electrolyte interphase (SEI) during the first cycles, which prevents the water molecules from undergoing irreversible redox reactions, as shown in Figure 1-2. Further study demonstrated that the anodic dissolution of aluminum was suppressed in such super-concentrated WiS electrolyte, enabling the use of cost-effective aluminum current collectors for WiS-based aqueous lithium-ion batteries [29]. Apart from the formation of the SEI, the significant decrease of “free” water (i.e., water molecules that remain uncoordinated by any lithium cations) at super-concentrated WiS electrolytes also hinders the hydrogen and oxygen evolution

involved in water hydrolysis at positive and negative electrodes. In the original work, the amount of free water molecules remains more than 15% of all water molecules at most concentrated status (21 m).

Considering that the maximum solubility of LiTFSI in water is 21–22 m at room temperature, it is thus not possible to further decrease of the portion of free water molecules. To overcome this limit, two main strategies were proposed: Firstly, by adding a second lithium salt into WiS electrolytes [30], it was reported that the fraction of free water was reduced to 11%, which further enhanced the redox stability of the so-called “water-in-bisalt” electrolyte, and thus leads to impressive performance in aqueous Li-ion batteries. Secondly, hydrate-melt lithium salt was reported as a promising electrolyte for high energy density aqueous batteries [31]. In this work, an eutectic composition of $\text{Li}(\text{TFSI})_{0.7}(\text{BETI})_{0.3} \cdot 2\text{H}_2\text{O}$ (where BETI denotes $\text{CF}_5\text{SO}_2)_2\text{N}$ anion) is regarded as a lithium salt hydrate-melt, in which all water molecules are coordinated by lithium cations, i.e., without any free water. The water activity is further reduced compared to that of “water-in-salt” or “water-in-bisalt” electrolytes.

Moreover, regarding the transport properties of WiS electrolytes, the ionic conductivity of 21 m LiTFSI remains 8.2 mS/cm at room-temperature [27], which is close to that of non-aqueous solutions (9 mS/cm) used in commercial lithium batteries. For the hydrate-melt electrolyte [31], though the viscosity is high (≈ 200 mPa·s), the ionic conductivity (3 mS/cm) is still comparable to that of Li-salt-based non-aqueous electrolytes. Furthermore, on the basis of the Walden plot, where electrolytes can be classified in terms of their performance as ionic conductors [32, 33], the WiS (21 m LiTFSI) and hydrate-melt ($\text{Li}(\text{TFSI})_{0.7}(\text{BETI})_{0.3} \cdot 2\text{H}_2\text{O}$) electrolytes can be regarded as good-ionic and super-ionic solutions, respectively [31]. The unexpectedly good performance of ionic conductivity for super-concentrated aqueous electrolytes, which is decoupled from the viscosity, is attributed to the water molecules that accelerate the cation’s diffusion. As reported by Borodin *et al.*, for WiS electrolyte (21 m LiTFSI) the liquid adopts a nano-heterogeneous structure with a 3D percolating lithium water network that promotes the cationic transport [34].

1.2 Application of water-in-salts in batteries

In 1994, the first aqueous Li-ion battery was proposed by Dahn and co-workers, providing an average operating voltage window of 1.5 V [35]. Since then, numerous efforts have been devoted to developments of aqueous rechargeable batteries in order to replace the flammable organic electrolytes. Significant improvements have been reached in this intriguing area with new battery chemistries explored [36–41]. However, as shown in Figure 1-3, the ESW for traditional aqueous electrolytes remains below 2 V. It is mainly limited by the hydrogen evolution at the anode, which is far above where most anode materials of lithium-ion batteries operate. As we discussed in the previous section, the use of WiS electrolytes enables a significant increase of the ESW allowing to reach high-voltage aqueous lithium-ion batteries [27].

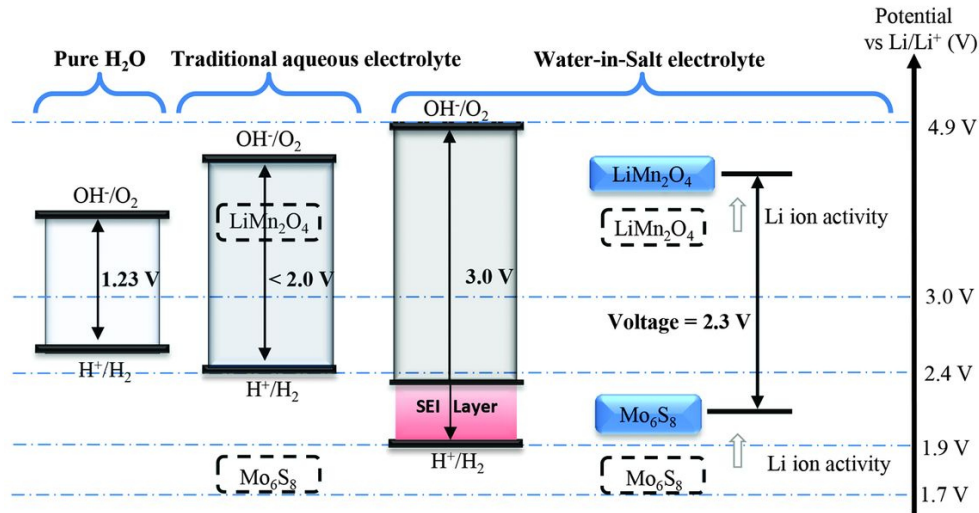


Figure 1-3: Illustration of the evolution of electrochemical stability window for aqueous electrolytes ranging from pure water to water-in-salt [27].

The successful applications of LiTFSI-based WiS electrolytes in batteries have attracted much attention since 2015, and numerous efforts have been made to expand the family of WiS electrolytes to other alkali metal-based (Li⁺, Na⁺, K⁺) electrolytes [28–30, 42–48, 48–54], multivalent metal-based (Mg²⁺, Ca²⁺, Zn²⁺) electrolytes [55–63], and even metal-free electrolytes containing NH₄⁺ cation [64].

It was demonstrated by Suo *et al.* that an alternative cathode material (LiFePO₄)

with larger electrochemical stability than the usual LiMn_2O_4 , has durability against a wide range of temperatures and superior performances, making it become a promising candidate for large-scale electric energy storage applications [42]. Apart from the application in lithium-ion batteries, WiS as an electrolyte for cathodically stable Li- O_2 battery operations was also reported very recently [45]. In Li- O_2 batteries, no reported organic electrolytes fulfill the stability requirements due to the high reactivity of oxygen in the system. However, the use of WiS electrolytes (21 m LiTFSI) without any organic solvents overcomes this limits. The WiS electrolyte, which has low water activity owing to the lack of free water, exhibits little reactivity towards Li_2O_2 or other oxygen species, leading to the stable operations of Li- O_2 battery.

Moreover, successive attempts aimed at exploring new Li-based WiS electrolytes have been reported, among them adding a second composition in water-in-LiTFSI solutions gained significant success. Inspired by the study of “water-in-bisalt” electrolyte containing 21 m LiTFSI and 7 m LiOTf (OTf = trifluoromethane sulfonate) [30], a hydrophilic polymer polyvinyl alcohol (PVA) was introduced into such electrolyte to form an aqueous gel [43]. It was reported that in this super-concentrated aqueous electrolyte, the unique sulfur chemistry involving a phase change from high-order polysulfide to low-order polysulfide experienced by the lithiation of sulfur was observed, leading to the application of WiS electrolytes for beyond Li-ion chemistry in Li-ion/sulfur cells with an excellent performance. Furthermore, the use of the same WiS-based gel polymer electrolyte, along with an extra protective SEI layer formed by pre-coating the graphite anode with a prepared gel, made it possible to achieve a 4 V class aqueous Li-ion battery, whose energy densities approach those of state-of-the-art Li-ion batteries but with significantly enhanced safety [28]. Similar electrolyte, where a homogeneous aqueous gel polymer formed at high temperature (95 °C) by dissolving 25 m LiTFSI and 10 wt% PVA in water, was prepared by Yang *et al.*. The reported superior energy (141 Wh kg^{-1}) and power (20.6 kW kg^{-1}) density, along with the flexible and robust electrodes in the symmetric cell, opens the way to manufacture lithium-ion batteries on the materials level.

The abundant and readily accessible features of sodium (Na) make it be inves-

tigated as an alternative ion of Li when targeting more economically competitive rechargeable batteries. Meanwhile, the development of aqueous sodium-ion batteries utilizing WiS electrolytes has made significant progress. Suo *et al.* demonstrated that a Na-ion WiS electrolyte containing 9.3 m NaOTf in water could expand the ESW to 2.5 V, owing to the formation of a Na⁺-conducting SEI along with the reduced water activity that prevents the hydrolysis reactions [50]. The combined analysis of Raman spectra and molecular dynamics simulations revealed that the frequent contacts between Na⁺ and F from the anions accompanied by a pronounced ion aggregation are mainly responsible for the formation of a stable SEI at much lower Na-salt concentration (9.3 m) than that of Li-salts discussed above. Kuhnelt *et al.* reported a sodium bis(fluorosulfonyl)imide (NaFSI) based WiS electrolyte at super-concentration of 35 m (this results may be questioned since several groups did not report such a high solubility), in which the molar ratio of water-to-salt is less than 2:1, can extend the ESW up to 2.6 V [48].

Multivalent metal-based batteries have attracted extensive interest as potential alternatives to lithium-ion batteries. Meanwhile, WiS electrolytes containing multivalent ions such as Mg²⁺, Ca²⁺, and Zn²⁺ have already applied in the field of rechargeable batteries [55–63]. Among them, aqueous Zn-ion batteries have been developed in particular. Zhang *et al.* reported that a concentrated aqueous electrolyte of Zn(OTf)₂, along with the cation-defected ZnMn₂O₄ as a stable cathode material, exhibited not only a wide ESW of 2.5 V but also the high efficiency and long-term stability for aqueous Zn-ion batteries [57]. Apart from these, the application of WiS electrolytes in hybrid Zn-ion based batteries were reported, in which the electrolytes are mixtures of Zn salt and other salts. By adding a small amount of Mn(OTf)₂ salt into the concentrated Zn(OTf)₂ electrolyte, Zhang *et al.* reported a Zn-MnO₂ battery system with high energy and power densities [59]. Hu *et al.* report that a formulated novel WiS electrolyte of 21 m LiTFSI and 1 m Zn(OTf)₂ enabled great improvements in both voltage platform and cycling stability for Zn/V₂O₅ aqueous hybrid-ion battery [58]. Moreover, a hybrid-Zn battery was reported by Wang *et al.* through the use of WiS electrolyte containing 1 m Zn(TFSI)₂ and 20 m LiTFSI [63].

The Zn metal anode combined with either LiMn_2O_4 or O_2 cathodes exhibited a high Zn reversibility along with high energy densities. Aqueous hybrid Zn/Na batteries were also reported by Li *et al.* very recently [62], in which 8 m NaClO_4 + 0.4 m $\text{Zn}(\text{OTf})_2$ WiS electrolyte was used.

So far, most reported WiS electrolytes including those above utilize fluorinated anions except for a few studies. However, Leonard *et al.* reported that the use of potassium acetate (KAc) aqueous solution at 30 m as a WiS electrolyte could provide an ESW of 3.2 V, broadening the exploration of new electrolytes for high-performance aqueous K-ion batteries [54]. Lukatskaya *et al.* reported that a mixed cation acetate WiS electrolyte (32 m KAc + 8 m LiAc) could be utilized to achieve high voltage (3 V) aqueous batteries, which has the reported lowest amount of water-to-salt ratio (1.3) that result in the absence of free water [47]. Moreover, aqueous Na-ion batteries with an inorganic electrolyte containing highly concentrated NaClO_4 salt dissolved in water were demonstrated to have high performances [49, 53]. Furthermore, an aqueous ammonium-ion (NH_4^+) battery based on a novel WiS electrolyte of 25 m $\text{NH}_4\text{CH}_3\text{COO}$ was reported by Holoubek *et al.* [64], which opens the way of exploring WiS electrolytes to the metal-free ones. Apart from these, a different battery utilizing all-organic (metal-free) electrodes together with WiS electrolyte (21 m LiTFSI) was reported by Dong *et al.*, which can deliver a supercapacitor-like high power density (32 kW kg^{-1}).

1.3 Application of water-in-salts in supercapacitors

Figure 1-4 shows the schematic of the Li-ion battery and supercapacitor. In contrast to batteries, supercapacitors rely on the highly reversible adsorption of ionic species at the electrode surfaces and the charging process is not limited by diffusion of ions in the bulk of the electrodes, allowing faster charging time, longer life cycles and higher power densities to be achieved but with a significantly lower energy delivery.

Therefore, supercapacitors can be regarded as promising energy storage systems that complement batteries or even replace them in high-power applications [65–67].

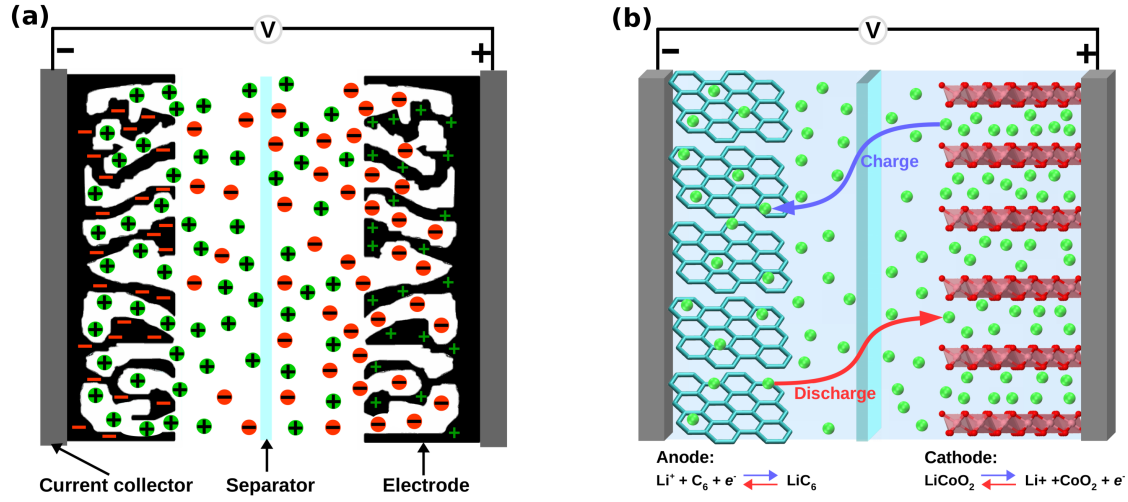


Figure 1-4: Schematic of (a) supercapacitor and (b) Li-ion battery.

The application of WiS electrolytes in supercapacitors have already attracted significant interest due to their successes in batteries [68–78]. Coustan *et al.* have recently obtained promising results by using a WiS electrolyte of 5 M (M = mol/L) LiTFSI (≈ 19 m), i.e., an increase of the ESW by 0.5 to 1 V depending on the chemical nature of the metallic electrode [68]. The authors attributed this effect to the presence of a negligible amount of free water molecules, which lead to an enhancement of the oxidative stability of the electrolyte on the positive electrode. The use of the same WiS electrolyte (19 m LiTFSI) in a MnO₂-based supercapacitor exhibited a slight increase of the potential stability range compared with that of salt-in-water electrolyte, while the electrochemical performance was not further improved when increasing the concentration to 21 m [69]. Moreover, Hasegawa *et al.* demonstrated that a high-voltage aqueous supercapacitor was achieved by employing activated carbon (AC) based electrodes with 5 M LiTFSI as the electrolyte. In this work, an expanded operating voltage of 2.4 V was reported for an aqueous AC/AC symmetric supercapacitor with good cycle performance.

Among questions raised by the above studies: on the one hand, high viscosity with a low ionic conductivity of WiS electrolyte, which is more sensitive in supercapacitors

than that in batteries, limits the use of WiS at very high concentrations of Li-salt above 19 m. On the other hand, in contrast to batteries, the SEI formed at the electrode surface reduce the effective surface area, leading to the direct decrease of capacitance in supercapacitors, which should be avoided here. All these emphasize the importance of optimizing the electrolyte and exploring new WiS electrolytes.

By investigating a wide range of salt molalities of LiTFSI as an aqueous electrolyte for supercapacitors, the operating voltage, power and energy densities, and electrochemical stability are compared by Lannelongue *et al.* [78], in which the 7 m LiTFSI WiS electrolyte was finally concluded to be the optimal one among them. A further study aimed at understanding the formation of SEI and eliminating its effects were reported. Coustan *et al.* investigated the electrochemical behavior of stainless steel electrode in 21 m LiTFSI WiS electrolyte, and pointed out that no SEI formed at potential cycling limited to a specific range, i.e., between 0 and -1.8 V, which gave new insight to design WiS-based electrolytes for supercapacitors [76].

Meanwhile the exploration of new WiS electrolytes have been reported by Reber *et al.* and Zhang *et al.* [72, 77], where Na-ion based WiS electrolytes for supercapacitors were proposed. The former group demonstrated that an 8 m NaTFSI solution exhibited a high ionic conductivity of 5 S/m, along with enhanced ESW, which had better capacitive performances using AC-based electrodes than that of 21 m LiTFSI electrolyte. Upon adding a redox additive (0.5 m KI) into 8 m NaTFSI, the AC/AC full cell can deliver a high energy density of 37.8 Wh kg⁻¹ with the operating voltage up to 1.8 V, which is comparable to the state-of-the-art non-aqueous supercapacitors. The latter group Zhang *et al.* reported that a MnO₂-based supercapacitor using 17 m NaClO₄ WiS as electrolyte displayed high energy and power densities and excellent cycle performance [77]. Moreover, a potassium acetate aqueous solution of 75 wt.% KAc (molar ratio of water-to-salt is 1.8) as WiS electrolyte was studied by Tian *et al.* [71]. The supercapacitor cell combined this electrolyte with AC/AC symmetric electrodes exhibited a high operating voltage of 2.0 V, along with enhanced energy densities compared with that of the normal concentration of the electrolyte.

Apart from these, Zhang *et al.* demonstrated that the use of a protected lithium

negative electrode and MO_2 or AC electrodes combined with WiS electrolyte (21 m LiTFSI) could expand the maximum cell voltages (4.4 V or 4 V) and operating voltages (1.5 V or 1.8 V), making them become high-performance hybrid supercapacitors [79]. Dou *et al.* developed a hybrid organic/aqueous electrolyte by introducing a co-solvent-in-salt system, i.e., acetonitrile was added into 21 m LiTFSI WiS electrolyte yielding a “acetonitrile/water-in-salt” (AWiS) hybrid electrolyte [74]. The optimal AWiS hybrid electrolyte with a salt concentration of 5 m provided improved conductivity, decreased viscosity and lowered freezing temperature compared with 21 m LiTFSI WiS while inherited the featured advantages of WiS electrolyte, i.e., moisture-tolerant, non-flammable, wide ESW of 3 V. The presence of acetonitrile molecules separates the Li cations and TFSI anions, and thus weakens the electrostatic cation-anion attractions, which ultimately results in the enhanced transport properties. Taking all these advantages, a model supercapacitor using the 5 m AWiS electrolyte displayed significant enhanced specific capacitance and high-rate capability, along with a wide operating voltage of 2.2 V.

1.4 Motivation and objective

Computer simulation studies have played a crucial role in understanding the mechanisms at play for electrochemical systems, in particular, molecular dynamics (MD) has become the more widely used approach to obtain a realistic picture of the systems at the atomistic/molecular-scale. Among the studies of WiS electrolytes, especially their applications in batteries and supercapacitors, MD simulations have served as important complements of experiments. In the original study of WiS electrolyte [27], the solvation property of Li cations was studied by MD simulations. The analysis of the coordination number of water molecules and TFSI anions in the first solvation shell of lithium and the fraction of free water, which illustrated the evolution of the Li cation primary solvation shell at salt concentration ranging from dilute (salt-in-water) to super-concentrated (water-in-salt). In Figure 1-5a, upon increasing the salt concentration, a decrease of the average number of water molecules coordinated by lithium

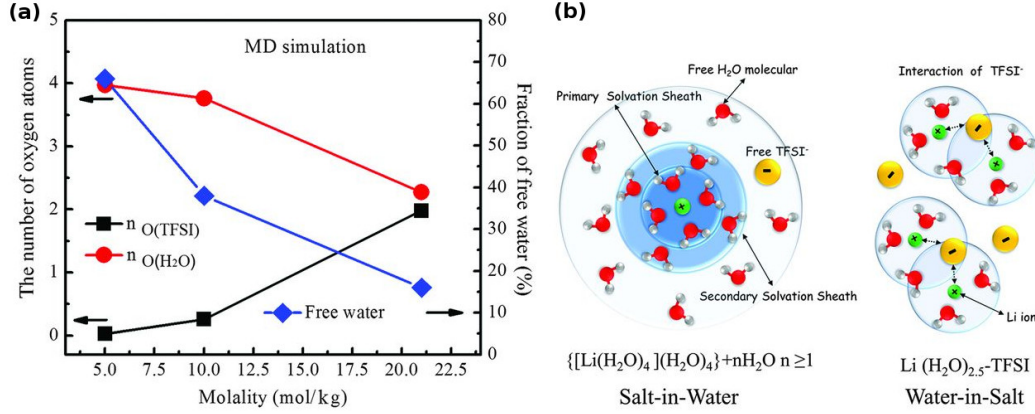


Figure 1-5: Solvation property of Li cations obtained from MD simulations. (a) Coordination number of O(water) and O(TFSI) in the first solvation shell of Li^+ and the fraction of free water not coordinated by any Li^+ . (b) Illustration of the evolution of the lithium primary solvation shell in dilute and water-in-salt solutions. Adapted from Suo *et al.* [27].

cation was observed, along with a significant abatement of the fraction of free water up to 15%, while the number of TFSI anions participated in the lithium solvation shell was growing. As a consequence, the primary solvation shell of the lithium cation experienced tremendous changes as illustrated in Figure 1-5b when switching from low to high salt concentration regime. Moreover, MD simulations have applied in several other studies of WiS electrolytes, in which the other structure properties, such as radial distribution function (RDF), ion aggregations [30, 31, 50], were investigated, in addition to the solvation properties [47, 63]. Apart from these, a paramount study of the bulk WiS electrolyte was reported, in which not only the above-mentioned structure properties but also the transport properties (such as diffusion coefficient and ionic conductivity) were investigated by molecular dynamics simulations in combination with small-angle neutron scattering and a variety of spectroscopic techniques [34]. A liquid structure of nano-heterogeneous domains was adopted at concentrated LiTFSI WiS electrolytes (from 10 to 21 m) due to the presence of disproportionate cation solvation induced by solvent-separated lithium cations, in which the lithium-water domain (without TFSI) served as a 3D percolating channel accounting for the fast transport of lithium cation.

As demonstrated above that the utility of MD simulations in the study of WiS

electrolytes enables a deep understanding of the bulk structure, and thus leading to a better design of new electrolytes for energy storage systems with enhanced electrochemical performances. While the microscopic picture of WiS electrolytes remains lack of information on the nature and characterization of the solvation complexes, motivating us to further investigate various properties of such systems in a wide range from diluted to super-concentrated solutions.

Thus, the first objective of this thesis is to comprehensive understanding the bulk properties of WiS electrolyte by performing MD simulations. To this end, the concentration dependence of the transport properties will mainly be discussed in chapter 3 and the detailed structural properties including analysis from the thermodynamic point of view, i.e., the strength of lithium solvation shell and water exchange rate inside which was seldom reported so far, will be discussed in chapter 4. However, an accurate MD simulation is entirely depended on a reliable model of the system to be investigated, i.e. the choice of an appropriate force field would determine the precision of the description of a given system. Diverse molecular dynamics simulations using either the classical force field [80] (where the conductivity and diffusion coefficients are underestimated by more than one order of magnitude at 20 m compared with those reported experimentally [27, 34]) or polarizable force field [27, 30, 34, 50] have all been performed in the aforementioned studies, among which different force field parameters were used even for the same system with identical compositions [27, 34], emphasizing the difficulty for precisely simulating WiS electrolytes. Thus, in this thesis, various transport properties including diffusion coefficient and viscosity, which are usually much more difficult to reproduce than the structural ones for concentrated electrolytes, are obtained using a set of different force fields in comparison to the experimental measurements and finally an optimum one is selected.

Interfaces between electrodes and electrolytes play a significant role in many processes for energy storage systems, such as electrochemical reactions in batteries and capacitance in supercapacitors. MD simulations have reported for the study of interfacial structures at electrode/WiS interfaces. As mentioned in the previous section where a 4 V aqueous Li-ion battery was reported [28], MD simulations were also

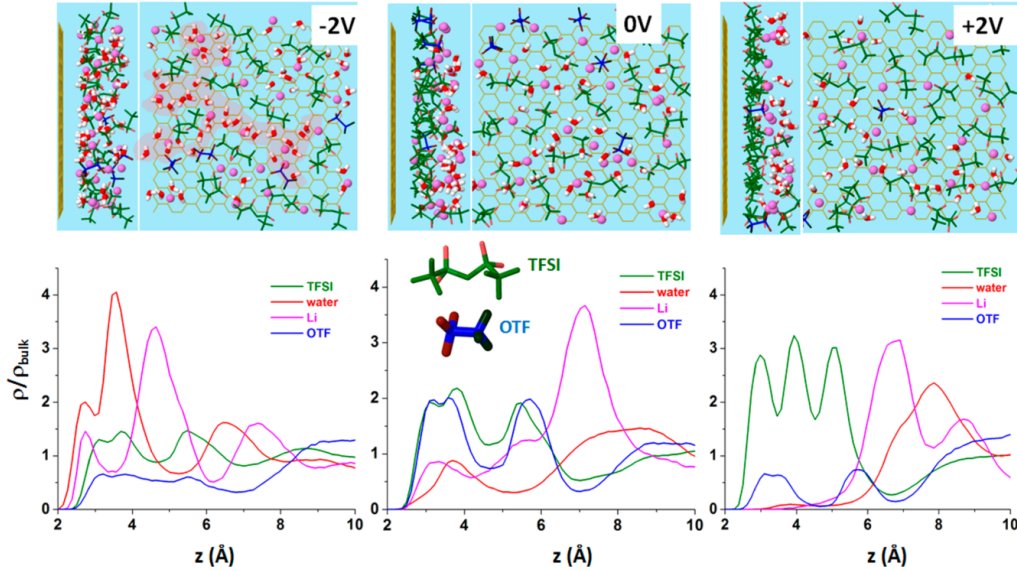


Figure 1-6: Snapshots of the interfacial layer for “water-in-Bisalts” electrolyte containing 21 m LiTFSI and 7 m LiOTf at planar graphite electrode surface (top) and the corresponding density profiles normalized by bulk density as a function of distance from the electrode (bottom) at -2, 0, and 2 V *vs* the potential of zero charge [81].

involved therein, which revealed the adsorbed structures of WiS electrolyte on electrode surfaces at different applied potentials. Further MD simulation study of the WiS electrolyte at planar graphite interfaces was reported by Vatamanu *et al.*, where the wide ESW of WiS electrolytes was explained through the investigation of density distributions for water and ions at interfacial layers [81]. Figure 1-6 shows the density profiles of ions and water at the potential of zero-charge (PZC) and the negatively and positively charged electrodes, along with corresponding snapshots of interfacial structures. At -2 V versus PZC, water molecules adsorb with hydrogens pointing toward the electrode surface at the interfacial layer. In contrast, at 2 V versus PZC, TFSI anions dominate the interfacial layer while water molecules are expelled from this region, corresponding to the favorable formation of SEI layer, which prevents the hydrolysis of WiS electrolyte at the positive electrode, and thus responsible for the large ESW of WiS. These simulation studies have revealed the basic microscopic picture of interfacial structures and provided insight into enhanced battery performances. While there is still lack of deep understanding of the dynamic processes at WiS/electrode interfaces, such as the adsorption of WiS electrolyte which plays a key

role in determining the performance of its application in supercapacitors.

Therefore, the second objective of this thesis is to fill the gap of quantifying the supercapacitor performance utilizing WiS electrolyte. To this end, the interfacial capacitance, which is one of the most important physical properties, intimately associated with the energy and power densities of supercapacitors, will be computed and analyzed in chapter 5 for a given WiS electrolyte (20 m LiTFSI) in supercapacitors. Moreover, its potential dependence behavior will also be discussed in light of the structural changes occurring inside the electric double-layer.

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Chapter 2

Methods

2.1 Molecular dynamics

2.1.1 General principle of molecular dynamics

Computer simulations generate information at the microscopic level, i.e. atomistic or molecular positions, velocities, etc. it is then possible to convert this very detailed information into macroscopic quantities, such as pressure, internal energy, etc. The experimentally observable properties associated with these macroscopic terms are reasonably assumed to be given by the temporal average:

$$\mathcal{A}_{\text{obs}} = \langle \mathcal{A}(t) \rangle_{\text{time}} = \lim_{t_{\text{obs}} \rightarrow \infty} \frac{1}{t_{\text{obs}}} \int_0^{t_{\text{obs}}} \mathcal{A}(t) dt \quad (2.1)$$

where $\mathcal{A}_{\text{obs}}$ is the macroscopic observable and the angle brackets denote the temporal average. The system is considered to obey to classical mechanics, so that the equations governing its time evolution are the well known Newton's equations of motion, which may be written:

$$m_i \ddot{\mathbf{r}}_i = \mathbf{f}_i \quad \mathbf{f}_i = -\frac{\partial}{\partial \mathbf{r}_i} U(\{\mathbf{r}_i\}) \quad (2.2)$$

where m_i , $\mathbf{r}_i$ and $\ddot{\mathbf{r}}_i$ are the mass of the particle i , its position coordinate and its acceleration. The total force $\mathbf{f}_i$ acting on the particle i is the gradient of the total potential energy $U(\{\mathbf{r}_i\})$.

Molecular dynamics (MD), which consists in modeling the evolution over time for an N-particle system therefore requires to solve the corresponding set of Newton's equation iteratively. With Equation 2.2, we immediately understand that the choice of the interaction potential U between the different particles, which is at the base of the computation of the forces $\mathbf{f}_i$, is of great importance for the reliability of the simulations. Since these forces are calculated at each step of the integration, the form of the interactions must be both sufficiently close to reality to correctly describe the evolution of the system and sufficiently simple for the computational cost of the forces to remain compatible with the current performance of computers.

So far as the calculation of the time averages is concerned, we clearly cannot hope to extend the integration of Equation 2.1 to infinite time, but might be satisfied to average over a long finite time, in which we solve Newton's equation for a given system until the properties of the system no longer change with time (i.e., equilibrate the system). After equilibration, the integration of Newton's equations makes it possible to generate a trajectory, i.e., a set of S configurations for the studied system. These configurations, or micro-states, correspond to particular macroscopic quantities and are obtained in a given statistical set. The determination of the macroscopic observables is carried out considering that the set of S configurations extracted from the trajectory is equivalent to a large number of independent configurations, which is also called the 'ergodicity hypothesis'. During a molecular dynamics simulation, a magnitude $\mathcal{A}$ can take a multitude of discrete values $\mathcal{A}_i$. Under the ergodicity hypothesis, the average value of a macroscopic observable $\mathcal{A}$ equals to the overall average over the whole S configurations. Thus, the Equation 2.1 can be rewritten as:

$$\mathcal{A}_{\text{obs}} = \langle \mathcal{A} \rangle_S = \sum_{i=0}^S p_i \mathcal{A}_i \quad (2.3)$$

where p_i is the probability of observing the value $\mathcal{A}_i$ for a given system.

2.1.2 Verlet algorithm

The algorithm used to integrate the equations of motion must be efficient and must make it possible to verify certainly important properties of Newton's equation: the conservation of the energy, the conservation of the total momentum, the conservation of the angular momentum and the reversibility of time. We will explain here as an example Verlet's algorithm [82, 83]. The positions of a particle at time $t \pm \Delta t$, with Δt the integration step, can be determined according to Taylor expansions:

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \frac{d\mathbf{r}_i(t)}{dt} \cdot \Delta t + \frac{d^2\mathbf{r}_i(t)}{dt^2} \cdot \frac{\Delta t^2}{2} + \frac{d^3\mathbf{r}_i(t)}{dt^3} \cdot \frac{\Delta t^3}{6} + \mathcal{O}(\Delta t^4) \quad (2.4)$$

$$\mathbf{r}_i(t - \Delta t) = \mathbf{r}_i(t) - \frac{d\mathbf{r}_i(t)}{dt} \cdot \Delta t + \frac{d^2\mathbf{r}_i(t)}{dt^2} \cdot \frac{\Delta t^2}{2} - \frac{d^3\mathbf{r}_i(t)}{dt^3} \cdot \frac{\Delta t^3}{6} + \mathcal{O}(\Delta t^4) \quad (2.5)$$

The Verlet's algorithm is then obtained by summing these two equations:

$$\begin{aligned} \mathbf{r}_i(t + \Delta t) &= 2\mathbf{r}_i(t) - \mathbf{r}_i(t - \Delta t) + \frac{d^2\mathbf{r}_i(t)}{dt^2} \cdot \Delta t^2 + \mathcal{O}(\Delta t^4) \\ &= 2\mathbf{r}_i(t) - \mathbf{r}_i(t - \Delta t) + \frac{\mathbf{f}_i}{m_i} \cdot \Delta t^2 + \mathcal{O}(\Delta t^4) \\ &\approx 2\mathbf{r}_i(t) - \mathbf{r}_i(t - \Delta t) + \frac{\mathbf{f}_i}{m_i} \cdot \Delta t^2 \end{aligned} \quad (2.6)$$

Thus, the position of the particle i at time $t + \Delta t$ is calculated from its positions at times t and $t - \Delta t$, and the force acting on it at time t . We must keep in mind from this development that the calculated trajectory numerically depends on the chosen integration step. If the time step is too long, the properties of conservation and reversibility of time associated with the Newton's equation will no longer be verified and the trajectory will not be exploitable.

The trajectory is generated from an initial configuration, which must be originally built. The closer the initial configuration is to a realistic situation, the easier it will be to produce a workable trajectory. The representativity of the trajectory obtained for the N particles is extremely important because all the macroscopic properties that

we seek to study are statistical averages of microscopic properties. As a result, if the trajectory is not realistic, due to a poor choice of interaction potential between particles or a too large time step, all the estimated properties will be tainted with errors. For the rest of this thesis, it is thus important to choose the force field and the initial configuration correctly, i.e., the formulation of the interactions between particles (more details will be discussed later) and the geometry of different constituents, to describe the system in a way adapted to the properties we wish to study.

2.1.3 Ensembles

There are many statistical sets (ensembles) commonly sampled in molecular dynamics.

Firstly, the microcanonical ensemble corresponds to an evolution of the system during which the Hamiltonian $\mathcal{H}$ of the system, i.e the sum of the kinetic energy and the potential energy, is preserved. This set is also called NVE ensemble because the evolution of the system is made of fixed number of particles (N), volume (V) and constant energy (E). The microcanonical partition function may be written:

$$\begin{aligned} Q_{NVE} &= \sum_{\mathbf{\Gamma}} \delta(\mathcal{H}(\mathbf{\Gamma}) - E) \\ &= \frac{1}{N!} \frac{1}{h^{3N}} \int d\mathbf{r} d\mathbf{p} \delta(\mathcal{H}(\mathbf{r}, \mathbf{p}) - E) \end{aligned} \quad (2.7)$$

where $\mathbf{\Gamma}$ represents the set of particle positions ($\mathbf{r}$) and momenta ($\mathbf{p}$), $\mathcal{H}$ is the Hamiltonian, and δ is the delta function which is proportional to the probability density for this ensemble.

Secondly, it is possible to simulate a system in equilibrium with a thermostat at a temperature T . The corresponding statistical set is the canonical set (NVT ensemble). The canonical partition function is:

$$\begin{aligned} Q_{NVT} &= \sum_{\mathbf{\Gamma}} \exp(-\mathcal{H}(\mathbf{\Gamma})/k_B T) \\ &= \frac{1}{N!} \frac{1}{h^{3N}} \int d\mathbf{r} d\mathbf{p} \exp(-\mathcal{H}(\mathbf{r}, \mathbf{p})/k_B T) \end{aligned} \quad (2.8)$$

The appropriate thermodynamic function is the Helmholtz free energy A

$$A/k_B T = -\ln Q_{NVT} \quad (2.9)$$

In the canonical ensemble, all values of the energy are allowed and energy fluctuations are non-zero. In practice, the system is coupled to a thermostat that changes the equations of motion to maintain the temperature at a fixed value. An algorithm often used to perform this type of simulation is the algorithm of Nosé-Hoover [84–86], which is based on the addition of a term to the Hamiltonian:

$$\mathcal{H}(\mathbf{r}, \mathbf{p}, p_s, s) = \sum_i \frac{\mathbf{p}_i^2}{2m_s^2} + \frac{1}{2} \sum_{ij, i \neq j} \mathcal{U}(\mathbf{r}_i - \mathbf{r}_j) + \frac{p_s^2}{2Q} + gkT \ln(s) \quad (2.10)$$

where g is the number of independent momentum degrees of freedom of the system, Q is an imaginary mass which should be chosen carefully along with systems. This additional term constrains the kinetic energy of the system to be equal to a chosen value. For simulating the bulk properties of WiS electrolyte in chapters 3 and 4, the NVT ensemble is used. Moreover, if we simulate a system using no external field and in which the center of mass is not fixed or if we have more than one conservation law, the Nosé-Hoover chains thermostat has to be employed to obtain the correct canonical distribution [87]. Other thermostats, such as velocity rescaling, the Andersen thermostat, the Berendsen thermostat and Langevin dynamics, can also be used to control temperature. Among them, Langevin thermostat is employed to simulate the WiS electrolyte at interfaces in Chapter 5. In this thermostat, the Newton's equations of motion are modified as:

$$m\ddot{\mathbf{r}} = -\frac{\partial}{\partial \mathbf{r}} U - \gamma \dot{\mathbf{r}} + \sqrt{2\gamma k_B T} R(t) \quad (2.11)$$

where γ is the viscosity and $R(t)$ is a delta-correlated stationary Gaussian process

with zero-mean, satisfying:

$$\begin{aligned}\langle R(t) \rangle &= 0 \\ \langle R(t)R(t') \rangle &= \delta(t - t')\end{aligned}\tag{2.12}$$

Apart from the two ensembles as mentioned above, there are two other common statistical ensembles, i.e., the isothermal-isobaric constant- NPT ensemble and the grand canonical constant- μVT ensemble. The coupling of the system with a thermostat and a barostat makes it possible to carry out simulations in the NPT ensemble, in which the volume (V) of the simulation box is then allowed to vary.

In general, the above mentioned thermodynamic variables are fixed for each ensemble, and other thermodynamic quantities must be determined by ensemble average. It is important to know in which ensemble the simulations are conducted to distinguish whether a macroscopic quantity is actually calculable from the trajectories.

2.2 Interactions: the force field

In molecular dynamics simulations, the formulation of interactions between particles involved in a system is diverse. Among them, the OPLS (or AMBER) force field is generally used in the classical molecular dynamics simulations when take into account all the atoms from the molecules as interaction sites. In OPLS [88] (or AMBER [89, 90]) force field, the total interaction potential is composed of bonded and non-bonded terms:

$$E_{\text{total}} = E_{\text{bonds}} + E_{\text{angles}} + E_{\text{dihedrals}} + E_{\text{non-bonded}}\tag{2.13}$$

2.2.1 Bonded interactions

The bonded (i.e., intramolecular) interactions include the first three terms, E_{bonds} , E_{angles} , $E_{\text{dihedrals}}$, in Equation 2.13, which take the following forms:

$$E_{\text{bonds}} = \sum_{ij}^{\text{bonds}} \frac{k_{ij}^r}{2} (r_{ij} - r_{ij}^{\text{eq}})^2\tag{2.14}$$

$$E_{\text{angles}} = \sum_{ijk}^{\text{angles}} \frac{k_{ijk}^{\theta}}{2} (\theta_{ijk} - \theta_{ijk}^{eq})^2 \quad (2.15)$$

$$E_{\text{dihedrals}} = \sum_{ijkl}^{\text{dihedrals}} \sum_{m=1}^4 \frac{V_{ijkl}^m}{2} [1 + (-1)^m \cos m\phi_{ijkl}] \quad (2.16)$$

The sums respectively run over the full set of instantaneous bonds r_{ij} , angles θ_{ijk} and dihedrals ϕ_{ijkl} , which must be defined prior to the simulations, i.e., the bonds are not allowed to break or form during the simulation. The quantities $k_{ij}^r, r_{ij}^{eq}, k_{ijk}^{\theta}, \theta_{ijk}^{eq}$ and V_{ijkl}^m are parameters of the force field. Specifically, in [Equation 2.14](#), the “bonds” typically involve the distance $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ of adjacent pairs of atoms in a molecular framework, and the form is assumed to be a harmonic with specified equilibrium bond distance r_{ij}^{eq} and spring constant k_{ij}^r . In [Equation 2.15](#), the “bend angles” are between successive bond vectors involving three atom coordinates, and this bending term is taken to be quadratic in angular displacement from the equilibrium value. Finally, in [Equation 2.16](#), the “torsion angles” are defined in terms of three connected bonds (i.e., four atom coordinates), and the torsion potential involves an expansion in periodic functions of order $m = 1, 2, 3, 4$.

2.2.2 Non-bonded interactions

The last term in [Equation 2.13](#) represents the non-bonded interactions, which is in principle composed of three contributions

$$E_{\text{non-bonded}} = E_{\text{repulsion}} + E_{\text{dispersion}} + E_{\text{electrostatic}} \quad (2.17)$$

In some simulations of complex fluids, it is sufficient to use the simplest models that faithfully represent the essential physics. In this thesis, we use the Lennard-Jones potential form, which gathers both the repulsion and dispersion terms in [Equa-](#)

tion 2.17 and is given by:

$$\begin{aligned} E_{\text{Lennard-Jones}} &= E_{\text{repulsion}} + E_{\text{dispersion}} \\ &= \sum_i \sum_{j>i} 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \end{aligned} \quad (2.18)$$

where r_{ij} is the distance between particle i and j . σ_{ij} and ϵ_{ij} are the finite distance at which the inter-particle potential is zero and dielectric constant (i.e., the depth of the potential well), respectively, which are obtained using the geometric combining rules $\sigma_{ij} = \sqrt{\sigma_i \sigma_j}$ and $\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$ in OPLS-like force field.

The last term of electrostatic interactions in Equation 2.17 is represented by the usual Coulomb potential

$$E_{\text{electrostatic}} = E_{\text{Coulomb}} = \frac{1}{4\pi\epsilon_0} \sum_i \sum_{j>i} \frac{q_i q_j}{r_{ij}} \quad (2.19)$$

where ϵ_0 is the vacuum permittivity, and q_i , q_j are the charges of particles i and j . Note that an integer value of the total charge for a single ion is set in most of the simulations. However, the total charge of ion is smaller than its formal value due to polarization or charge transfer effects. Therefore, the reduced charge strategy is used to mimic the polarization effects. In this thesis, both the formal charge and reduced charge methods are taken into account when perform the molecular dynamics simulations.

2.3 Simulating constant potential electrodes

2.3.1 Fluctuating charges model and its implementation

In molecular dynamics simulations of supercapacitors, the choice of an appropriate model for the electrode presents a substantial challenge due to the difficulty in defining a consistent classical atomistic model for a metallic electrode. In the majority of the MD simulations, the charges carried by the electrode atoms are assumed to be

constant during the simulation and homogeneously distributed on the surface of the electrode [91–94]. While the fluctuations of the charge on the electrode, which is neglected in the constant charge method, contain information on the microscopic correlations within the adjacent electrolyte solution and their effect on the electronic properties of the electrode-electrolyte interface. Thus, it is important to take into account such fluctuations, which could be achieved by introducing a polarizable model involving fluctuating charges.

There are several ways to include polarization in classical MD simulations. In all cases, the introduction of polarizability induces an additional calculation cost. However, in systems such as supercapacitors, where electrostatic interactions and electronic conduction play a crucial role in the determination of properties, it appears essential to represent this polarizability. The polarizability of atoms, ions or molecules is the ability of the electron cloud to deform under the effect of an electric field. For electrodes, we denote the polarizability as the ability of the material to conduct the current, i.e., the redistribution of the charges on different atoms constituting the solid electrode under the effect of an electric field. To take into account the polarizability of atoms, ions or molecules, several models exist. A first option is to assign the atoms a point dipole. The dipoles are then considered as additional degrees of freedom determined at each time step by a procedure for minimizing the total polarization energy [95]. A second option consists in assigning to each polarizable atom a Drude oscillator [96], that is each atom/ion carries two point charges separated by a spring [97]. A variant of this model is to consider a rigid “rod” of a certain length replace the spring. The rotation of the rod makes it possible to model the polarizability. This second approach has been successfully used to model the interface between an ionic liquid and a metal surface in order to study the stabilization of metal nanoparticles in an ionic liquid medium, the friction properties of these liquids or the structure of the liquid at the interface [98–101].

The main limitation of the two approaches described so far is the effective way to apply a potential difference between the electrodes. In molecular dynamics simulations, Siepmann and Sprik [102] have introduced a method for treating atomic charges

of the electrode as additional degrees of freedom. That is, the polarization is not represented by the assignment of a dipole to the atoms but by the fluctuation of the charge they carry. In the original work, the charges evolved following Car-Parrinello dynamics in order to maintain the electrode potential close to a target value. This model has been adapted by Reed *et al.* [103] in the case of Born-Oppenheimer dynamics for which it is assumed that the electronic degrees of freedom relax instantaneously relative to the movement of ions/molecules. In practice, the charges of the electrode atoms are represented by Gaussian charge densities centered on the atoms. They are calculated at each time step by minimizing the expression:

$$U = \sum_i q_i(t) \left[\frac{\Psi_i(\{q_j\})}{2} + \frac{q_i(t)\kappa}{\sqrt{2\pi}} - \Psi^0 \right] \quad (2.20)$$

where q_i is the charge carried by the atom i , κ is the width of the Gaussian distributions, $\Psi_i(\{q_j\})$ is the potential at position i due to all other atoms and ions; the second term comes from the interaction of the Gaussian with itself and Ψ^0 is the applied potential. At each simulation step, all the charges must be determined in a self-consistent way by minimizing the Equation 2.20 using the conjugate gradient method. This methodology has been successfully applied to a number of electrode-electrolyte interfaces [81, 103–116]. Compared with other faster methods [117], this technique has the advantage of being directly applicable to the case of non-planar and irregular electrodes.

2.3.2 Importance of polarizability of electrode

During an electrochemical experiment, a potential difference is applied across the supercapacitor and the local charge, which fluctuates over time, depends both on the imposed potential and on the molecules surrounding the surface. Thus, modeling the electrodes in a polarizable way, i.e., allowing the fluctuations of charges on the electrode atoms as we discussed above, make MD simulations possible to become more reliable and comparable to the experiments. The first thing we notice during the simulations is the inhomogeneity of the charges on the surface of the electrode in

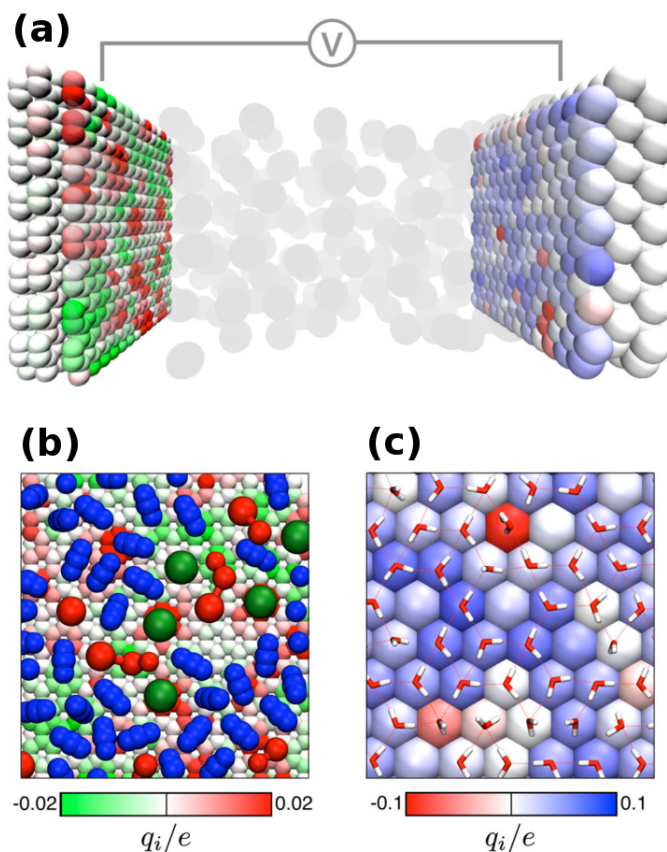


Figure 2-1: (a) Illustration of electric double layer capacitors with two electrodes maintained at constant potential difference. The atoms of the electrode are colored according to the instantaneous charge q_i they carry, with the corresponding scale shown at the graphite electrode (b) a representative configuration of the first adlayer of the 1.5M 1-butyl-3-methylimidazolium (red) hexafluorophosphate (green) in acetonitrile (blue) solution in contact with it and the 111 crystal facet of a platinum electrode (c) a representative configuration of the first adlayer of the water in contact with it [118].

contact with the electrolyte.

Figure 2-1 shows the instantaneous atomic charges of a carbon electrode of the graphitic structure in contact with liquid electrolytes. In this figure, we see that the charges are not homogeneously distributed on the surface of the electrode. The charge carried by an electrode atom depends both on the imposed potential difference and the electrolyte present in the vicinity. Thus, each positive (respectively negative) charge is observed near an anion (or a cation, respectively). Taking polarizability into account thus modifies the representation of electrostatic interactions at the electrode-

electrolyte interface.

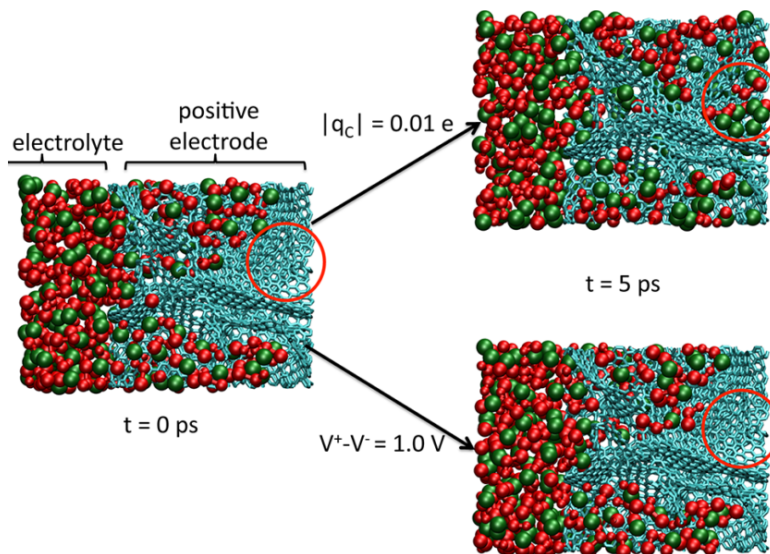


Figure 2-2: Evolution of the structure inside a positive nanoporous carbon electrode upon application of a constant charge (top) or a constant applied potential (bottom) simulation. The initially empty pore region is highlighted with a red circle [115]. Green spheres: anions; red spheres: cations.

The introduction of polarizability has consequences on the structure of the liquid at the interface with the electrode. Moreover, the effect on dynamic processes is very marked as reported by Merlet *et al.* [115]. As shown in Figure 2-2, the way to study the charge dynamics of a supercapacitor is to start from an initial configuration corresponding to a zero potential and instantly apply a non-zero potential difference across the supercapacitor. The response of the system to this disturbance provides a lot of information. To show the importance of polarizability, Merlet *et al.* performed two simulations from an initial configuration corresponding to zero potential (see Figure 2-2). From this initial configuration, they conducted two simulations: one is constant potential with a potential difference of 1 V between the two electrodes; the other is constant charge with an atomic charge of $0.01 e$, i.e., neglecting the polarizability of the electrodes.

It should be noted that the constant charge has been chosen such that the potential difference, reconstructed from the charge density, is equal to 1 V for a simulation at equilibrium. In Figure 2-2, we note that after 5 ps, the "pocket" (circled in red), which

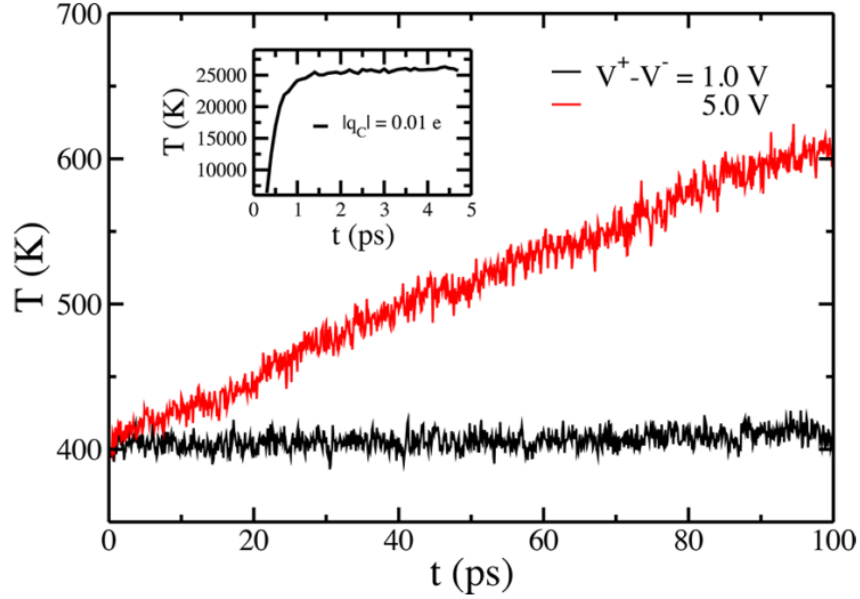


Figure 2-3: Temperature drift when a constant potential difference is suddenly applied (inset: when a constant charge is assigned to each carbon atom) [115].

was empty in the initial configuration, is filled in the case of constant charge simulation and still empty in the case of constant potential simulation. This suggests that the use of constant charge accelerates the dynamics of the system. Moreover, in Figure 2-3, a temperature increase due to the Joule effect, is observed during the simulations. For constant potential simulation, the temperature gradient is consistent with a simple estimate based on Ohm's law [115]. In contrast, for constant charge simulation, the temperature reaches 25,000 K in 1 ps, which is absolutely not realistic. This type of simulation should not be used to study dynamic phenomena. Therefore, it is conceivable to firstly impose a constant charge on the system to access a configuration close to equilibrium; the determination of the properties should be then performed at the constant potential.

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Chapter 3

Transport properties of water-in-salts: force field dependence

3.1 Simulation cell

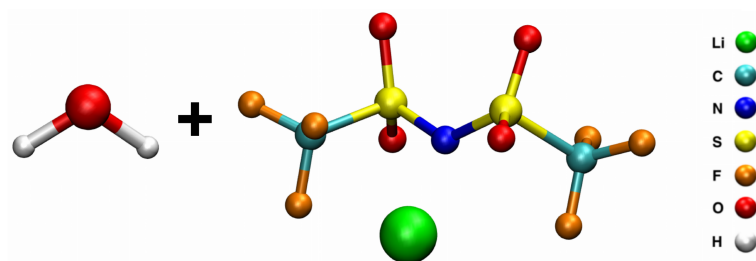


Figure 3-1: Structure of the mixture of water molecule, Li cation, and TFSI anion.

The simulation cells consist of a mixture of water molecules and LiTFSI salt ([Figure 3-1](#)), with molalities of LiTFSI ranging from 0.3 to 20 m (mol/kg). Specifically, the studied molalities are 0.3 m, 3.5 m, 7 m, 12 m, 15 m, and 20 m, in which the first two are in the salt-in-water region and the remaining ones are in the water-in-salt region as defined in chapter 1. Three representative structures of simulation cells are

shown in Figure 3-2 at 0.3 m, 3.5 m, and 15 m, respectively.

The density profile as a function of molality is shown in Figure 3-3, where experimental densities were measured by R. Bouchal. It is clear that the increase of molality with salt-to-water ratio growing makes systems being denser. Though there is a well agreement between simulated and measured density at various concentrations, we still fix to use the measured density to do better comparisons with experiments. The detailed parameters of the simulation cells are shown in Table 3.1.

Table 3.1: Simulation cell parameters for water and LiTFSI mixtures			
Molality (mol/kg)	Cell size ¹ (Å)	Number of LiTFSI	Number of water
0.3	35.88	8	1480
3.5	28.38	32	507
7.0	31.34	64	507
12.0	29.16	64	296
15.0	35.57	128	473
20.0	34.70	128	355

1. The cell size is calculated based on the experimental density.

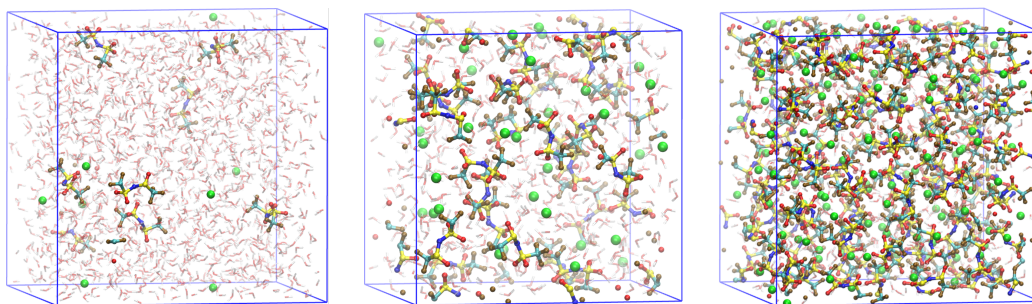


Figure 3-2: Simulation cells of water and LiTFSI mixtures at 0.3 m (left), 3.5 m (middle), and 15 m (right). Same color labels as in Figure 3-1 except that the water molecules are shadowed for clarity.

The MD simulations were performed using LAMMPS molecular dynamics simulation package [119]. The SPC/E water model was used in present systems [120]. An atomistic model of TFSI anion were considered. In a first step, a modified OPLS force field was used in case of this anion (here, we call this force field as **FF1**), where the parameters were taken from Ref [121]. The simulations were conducted in the NVT ensemble, with the temperature set at 298.15 K. The simulation cells were cubic and constructed using experimental densities, and the details are provided in Table 3.1.

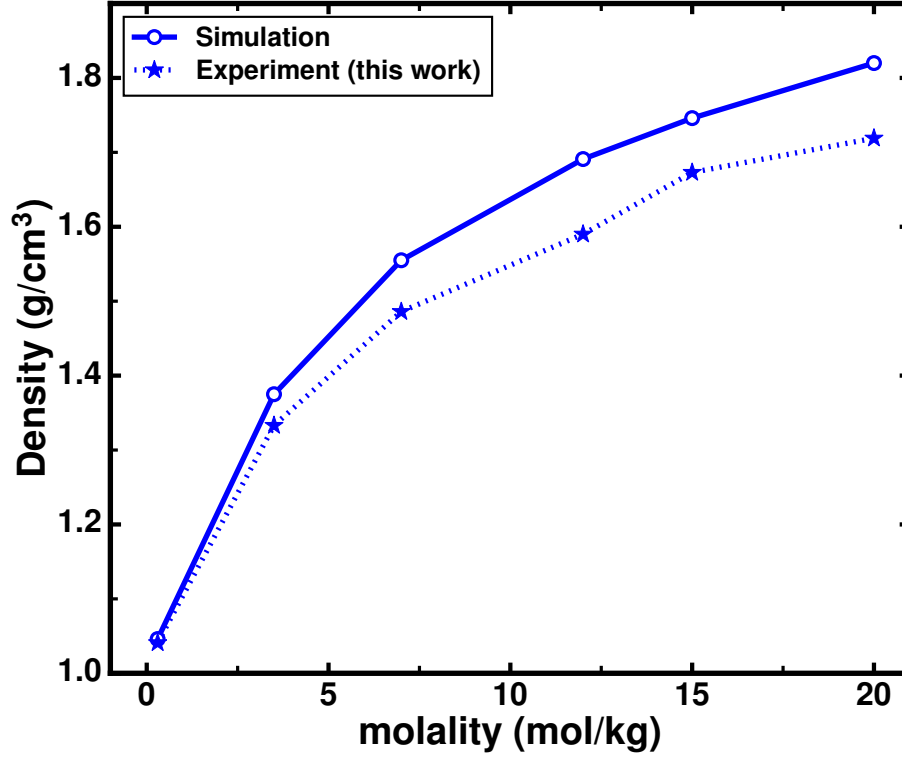


Figure 3-3: Simulated and measured densities at various concentrations.

For all of the simulations, the velocity-Verlet algorithm with a time step of 1 fs was used, the dynamics properties were obtained from the production runs with timescale over 60–110 ns after long equilibration runs (60 ns). The atomic coordinates were saved every 1 ps for post-analysis.

3.2 Viscosity

3.2.1 Methods

The shear viscosity of a liquid is calculated from the time integral of the shear stress autocorrelation function of the off-diagonal elements of the stress tensor. It is known as the Green-Kubo relation, which given by:

$$\eta = \frac{V}{k_B T} \int_0^\infty \langle \sigma_{\alpha\beta}(0) \cdot \sigma_{\alpha\beta}(t) \rangle dt \quad (3.1)$$

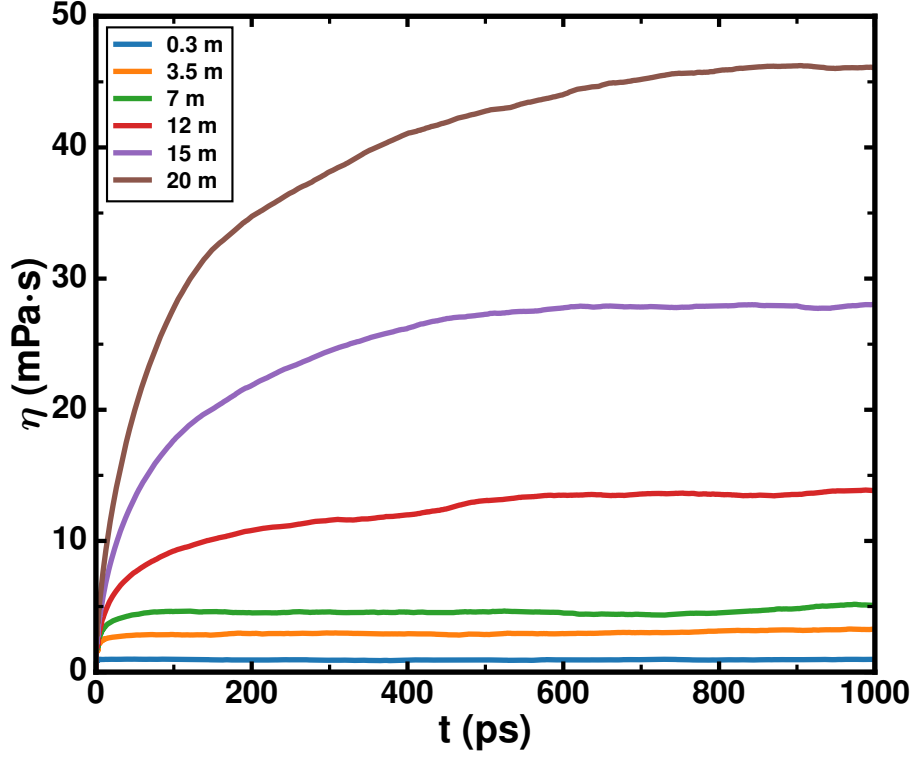


Figure 3-4: Evolution of viscosity data calculated by Equation 3.1 as a function of time at various concentrations. The final value of viscosities are given by the plateaus.

where V and k_B are the volume of the simulation cell and Boltzmann constant, respectively. $\sigma_{\alpha\beta}$ can be any of the five independent anisotropic components of the stress tensor (i.e. σ_{xy} , σ_{xz} , σ_{yz} , σ_{xx-yy} , $\sigma_{2zz-xx-yy}$). To get better statistics, an average over these five components is used. As shown in Figure 3-4, the value of the integral in Equation 3.1 converges to a plateau after a certain time, which varies with the system molality — we will discuss this point later. For the dilute solutions, the integral converges in a few picoseconds, while it takes several hundreds of picoseconds to converge to a plateau at super-concentrated states. The viscosity can then be obtained by the plateau value of the running integral.

The structural relaxation time, or Maxwell relaxation time τ_{Maxwell} , measures the time taken by the fluid relax to a new configuration when it is sheared. This quantity can be extracted from the time for which the evolution of viscosity with respect to

time (Figure 3-4) satisfies the following equation:

$$\eta(\tau_{\text{Maxwell}}) = \eta(t \rightarrow \infty) \left(1 - \frac{1}{e}\right) \quad (3.2)$$

3.2.2 Results

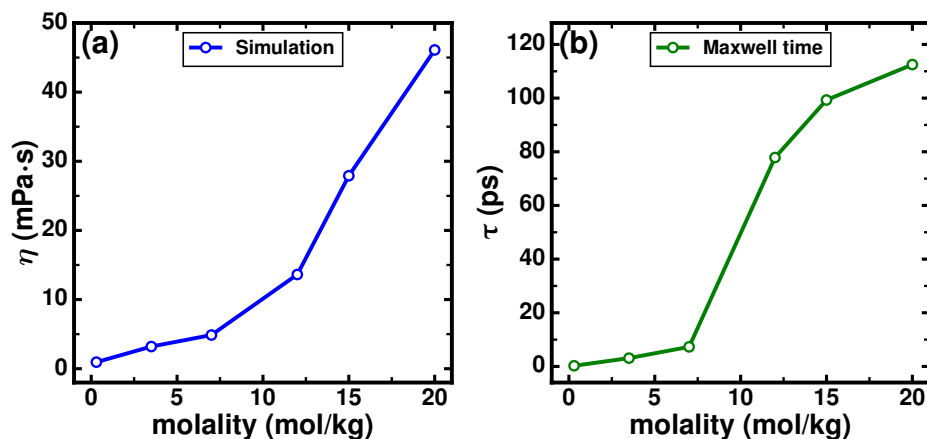


Figure 3-5: Calculated viscosities (a) and Maxwell relaxation times (b) at various concentrations.

In a phenomenological description, the viscosity is written as the product of a shear modulus and the Maxwell relaxation time τ_{Maxwell} , however, the shear modulus shows only weak compositional and temperature dependence [122]. Thus, there could be positive correlations between the viscosity and corresponding Maxwell relaxation time. The calculated values for both quantities are compared in Figure 3-5. The viscosity increases progressively with concentration by one order of magnitude when switching from low to high salt concentration regime. It is clear that the Maxwell relaxation time increases with viscosity.

In Figure 3-6, the simulated viscosities are plotted along with results from experimental measurements. The experimental results include both the measured values from our collaborators C. Rizzi and R. Bouchal and the values adopted from ref [27]. As can be seen that the simulated viscosities are agreed well with both experimental results. The latter show a slight discrepancy for the larger concentration which may be due to difficulties for controlling the composition at large salt/water ratios.

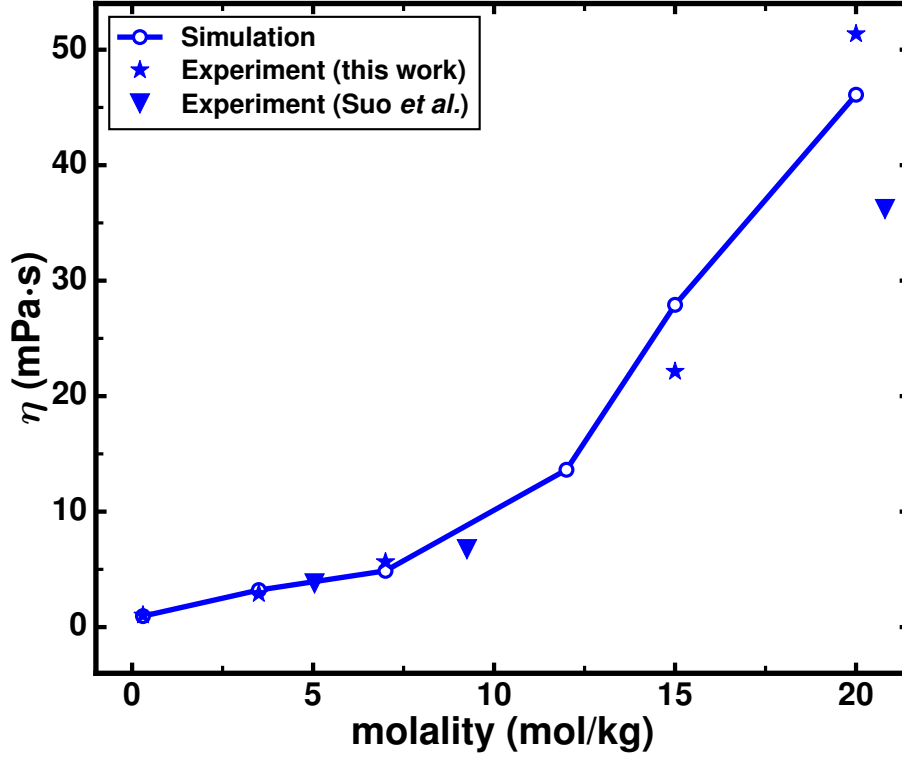


Figure 3-6: Comparison of the calculated and experimental viscosities. The circles, stars, and triangles represent the calculated results by our simulations, measured results by our collaborators, and experimental results from ref [27], respectively.

3.3 Diffusion coefficient

3.3.1 Methods

The self-diffusion coefficient is computed from the slope of the mean-squared displacement average over the whole trajectory of individual species using the Einstein relation, which is defined as:

$$D_\alpha = \lim_{t \rightarrow \infty} \frac{1}{6t} \langle |\delta \mathbf{R}_i(t)|^2 \rangle \quad (3.3)$$

where D_α is the self-diffusion coefficient of species α , the angle brackets denote average over all configurations, and $\delta \mathbf{R}_i$ is the displacement of an individual ion i of species α .

In fact, the use of periodic boundary conditions induces a box length dependence

of the measured diffusion coefficient due to the restriction of diffusion from long-range hydrodynamic interactions [123,124]. The term of finite size correction (FSC) to the self-diffusion coefficient should be added to obtain the value of the diffusion coefficient finally, and this quantity is given by:

$$\Delta D^{FSC} = \frac{2.837k_B T}{6\pi\eta L} \quad (3.4)$$

where η is the viscosity as discussed in the previous section, and L is the length of the simulation periodic cell.

3.3.2 Results

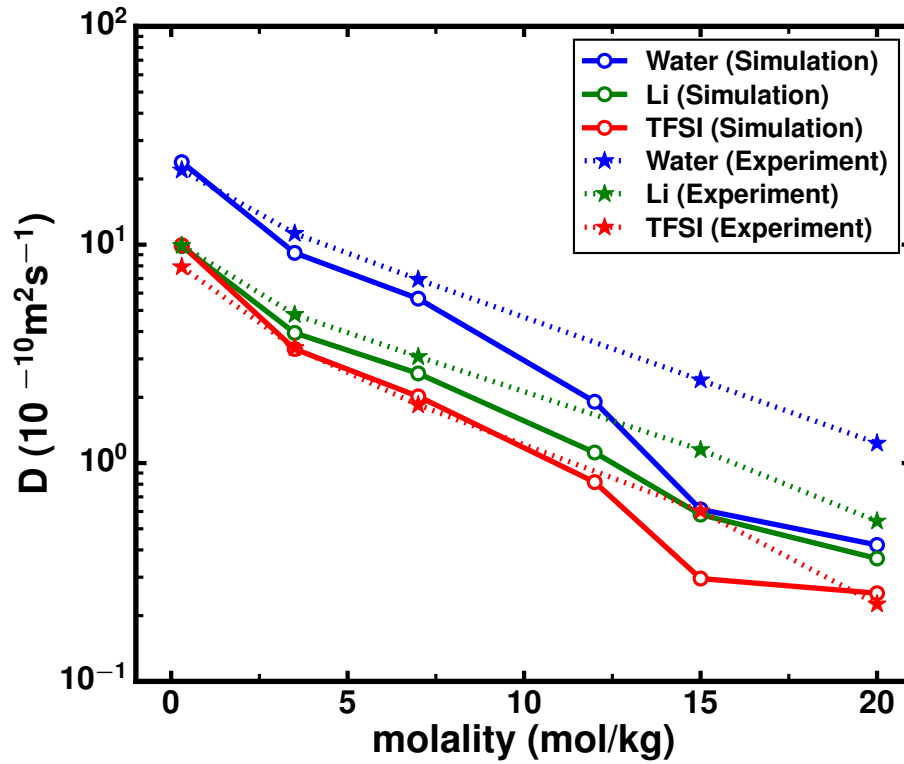


Figure 3-7: Simulated and measured diffusion coefficients for the water molecule, Li cation, and TFSI anion at various concentrations. Experimental results were obtained by A.-L. Rollet and R. Bouchal using pulse-field gradient NMR.

The results of the diffusion coefficients of the water molecule, Li cation, and TFSI anion are shown in Figure 3-7. The diffusion coefficients of all the species decrease

progressively with concentration by more than one order of magnitude, which is related to the increased viscosity as discussed in the previous section. The experimental results indicate linear decreasing on the log-scale for all the species. However, different pictures are found for the simulated results. The obvious decrease of diffusion coefficients of all the species is almost the same as the trend found for measured results. The values are consistent with experimental results at the concentrations below 12 m, but they become lower than experimental values above 15 m. Especially, we observe very close values for the diffusion coefficients of the water molecules and the Li cations at 15 m and 20 m in the simulations, which is quite different from the measurements in which the values for the water molecules are two times larger than that for the Li cations. Therefore, it seems that the force field **FF1** might not be applicable to precisely describe the transport in the super-concentrated systems above 12 m.

3.4 Conductivity

3.4.1 Methods

The conductivity is obtained from the long-time slope of a plot of the mean-squared displacement of the charge density versus time:

$$\lambda = \frac{e^2}{k_B T V} \lim_{t \rightarrow \infty} \frac{1}{6t} \langle |\sum_i q_i \delta \mathbf{R}_i(t)|^2 \rangle \quad (3.5)$$

where q_i and $\delta \mathbf{R}_i$ are the charge and displacement of ion i , respectively. The sum runs over all cations and anions, which means that the mean-squared displacement in the brackets includes not only the self terms of an individual ion i but also the distinct terms (correlations between the displacements of different ions). Thus, the total conductivity can be decomposed to two parts (self and distinct). The Nernst-Einstein approximation for the conductivity can be obtained by neglecting the correlations of

the distinct terms, i.e., $\langle \delta \mathbf{R}_i(t) \cdot \delta \mathbf{R}_j(t) \rangle = 0, i \neq j$, it is thus given by:

$$\lambda^{NE} = \frac{Ne^2}{k_B TV} \sum_{\alpha} q_{\alpha}^2 D_{\alpha} \quad (3.6)$$

where q_{α} is the charge of species α and D_{α} is the diffusion coefficient of species α as defined in Equation 3.3.

3.4.2 Results

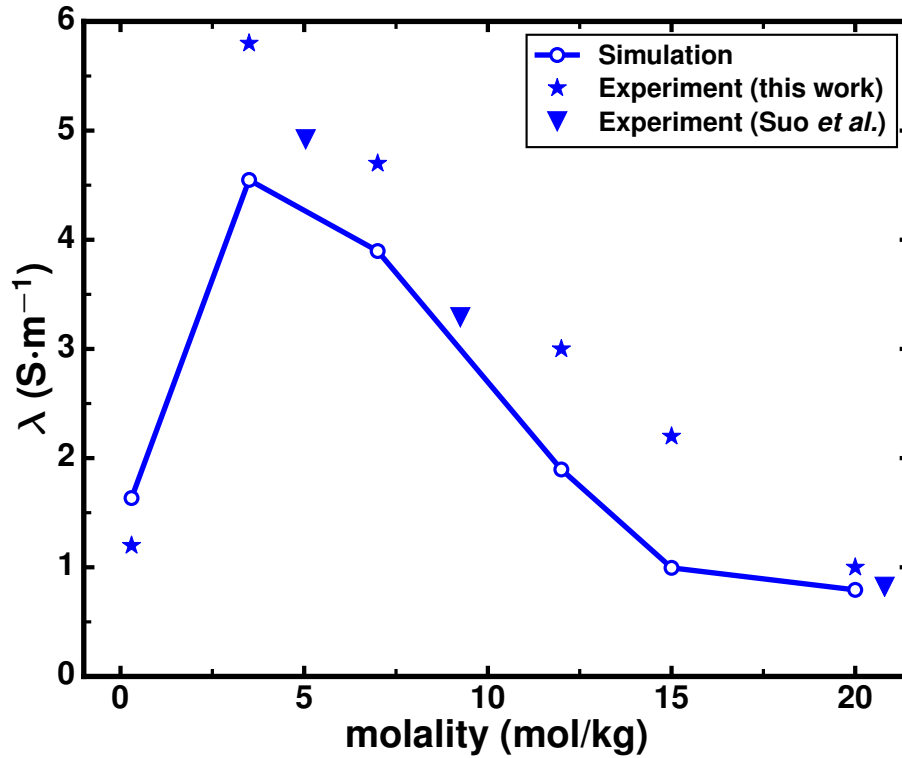


Figure 3-8: Simulated and experimental conductivities at various concentrations. Experimental results were obtained by R. Bouchal.

The conductivity obtained using Equation 3.5 are plotted in Figure 3-8 together with the experimental results. We can see that the conductivity increases at low concentration with the number of charge carriers before reaching a maximum at 3 m, it then decreases at larger concentrations but remains 1 S/m at 20 m comparable to that of commercially used electrolytes in electrochemical storage devices. The simulated results agree well with the experimental values on the whole. The smaller values

obtained from simulation compared with experimental results are mainly attributed to the underestimated values of diffusion coefficients of the Li cation and TFSI anion shown in Figure 3-7.

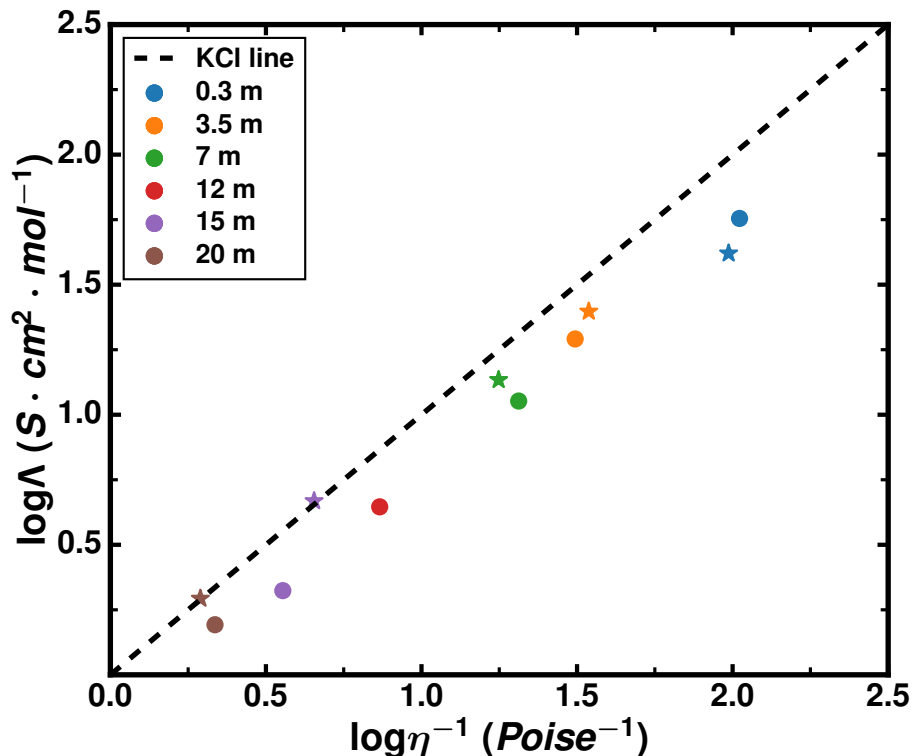


Figure 3-9: Walden plots of the simulated results (circles) and measured results (stars). The dashed line is the results for the ideal KCl aqueous.

The conductivity is linked to the viscosity through a plot based on the Walden rule, i.e., $\Lambda\eta^\alpha = \text{constant}$, where the Λ is the molar conductivity and α represents an adjustable parameter. The Walden plots in Figure 3-9 shows the relationship between the logarithm of molar conductivity (Λ) and the logarithm of fluidity (η^{-1}), which can be used to classify electrolyte solutions regarding their performance as ionic conductors. The dashed line represents the ideal KCl aqueous in which the KCl is completely dissociated. The electrolyte solution is classified as poor-ionic electrolyte whose Walden plot lies much lower than the ideal line. The regions lie below the ideal line but close to it, corresponding to good-ionic electrolytes. The electrolytes are considered as super-ionic conductors whose Walden plots lie above the ideal line [32, 33]. As shown in Figure 3-9, the plots of the systems at various concentration are

locating at the good-ionic region, close to the ideal line when switching from low to super-concentrated states. Apart from these, the experimental results at 15 m and 20 m are on the ideal line, leading to even better performance as ionic conductors compared with the remaining concentrations. These could partially account for the high performance of using water-in-salt electrolytes in electrochemical storage devices, like lithium-ion batteries and supercapacitors.

3.5 Comparison with other force fields

3.5.1 Type of force fields

As discussed above in this chapter, the simulated viscosities and conductivities can be well reproduced with experimental results for the whole studied concentrations by using the force field **FF1**. Also, the simulated diffusion coefficients of all the species agree well with the experimental measurements at concentrations below 12 m. However, the **FF1** force field is failed to reproduce the value of diffusion coefficients at super-concentrated states (15 m and 20 m). The significant differences between the ratio of $D_{Water} : D_{Li}$ from experiment ($\approx 2:1$) and that from the previous simulations ($\approx 1:1$) at 15 m and 20 m would have significant effects on the structural properties, such as the property of solvation shell of Li and/or water molecules, which we will discuss in the next chapter. Therefore, we need to modify the force field, such as using reduced charge strategy to mimic polarization effects, or to chose another parameterization of the force field to improve the ability describing the electrolytes at super-concentrated states.

We implement three different sets of parameters for the force field to perform a new set of simulations at 15 m, in which the changes are as following:

1. **FF2**: Charges of Li cation and TFSI anion are uniformly scaled by a factor of 0.8 based on **FF1**, all the remaining parameters are the same as **FF1**;
2. **FF3**: Intermolecular parameters of TFSI anion are taken from ref [125] in which the charge of Li cation and TFSI anion are set to +1 and -1, respectively, the

intramolecular parameters are the same as **FF1**;

3. **FF4**: Scaled charges of Li cation and TFSI anion with a factor of 0.8 based on **FF3**, all the remaining parameters are the same as **FF3**.

Note that the water molecule is always without scaled charges; we keep using SPC/E model during all the simulations. Each of the simulations with new force fields is performed with equilibration runs for 60 ns, followed by 60 – 90 ns production runs for data collections. The specific charges of Li cation and TFSI anion for the four force fields are listed in [Table 3.2](#).

Table 3.2: Charges of Li cation and TFSI anion

Force field	Li	C	F	O	S	N
FF1	1.0	0.2988	-0.1176	-0.3588	0.4845	-0.4258
FF2	0.8	0.23904	-0.09408	-0.28704	0.3876	-0.34064
FF3	1.0	0.35	-0.16	-0.53	1.02	-0.66
FF4	0.8	0.28	-0.128	-0.424	0.816	-0.528

3.5.2 Results

In [Figure 3-10](#), the simulated viscosities obtained by using the different type of force fields are compared with the experimental value at 15 m. Largest value is given by **FF3** force field, which is more than 2 times larger than the experimental measurement, compared with those from all the other type of force fields. The **FF2** force field underestimates the viscosity showing a value only half of the experimental one, which is in contrast with the general fact that viscosity is often overestimated from simulations. This could be attributed to the excessive reduction of the charge in **FF2**. The **FF1** and **FF4** force fields give closer values compared with the other two with the former slightly larger than the experimental one and the latter in verse. Thus, both the **FF1** and **FF4** force fields seem to be applicable to the water-in-salt electrolytes at 15 m based on the viscosity comparison.

The comparison result of diffusion coefficients of the water molecule, Li cation and TFSI anion is shown in [Figure 3-11](#). As mentioned above, two important criterion of

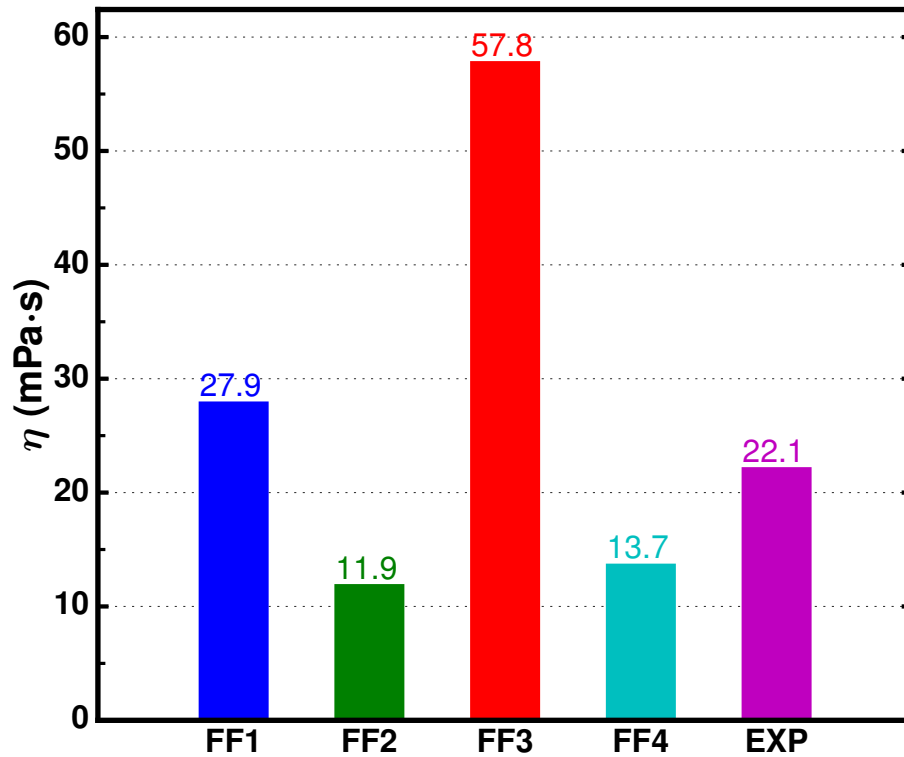


Figure 3-10: Calculated viscosities from the different type of force fields compared with the experimental result.

the simulated results should be considered in particular to determine the optimized type of force field to describe the water-in-salt electrolytes at 15 m. The first one is of course that the simulated results should give relatively close values to that of experimental ones. The second but more important is that the ratio of $D_{Water} : D_{Li}$ should be around 2:1 in accord with the experimental measurement at 15 m. It can be seen that none of the first three force fields (**FF1**, **FF2**, **FF3**) fulfill the two criterion, the absolute values are smaller than experiments and the ratio of $D_{Water} : D_{Li}$ is either close to 1 or more than 3. However, the diffusion coefficients obtained from **FF4** force field can well reproduce the experimental results with an only slightly smaller value for the water molecules. Thus, the use of **FF4** force field can be confirmed to investigate further the structural properties of water-in-salt electrolytes at super-concentrated states.

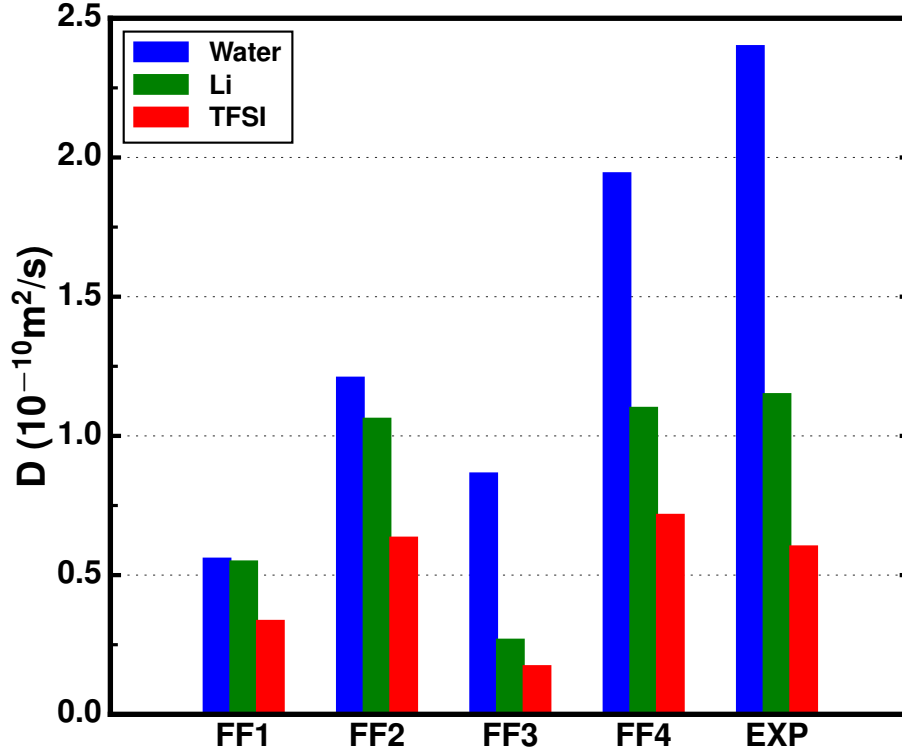


Figure 3-11: Simulated diffusion coefficients for the different type of force fields compared with experimental measurements.

3.6 Conclusions

In this chapter, we studied the water and LiTFSI mixtures at various concentrations from dilute solutions to super-concentrated solutions, including the water-in-salt region. The dynamic properties, such as the viscosity, diffusion coefficient and conductivity, of the mixtures were computed and compared with experimental results.

The dependence of dynamic properties on concentrations is clearly found by using a uniform force field (**FF1**): the system becomes viscous with increasing viscosity and decreasing diffusivity when switching from low to high concentration regime, in which the drastic changes occur at concentrations above 12 m. These results are consistent with both the simulated and experimental values recently reported [34]. The extent of the decrease in diffusivity is similar to the case of all mixtures of ionic liquids with solvents, and the main consequence is that the choice of the optimal concentration for EDLC applications is likely to consist in a compromise between an

improved electrochemical stability window as reported [27] and a poorer diffusivity of the lithium ions (unlike batteries, for which the formation of a protective interphase at the surface of the electrodes is crucial [28]). This competition is also reflected on the electrical conductivity, which first increases to a maximum and then decreases at water-in-salt region. Based on analysis of the Walden plots, we confirm that the water-in-salt electrolytes at super-concentrated states have better performances as ionic conductors than the less concentrated systems.

In order to better reproduce the dynamic properties, especially the diffusion coefficients, with experiment at super-concentrate states, the different type of force fields are utilized to study the water-in-salt electrolytes at 15 m. The combined analysis based on both viscosity and diffusion coefficient shows that the **FF4** force field can give results in good agreement with experimental measurements. Such transport quantities are usually much more difficult to reproduce than the structural ones for concentrated electrolytes, so their reproduction validates the use of **FF4** force field to analyze the structure and the thermodynamics of the system.

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Chapter 4

Structural properties of water-in-salt electrolyte

As discussed in chapter 3, the dynamic properties significantly change with the increase of concentrations, which could be attributed to the variation of structural properties, such as the solvation shell and speciation. Therefore, the structural properties of water-in-salt electrolytes at 15 m are discussed in this chapter not only to account for the dynamical performances but also to have deep understandings of the microscopic pictures of water-in-salt electrolytes at super-concentrated states. Although the **FF4** has proven to be the best choice describing the systems at 15 m among the four studied force fields, it is also interesting to compare them when studying the structural properties. The results from this comparison are expected to shed new light on influence/role of the salt and water correlations.

4.1 Solvation shell of Lithium

4.1.1 Coordination number of Lithium

The average coordination number of a reference particle A , i.e. the number of observed particles (B) surrounding each A on average, is calculated by integrating the radial

distribution function (RDF) of the A - B pairs through

$$\bar{n}(r') = 4\pi\rho \int_0^{r'} r^2 g(r) dr \quad (4.1)$$

where r is the distance between A and B , $g(r)$ is the radial distribution function of the A - B pairs, and ρ is the number density of particle B in the simulation cell.

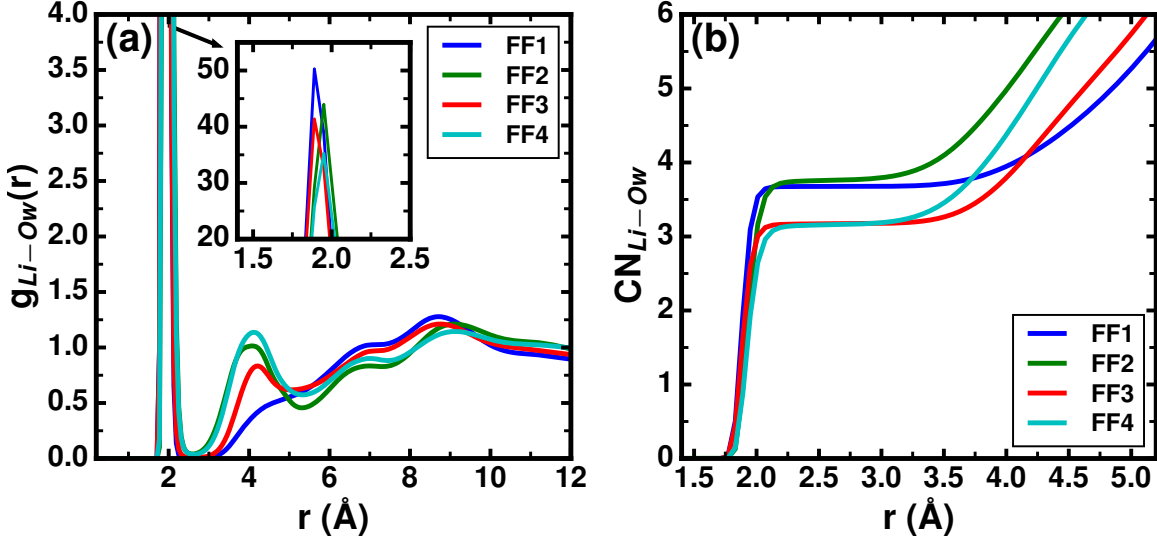


Figure 4-1: (a) Radial distribution functions of Li-water pair, and (b) corresponding coordination numbers as a function of Li-water distance.

The $g(r)$ between Li cation and water molecule obtained with the four force fields are shown in Figure 4-1a. In all cases, the first shell of tightly bound water molecules surround the Li cations with a distance around 1.8 Å (the first peak in Figure 4-1a) but with different peak values. We will discuss these peak values in the next section. Moreover, all the force fields give almost the same position for the first minimum, located at around 2.57 Å and thus we take this value as the cutoff distance for the Li first solvation shell (i.e., hydration shell when the solvent is water).

Figure 4-1b shows the corresponding coordination numbers (hydration numbers) of water molecules surround the Li cation. The plateau ranging from 2.1 Å to 3–3.5 Å for each of the force fields corresponds to the boundary between the Li first hydration shell and the second solvation shell, which is much more loosely bound. The hydration numbers of the Li are around 3.7 for **FF1** and **FF2** and 3.2 for **FF3**

and **FF4**. It is well established from the combination of experimental (neutron and X-ray diffraction) and simulation data that at infinite dilution the hydration number of lithium is 4, which means that some Li cations become under-hydrated at 15 m. Note that the charges of Li cation and TFSI anion are reduced in **FF2** (**FF4**) compared with that in **FF1** (**FF3**), but they have the same LJ parameters. Therefore, the hydration number of the Li first solvation shell seems to be nonsensitive to the Coulombic interactions but to be controlled by the Lennard-Jones terms.

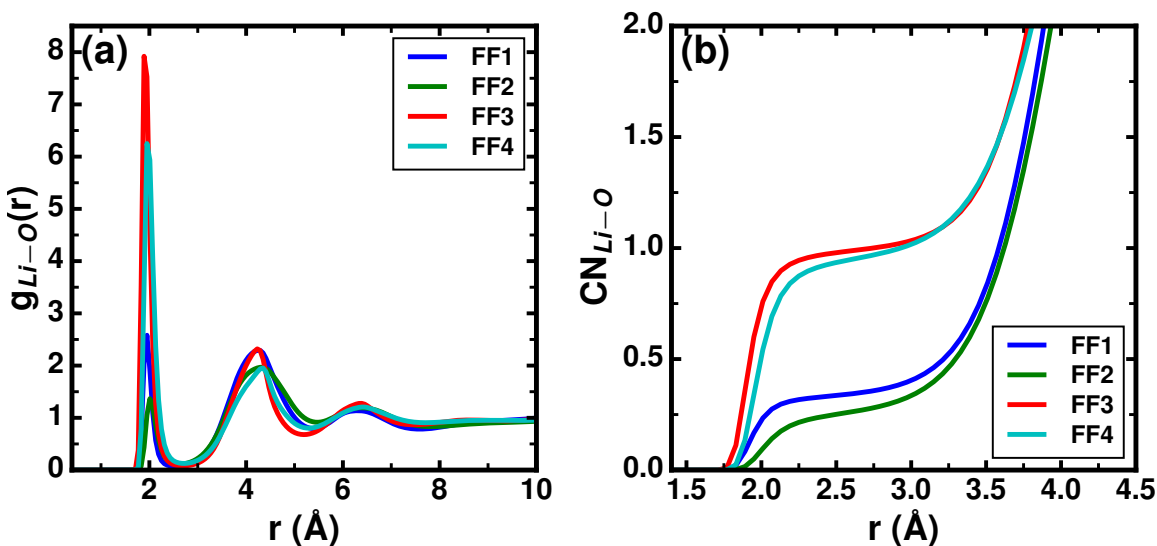


Figure 4-2: (a) Radial distribution functions of Li-O(TFSI) pair, and (b) corresponding coordination numbers as a function of Li-O(TFSI) distance.

To account for the differences of the hydration number of the Li first solvation shell, we also calculate the radial distribution function of Li cation and O atoms from TFSI anion pairs and the corresponding coordination numbers (Figure 4-2a and b). Very different values of the first maxima are observed in Figure 4-2a, which leads to different values for the corresponding coordination numbers. The **FF1** and **FF2** give a value around 0.25, which is smaller than that of **FF3** and **FF4** (around 0.9). It is clear that there is a competition between water molecules and O atoms from TFSI anions to participate in the Li first solvation shell. The more O atoms from TFSI anions involved in the Li first solvation shell, the lesser the number of water molecules inside.

4.1.2 Residence time of water

The first solvation shell is generally characterized by two main quantities: the average coordination number of the cation, which we have already discussed in the last section, and the mean residence time τ of a water molecule inside the shell.

The residence time, measuring the rate of the break-up of the first coordination shell of the lithium cations, is obtained by using the cage correlation function analysis [126]. The instantaneous set of neighboring water molecules of any lithium ion i is defined by a neighbor list which is stored in a vector $\mathbf{I}_i(t)$ ($i \in [1, N_{Li+}]$). This vector has a dimension N_{H_2O} ; the j -th component equals 1 if the corresponding molecule lies within the first coordination shell of i , and 0 otherwise. As for the coordination number, a simple geometric criteria $r_{ij} < r_{cut} = 2.57 \text{ \AA}$ was used to attribute the water molecules to the first coordination shell. Within that formalism, the hydration number of i at time t is given by $|\mathbf{I}_i(t)|^2$, and the number of water molecules that have left their original neighbor list in the subsequent time interval δt is

$$n_i^{out}(t, t + \delta t) = |\mathbf{I}_i(t)|^2 - \mathbf{I}_i(t) \cdot \mathbf{I}_i(t + \delta t) \quad (4.2)$$

The cage-out correlation function for the Li + ions solvation shell then is given by

$$C^{out}(t) = \frac{1}{N_{Li+}} \left\langle \sum_{i=1}^{N_{H_2O}} \Theta(1 - n_i^{out}(0, t)) \right\rangle \quad (4.3)$$

where Θ is the Heaviside step function. So defined, the cage-out correlation function measures the rate at which a single molecule leaves the cage. Using similar definitions, it is also possible to calculate the correlation functions measuring rates for a molecule to enter into the cage (cage-in), but also for an ion to enter or to leave it (cage-in-or-out).

Herein, the calculated cage-out correlation function and the corresponding residence time obtained from different type of force fields are shown in Figure 4-3 and Figure 4-4, respectively. The decay rate of the cage-out correlation function using FF1 (blue line in Figure 4-3) is extremely slow compared with the other three type

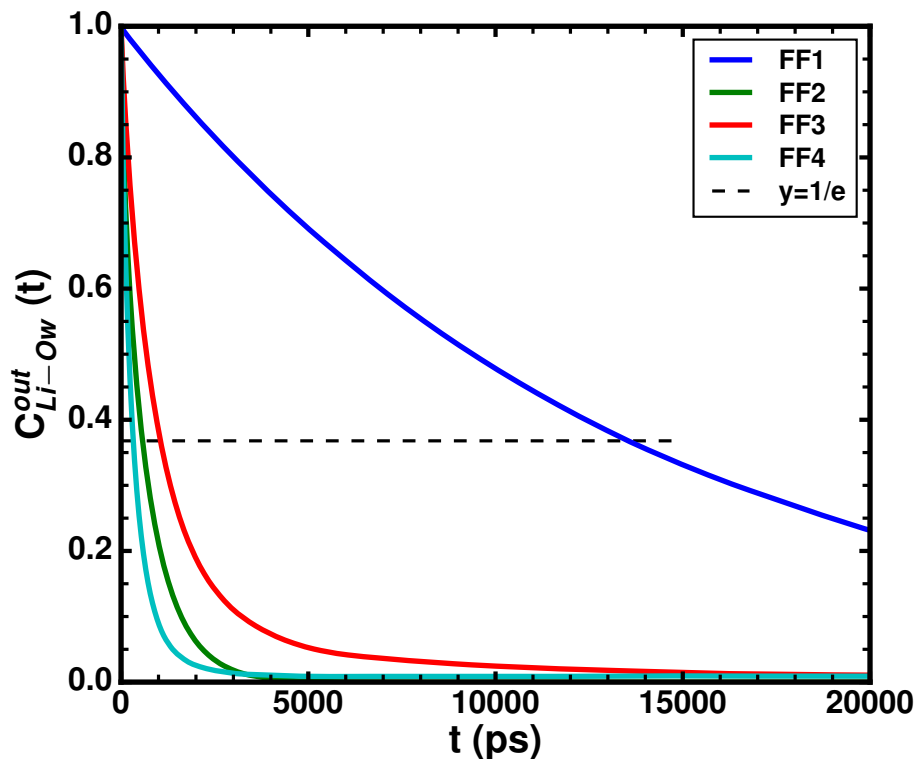


Figure 4-3: Cage-out correlation functions with respect to time calculated through Equation 4.3.

of force fields, resulting in a residence time τ of 13.6 ns (Figure 4-4). Such a large residence time obtained from **FF1** is associated with the large deviation of the diffusivity from experimental results (as discussed in Chapter 3), which makes the value unreliable. Apart from this, using **FF4** force field, the given residence time (300 ps) is in agreement with reported results in the literature which are diverse (25–400 ps) depending on the simulation method [127]. The **FF2** force field, which uses modified Coulombic interactions from **FF1** with reduced charges, gives a value of 600 ps, which is close to that from **FF4**. Finally the residence time (1 ns) is three times larger for **FF3**, in which the charges are not reduced, than that of **FF4**. Therefore, in contrast with the dependence of coordination numbers, the residence time is mainly affected by the Coulombic interactions rather than by the Lennard-Jones terms.

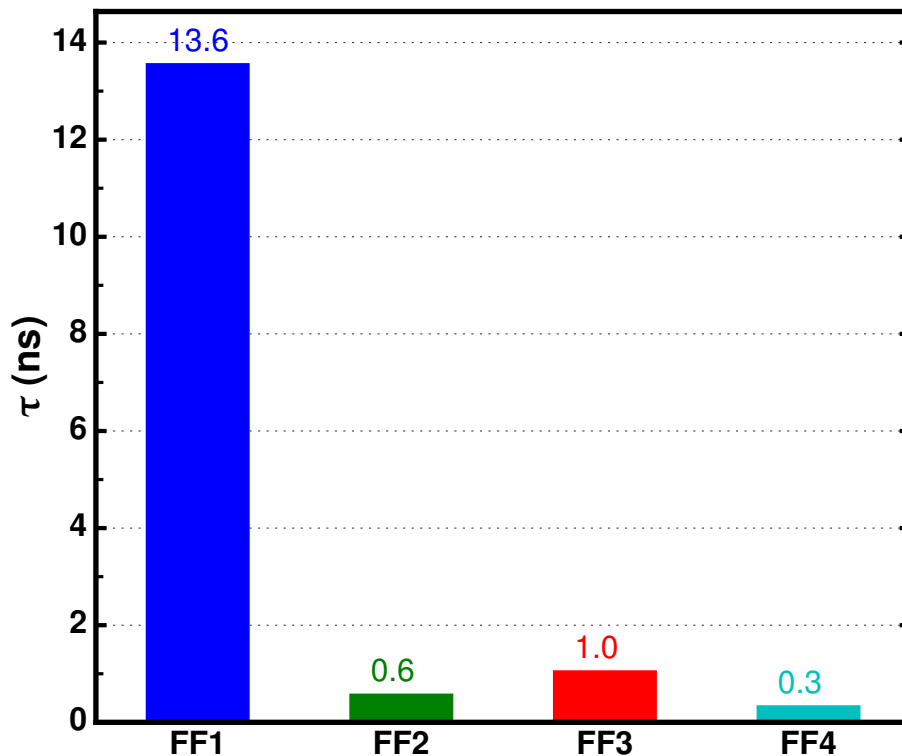


Figure 4-4: Residence times obtained from cage-out correlation functions for which the function equals $1/e$ (dashed line in Figure 4-3).

4.1.3 Potential of mean force

In order to analyze the thermodynamic aspect related to the Li solvation shell strength, we compute the potential of mean force (PMF) for the escape of water molecules (or TFSI anions represented by O atoms) from the solvation shell of Li cations, which is given by

$$\text{PMF} = -k_B T \ln g(r) \quad (4.4)$$

where k_B and T are the Boltzmann constant and temperature, respectively.

Figure 4-5a shows the PMFs for water molecules escaping from the solvation shell of Li cations. The first minimum corresponding to the first peak in Figure 4-1a, indicates the strength of the Li-water interaction, which is represented by the energy gap (ΔE) between the first minimum and the reference value (arbitrary fixed at 0 kJ/mol). The energy gaps (stabilization energies), ΔE , extracted from Figure 4-5a are shown in Figure 4-5b. We can see that the water molecules are stabilized by 8.8 to

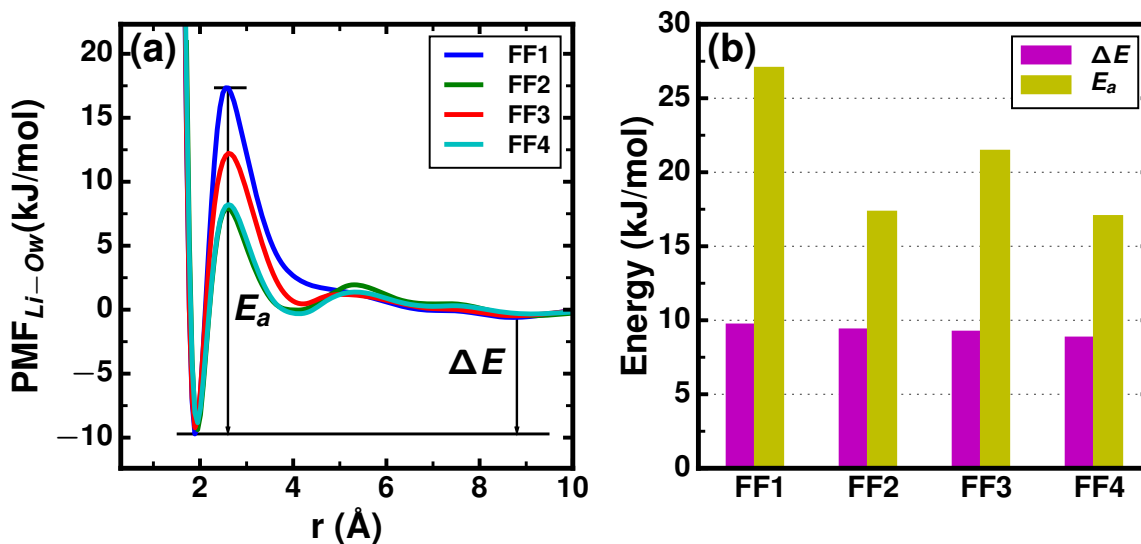


Figure 4-5: (a) Potential of mean forces for breaking of a lithium-water “bond”. (b) Stabilization energies (ΔE) and barrier heights (E_a) calculated from the PMFs.

9.7 kJ/mol when entering this first solvation shell, a large number which is due to the small ionic radius and the large polarizing power of this cation. Moreover, the barrier height, E_a , defined by the energy difference between the maximum and the minimum of PMF (in Figure 4-5a), can be obtained from the PMF as well. There is more discrepancy of this quantity since it ranges from 17 to 27 kJ/mol. Even though the reduction of charges in **FF2** or **FF4** decreases the barrier height compared with that without reduced charges (**FF1** or **FF3**), it remains a high barrier for water molecules escaping from the first solvation shell of Li cations. This is due to the under-hydrated state of Li cation at 15 m, leading to the lack of free water molecules beyond the Li first hydration shell.

Considering that several TFSI anions are also involved in the Li first solvation shells, the PMFs for TFSI anions escaping from the solvation shell of Li cation is calculated as well as the corresponding energy differences (in Figure 4-6). Both the stabilization energy (ΔE) and barrier height (E_a) of TFSI anions are much smaller than that of water molecules, which indicates that the former is much more loosely bound and more dependent on the force field.

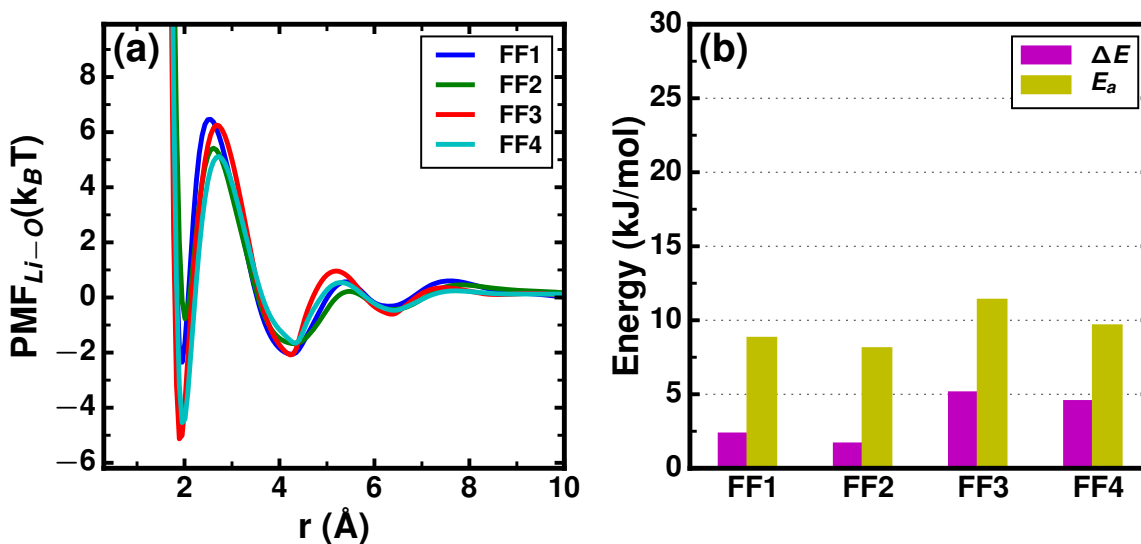


Figure 4-6: (a) Potential of mean forces for breaking of a Li-O(TFSI) “bond”. (b) Stabilization energies (ΔE) and barrier heights (E_a) calculated from the corresponding PMFs.

4.1.4 Fraction of free water

Water molecules that do not belong to any Li first solvation shells are considered as free water in our work. The fraction of free water can then be obtained through the coordination analysis from the trajectory, the results for different force fields are shown in Figure 4-7. The first two force fields (**FF1** and **FF2**) show smaller fraction of free water molecules compared with the other two (**FF3** and **FF4**). It is due to the larger average hydration number of water molecules observed in Figure 4-1b that requires more water in the presence of the Li first solvation shell, resulting in the decrease in the amount of free water.

Moreover, it is clear that the **FF1** gives a distinct value (0.6 %) compared with the others. Such a smaller value is also partially attributed to the absence of a second minima in the region around 4 Å in the Li-O(water) PMF (Figure 4-5a), which leads to an easier release of water molecules since they can access the adjacent lithium’s first solvation shell. On the contrary, larger values of the fraction of free water are found for the rest of the force fields, owing to the valley appearing at around 4 Å in Figure 4-5a. In Particular, the **FF3** and **FF4** give similar value which is in agreement

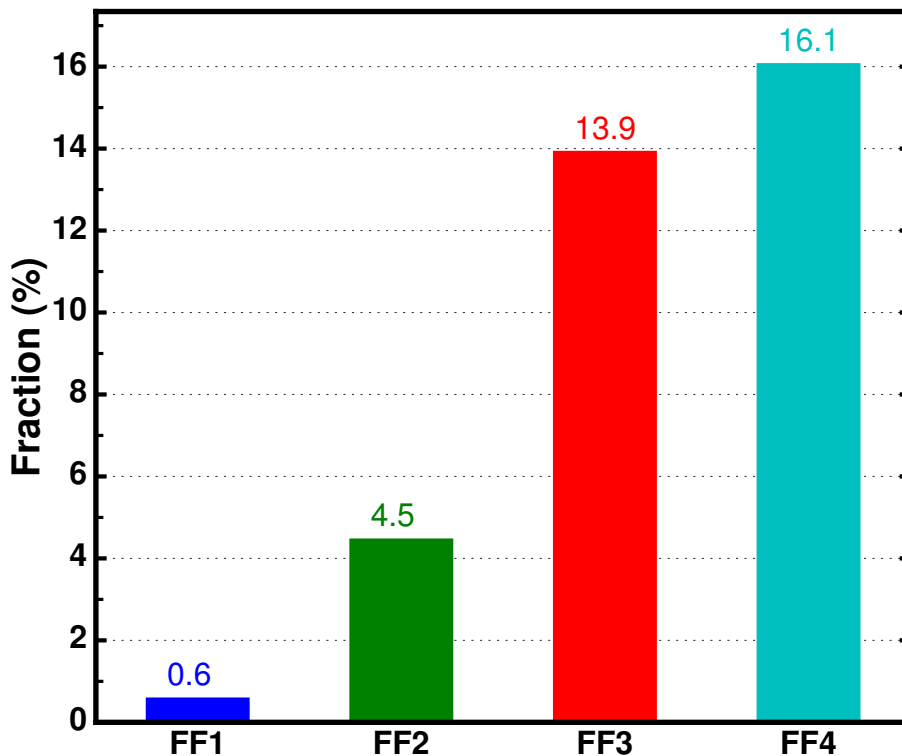


Figure 4-7: Comparison results of the fraction of free water molecules for different force fields.

with that reported by Borodin *et al.* [27, 34].

The fraction of free water is linked to the behavior of the diffusivity of water molecules and lithium ions. The limited fraction for **FF1** (**FF2**) means that most water molecules are diffusing together with lithium ions resulting in similar values between water and lithium ions. In contrast, the relatively larger fraction of free water for **FF3** (**FF4**) enables a portion of water molecules to diffuse with more freedom, which increases the average value of the diffusion coefficient of water molecules.

4.1.5 Lithium-lithium dimer

The first solvation shell of lithium ions is well understood based on the analysis in previous sections. In this section, we will discuss the structural properties beyond the first solvation shell of Li cations.

We calculate the radial distribution functions of lithium-lithium dimer for different force field as shown in Figure 4-8. The first peak in $g_{Li-Li}(r)$ predicted by **FF2** (**FF4**)

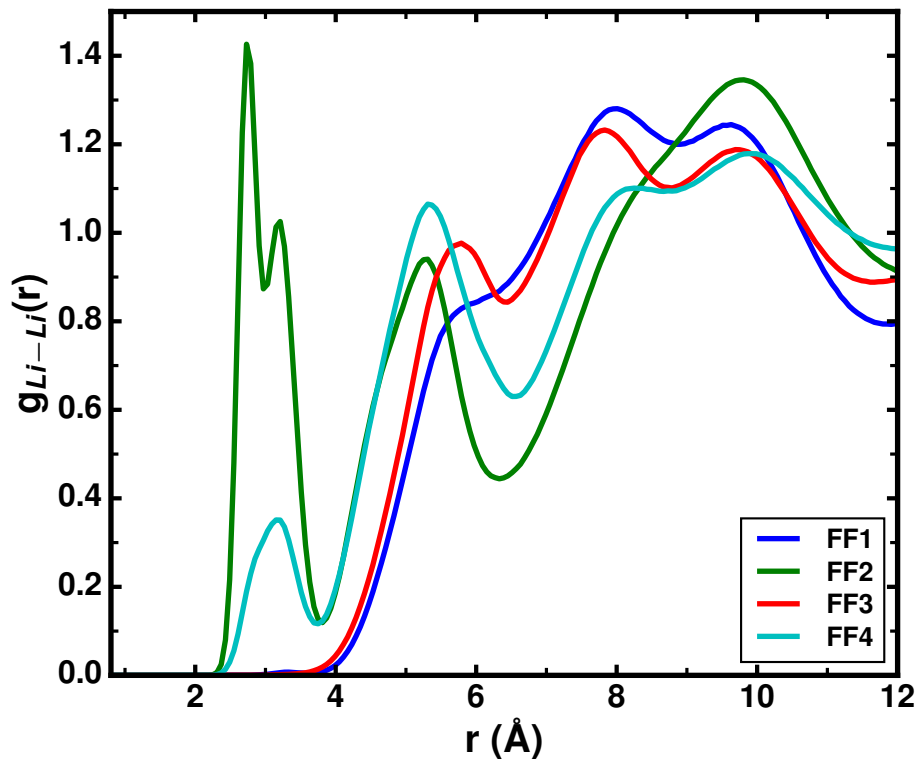


Figure 4-8: Radial distribution functions of lithium-lithium pair.

locates at 2.8 Å (3.1 Å), indicating that some lithium-lithium dimers start to form at this distance. Such a short distance is generally highly unlikely due to their strong Coulombic repulsion. Here it is made possible by the dehydration of the first solvation shell of Li cations, which allows them to share the central water molecules. However, there is no pronounced peaks in $g_{Li-Li}(r)$ for **FF1** (**FF3**) when the dimer distance is lower than 3.8 Å, which might be attributed to the larger charge of Li cation (1.0 e) and thus to a stronger Coulombic repulsion compared with the case where reduced Li charges (0.8 e) are used for **FF2** (**FF4**).

The non-trivial feature found in Figure 4-8 motivates us to further study the local coordination structures of lithium-lithium dimers at short distances in particular. For example, do these dimers share a water molecule or a TFSI anion? To ascertain this, we calculate the combined distribution function (CDF) obtained from calculating two joint radial distribution functions, which is able to identify the local environments of Li-Li dimers. In Figure 4-9 and Figure 4-10, the combinations of two radial distri-

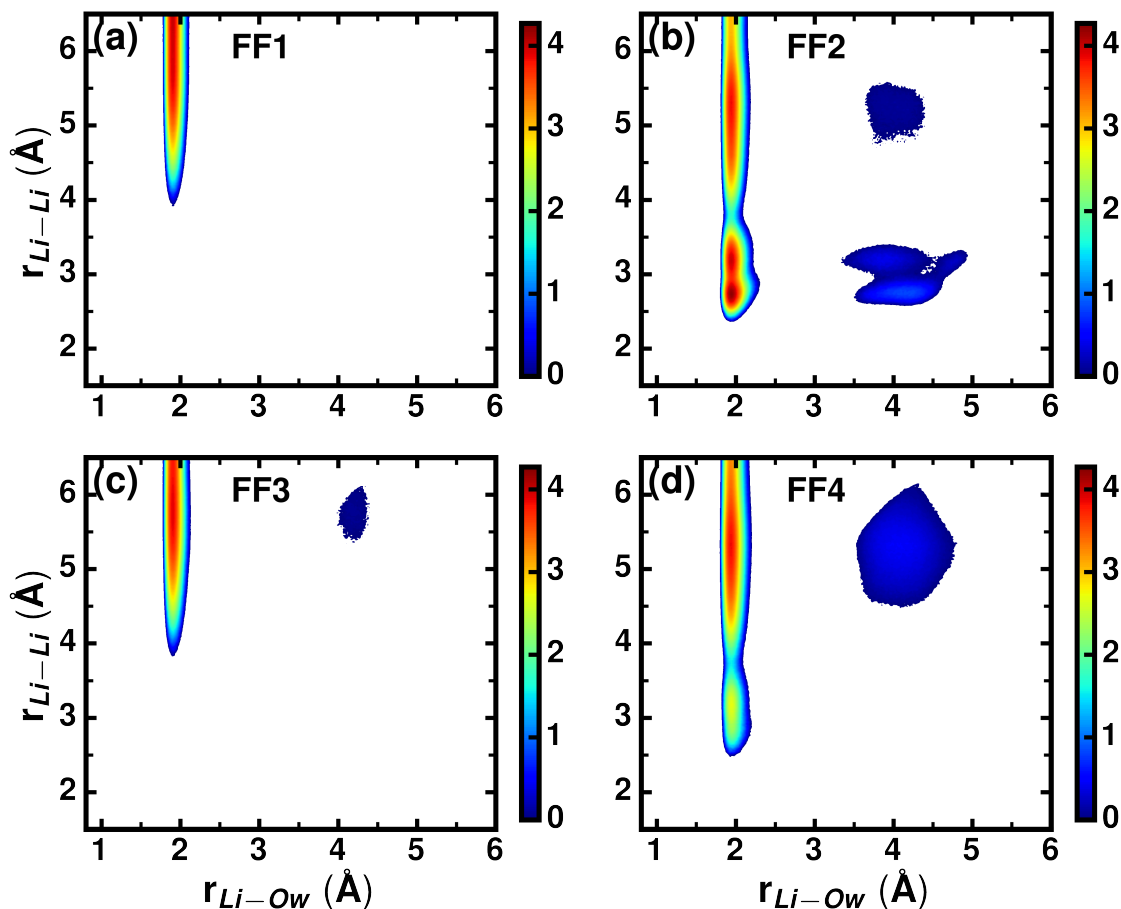


Figure 4-9: Combined radial/radial distribution functions for the Li-Ow(water) pair (x axis) and Li-Li pair (y axis). The color bars represent the intensity of the contour plots, in which the values are shown in logarithmic scale for clarity.

bution functions (lithium-water pair and lithium-lithium dimer in Figure 4-9, and Li-O(TFSI) pair and Li-Li dimer in Figure 4-10) are shown for each of the force field.

On the one hand, there is no distribution found for **FF1** and **FF3** when the lithium-lithium dimer distance is shorter than 3.8 Å (in Figure 4-9) or 4.2 Å (in Figure 4-10), which is in agreement with the absence of peaks (Figure 4-8) for these two force fields at short distances. In contrast, there are some occurrences for **FF4** (in both Figure 4-9 and Figure 4-10) and **FF2** (in Figure 4-9) within the dimer distance, i.e. lesser than 3.8 Å. On the other hand, Figure 4-10 shows that all the force fields give quite similar results for the radial distribution of Li-O(TFSI) “bond” appearing around Li-Li dimers, while the overall intensities are much smaller than that in Figure 4-9. Such a large difference of intensity indicates that the water

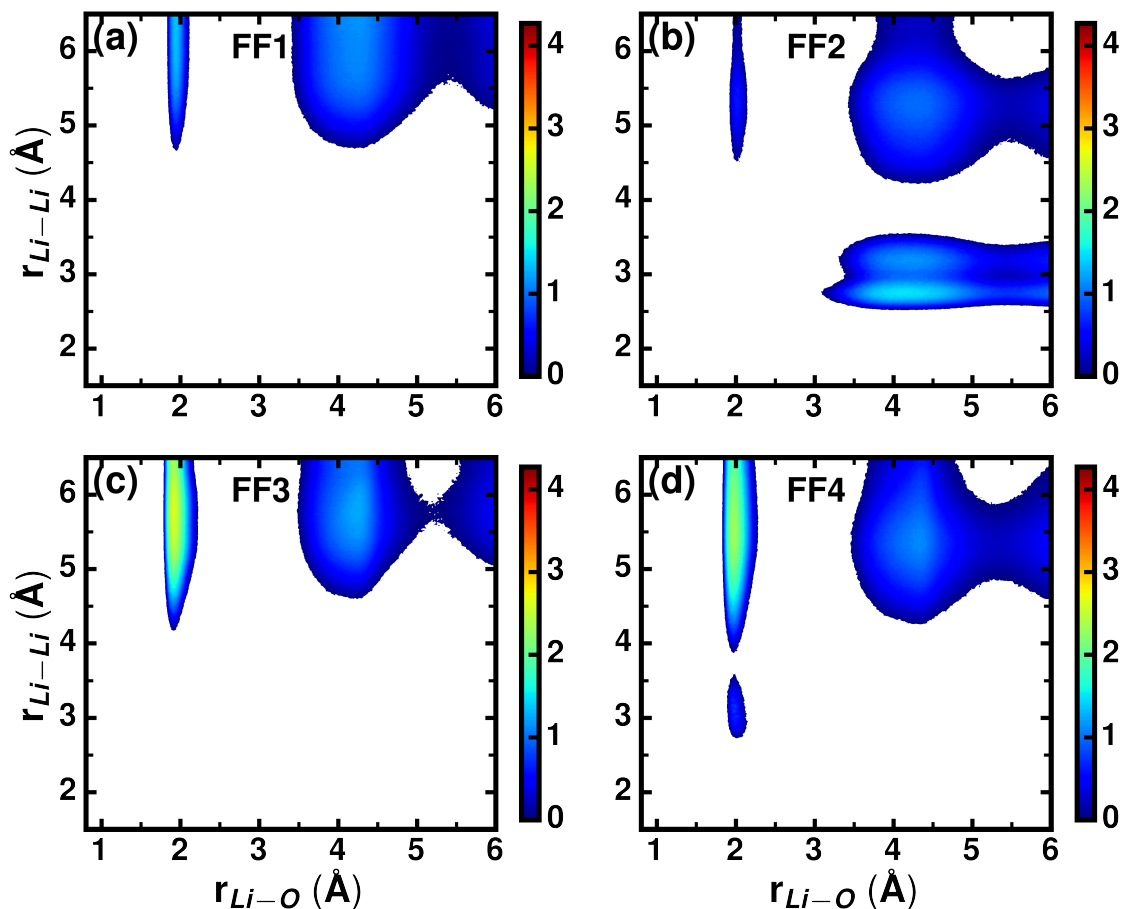


Figure 4-10: Combined radial/radial distribution functions for the Li-O(TFSI) pair (x axis) and Li-Li pair (y axis). The intensities have the same range as in Figure 4-9 for comparisons.

molecules are more likely to be involved in the solvation shell of the lithium-lithium dimer compared with TFSI anions. In particular, comparison between Figure 4-9b (c) and Figure 4-10b (c) indicates that the “first” solvation shell of lithium-lithium dimer ($r_{Li-Li} < 3.8 \text{\AA}$) is almost fully occupied by water molecules rather than O atoms from TFSI. This is different from the analysis of the first solvation shell of single lithium ion in Section 4.1.1, where a considerable portion of O(TFSI) atoms are involved in the first solvation shell, i.e. TFSI anions are excluded from the first solvation shell of lithium ions when these Li form dimers at short distances ($< 3.8 \text{\AA}$).

4.2 Role of water

4.2.1 Coordination number of water

The properties of “solvation shell” of water molecules are discussed in this Section. Firstly, the RDFs of water-TFSI pairs and corresponding coordination numbers are shown in Figure 4-11a and b. Different from the results of lithium ions, the RDF

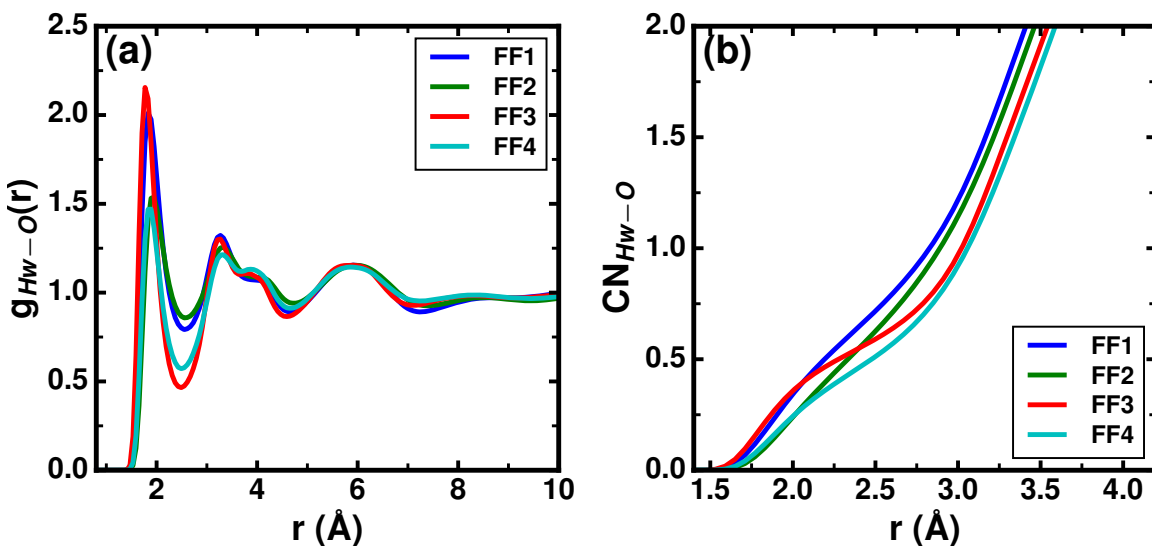


Figure 4-11: (a) Radial distribution functions of Hw(water)-O(TFSI) pair, and (b) Corresponding coordination numbers as a function of Hw(water)-O(TFSI) distance.

of water-TFSI pair and coordination number always experience great changes when switching from one force field to another.

The PMFs of the water-TFSI pair are studied to characterize the “solvation shell” of water molecules as well. As shown in Figure 4-12a, force fields with un-scaled charges (**FF1** and **FF3**) exhibit deeper minima (≈ -1.8 kJ/mol), corresponding to larger values of ΔE in Figure 4-12b, compared to those with scaled charges (≈ -1 kJ/mol). The first two force fields with same non-Coulombic parameters (**FF1** and **FF2**) give similar value of the first peak in the PMFs, while they are smaller than those of the last two force fields (**FF3** and **FF4**). As a consequence, the barrier height E_a for **FF3** is the largest one compared with the other force fields, corresponding to the strongest strength of water-TFSI “bonds”.

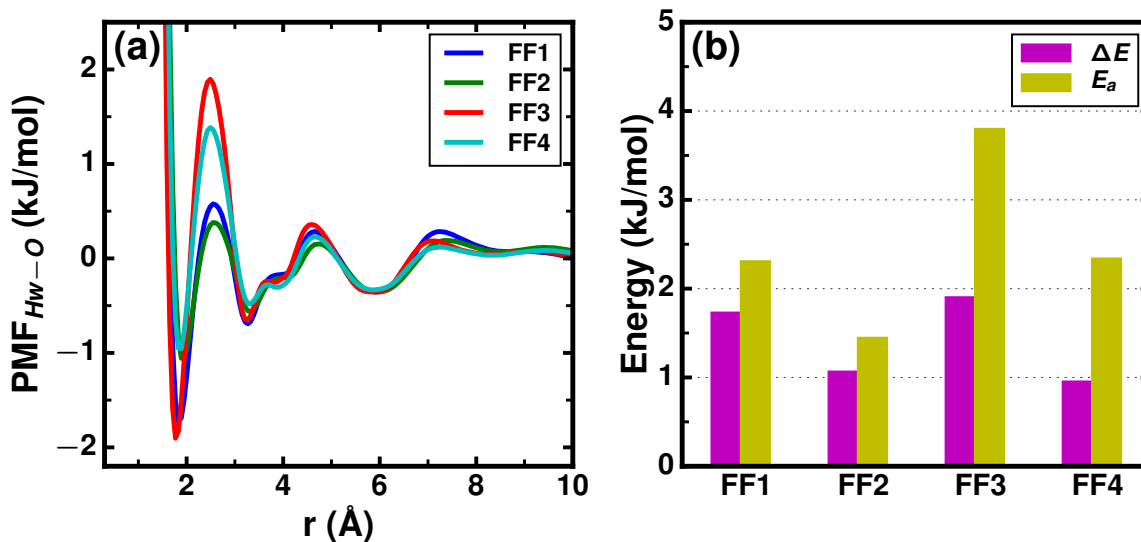


Figure 4-12: (a) Potential of mean forces for breaking of a Hw(water)-O(TFSI) “bond”. (b) Stabilization energies (ΔE) and barrier heights (E_a) calculated from the PMFs.

4.2.2 Competition between Li and TFSI

To understand whether the water molecules located in the vicinity of the TFSI (first peak of the $g(r)$ shown in Figure 4-11a) are free or Li-bounded, the combined radial/radial distribution functions of the water-TFSI pair and water-Li pair are calculated for the different force fields. Figure 4-13 shows the results within the first solvation shell of lithium ions ($r_{Ow-Li} < 2.4$ Å). Similar as for the RDFs, two more likely regions (red or orange region) centered at around 2.8 Å and 5.5 Å are found for O atoms from TFSI surrounding water molecules within the first solvation shell of lithium ions, which shows that the water molecules can be bounded to both the lithium and the TFSI ions. Moreover, **FF4** has the smallest value of intensity at short distances compared with the other force fields, which corresponds to the smallest probability of finding TFSI anion around water molecules. This shows that TFSI anions have a stronger hydrophobic character with this force field. On the contrary, the TFSI anions are more hydrophilic in **FF1** compared with the other force fields.

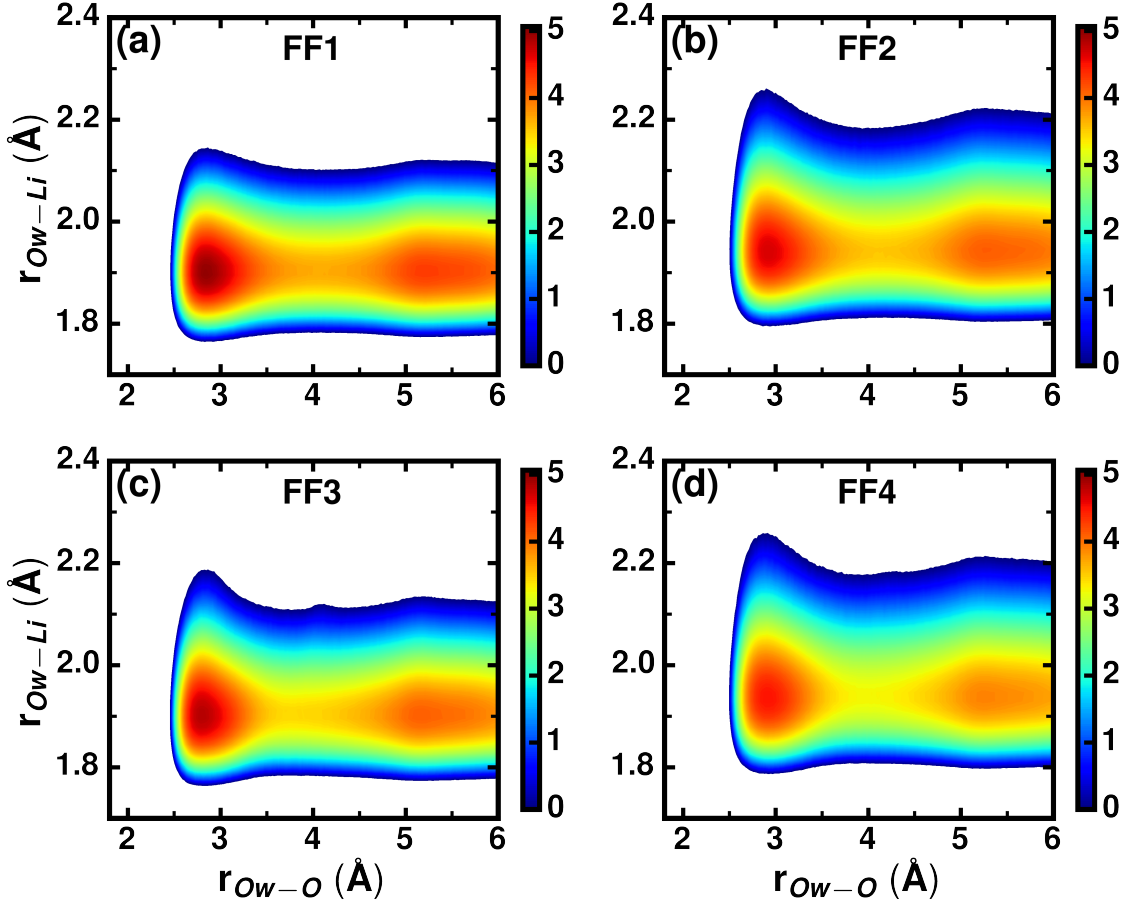


Figure 4-13: Combined radial/radial distribution functions for the Ow(water)-O(TFSI) pair (x axis) and Ow(water)-Li pair (y axis). The color bars represent the intensity of the contour plots, in which the values are shown in logarithmic scale for clarity.

4.3 Conclusions

In this chapter, we studied the structural properties of water-in-LiTFSI with the molality of LiTFSI at 15 m. The solvation shell of lithium ions was investigated in terms of the radial distribution function, coordination number, residence time of water molecule, and the potential of mean force for water molecules (TFSI anions) escaping from the solvation shell of Li cations. From the speciation point of view, the water/lithium ratio becomes lower than 4, which means that some Li^+ become under-hydrated, forming $\text{Li}(\text{H}_2\text{O})_3^+$ and even $\text{Li}(\text{H}_2\text{O})_2^+$ species. The missing water molecules are then replaced by the oxygen atoms of the TFSI anions, but the latter

is much more loosely bound based on the PMF analysis. Moreover, the analysis of residence time and the fraction of free water suggest a high dependence on the choice of force fields. In particular, the larger fraction of free water with a relatively smaller residence time for **FF4** compared with the others leads to the larger difference of diffusion coefficients between water molecules and Li^+ cations, which is in agreement with the experimental measurement. Apart from these, lithium-lithium dimers with short distance ($r_{\text{Li-Li}} < 3.8 \text{ \AA}$) are found for **FF4** and **FF2**, and these dimers are mostly coordinated by water molecules other than TFSI anions based on the analysis of combined radial/radial distribution functions.

The role of water molecules and their “solvation” properties were also investigated by the analysis of coordination number, combined distribution functions and so on. A hydrophobic behavior of TFSI anions is found for **FF4** while a more hydrophilic tendency is observed for **FF1**.

Chapter 5

Water-in-salt electrolyte at interface

The main physical property quantifying the performance of EDLCs for energy storage applications is the interfacial capacitance [128–130]. This quantity is highly dependent on the electrode/electrolyte couple as reported in previous works [131, 132]. In general, the main changes are attributed to the interfacial layer structure (or local structure) of the liquid electrolyte [112, 133]. Different pore sizes in nanoporous electrodes accompanying complex local structures have a large impact on the capacitance compared with non-porous electrodes. However, the capacitance can also take a wide range of values both in experiment and simulation even if the electrodes are planar [116, 134–136]. It is mainly the process of adsorption of cations and anions at the surface that controls the capacitance. The structure of the electrolyte at an interface differs from the bulk one, and it may change drastically when an electric potential is applied to the electrode. For example, Merlet *et al.* reported that the structure of an ionic liquid adsorbed on graphite electrodes can be either ordered or disordered depending on the applied voltage [116]. In this study, the structural changes were explained by a substantial change in the charge distribution across the interfacial region that led to changes in the differential capacitance with applied voltage. Limmer performed systematic simulations for dense ionic solutions near charged planar electrodes and showed that first-order transitions and spontaneous charge density

ordering at the interface might result in potential-driven anomalous differential capacitances [137]. More recently, Ma *et al.* reported that the differential capacitance might be strongly influenced by the charge-driven lateral structural evolution of the ions in EDLCs [138]. It is therefore very difficult to predict the interfacial structure without using complex simulation and/or experimental characterization techniques.

For the application of water-in-salt to EDLCs, several experimental works have been reported including some capacitance measurements [68–70, 78]. In addition, a few studies have aimed at understanding the interfacial structure of these electrolytes near electrodes [81, 139, 140], but their capacitive behavior has not been analyzed so far. Among the questions to be solved, an important one is whether water-in-salts behave as ionic solutions or ionic liquids. Thus, in this work, we performed molecular dynamics (MD) simulations at various applied potentials for an electrochemical cell consisting of a water-in-salt electrolyte at a concentration of 20 m (mol/kg) LiTFSI, placed between two planar graphite electrodes, in order to obtain a microscopic picture of the structure and the capacitive behavior on the interfaces and their dependence on the applied potentials. We discuss in particular the differential capacitances of either a single electrode or of the full electrochemical cell. We show the variation of the differential capacitance and relate them to structural changes at specific potential ranges.

5.1 Model and computational details

We use MD to simulate a cell consisting of 20 m LiTFSI placed between two graphite electrodes. The simulation box contains 255 Li cations, 255 TFSI anions and 707 water molecules (Figure 5-1). We use the FF1 force field described in Chapter 3 [120, 121]. As we discussed in chapter 3, the use of FF1 yields an electrical conductivity of 0.79 S/m a viscosity of 46.1 mPa·s, which are in good agreement with experimental results of Suo *et al.* (0.82 S/m and 36.2 mPa·s, respectively, albeit for a slightly larger concentration in salt of 20.8 m) [27]. The electrodes consist of three fixed graphene layers on each side (Figure 5-1) with in-plane dimensions of $L_x = 32.25 \text{ \AA}$ and L_y

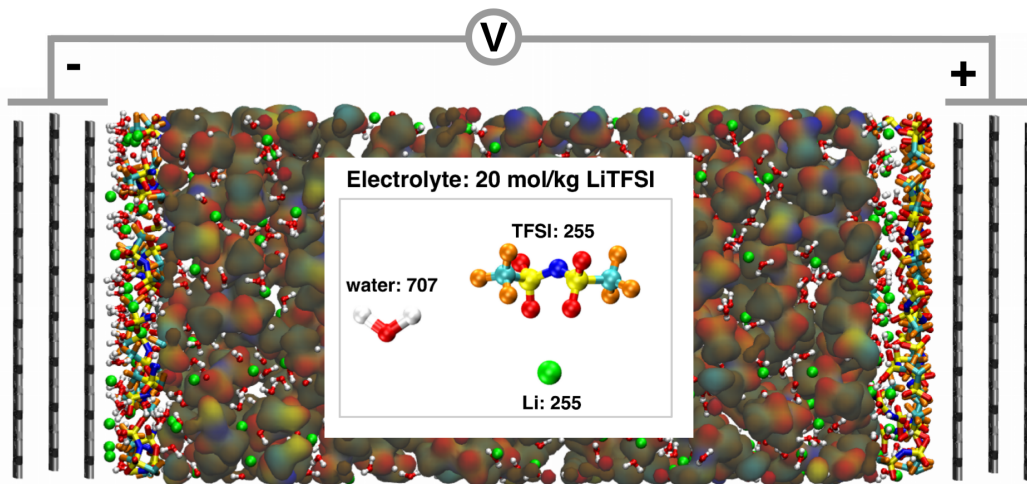


Figure 5-1: The snapshot of simulation cell consisting of 20 m LiTFSI confined between two three-layered graphite electrodes, in which the all-atom model of electrolyte is shown at the interfaces with H (white), O (red), Li (green), F (orange), C (cyan), S (yellow), and N (blue) atoms, respectively. The TFSI anions beyond interfaces are represented by isosurface instead. The carbon walls are shown in side views.

$= 34.37 \text{ \AA}$. The length of the cell in z -direction was set to $L_z = 96 \text{ \AA}$ to match the experimental density of 20 m LiTFSI in the bulk region of the simulation cell. The carbon atom charges on the electrode were allowed to fluctuate by imposing a constant potential method implemented in LAMMPS code [102, 103, 119, 141], which ensured an adequate description of the surface polarization by ions and water during simulations. A vacuum region was added in the z -direction and the Yeh-Berkowitz condition for slab correction was used to mimic the 2D periodic boundary condition. Its length was set to eight times L_z , which was the minimal value to ensure that the calculated carbon atom charges were converged. Simulations were performed for 11 applied potential differences between the two electrodes, $\Delta\Psi$, varying from 0 to 3 V in order to obtain good statistical properties. The simulations were conducted in the NVT ensemble with a time step of 1 fs at room temperature (298.15 K). The system was first equilibrated during 80 ns at zero constant charge on each electrode and followed by a 12 ns equilibration at the constant potential for each $\Delta\Psi$. The data was then collected in a 25 ns production run at the constant potential with configurations saved every 1 ps for each simulation.

5.2 Number density and charge density

For each simulation within the studied potential range, positive and negative electrodes were assigned equal but opposite potential, so that $\Delta\Psi$ follows the [Equation 5.1](#):

$$\Delta\Psi = \Psi^+ - \Psi^- = 2\Psi^+ = -2\Psi^- \quad (5.1)$$

The number densities are computed along the z -direction normal to the graphite

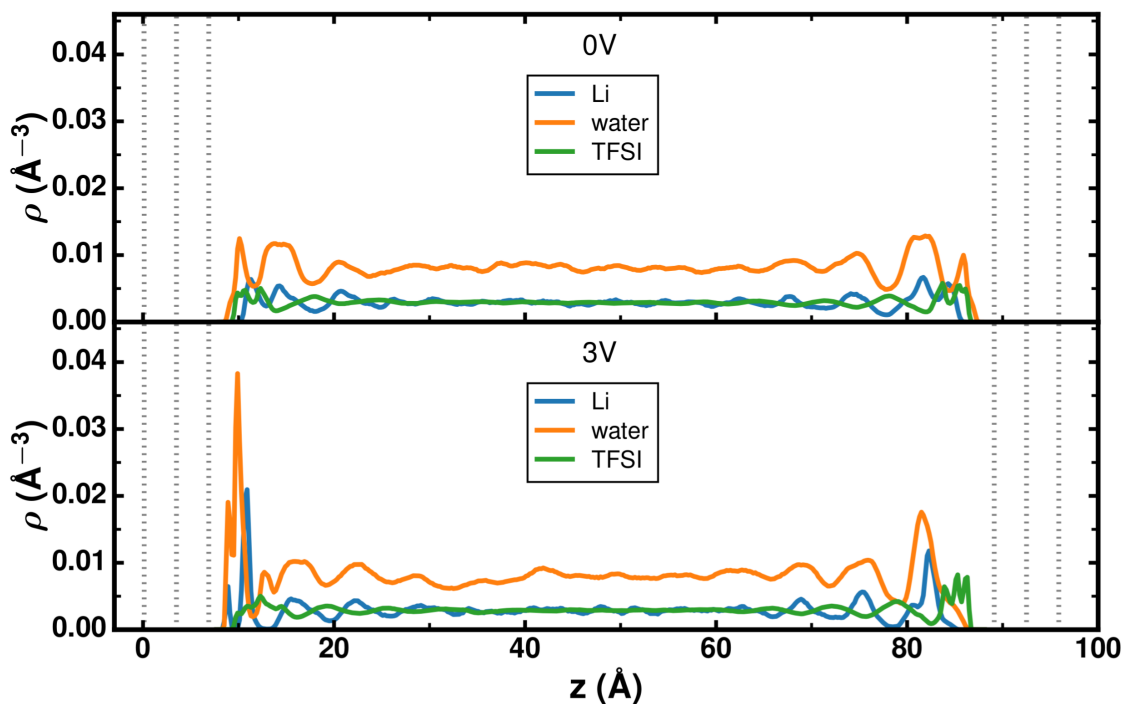


Figure 5-2: Number density profiles of Li cations, water molecules, and TFSI anions at applied potential differences $\Delta\Psi = 0$ V (top) and 3 V (bottom). Note that the density profiles of water and TFSI are represented by the average densities of atoms in their molecules, respectively, for better comparison.

surface. They yield bulk-like number density for each compound in the cell center (see the 0 V and 3 V cases in [Figure 5-2](#)), which ensures decoupling of the two interfaces.

At null potential difference ($\Delta\Psi=0$ V), layered structures of the water-in-salt electrolytes have already been observed (top of the [Figure 5-2](#)), reflecting the adsorption of all the species at electrode/electrolyte interface. The interactions in a given layer

are dominated by the short-range repulsion and the Coulombic interaction, in which the former controls the packing of ions and the latter occur between the various ions. Different sizes and shapes of the species lead to the variations in the distances between successive planes, and the bulk-like structure is then recovered after the density oscillations extend up to several tens of angstroms.

When a non-zero potential difference is submitted to the electrodes, as shown in the bottom of Figure 5-2 ($\Delta\Psi = 3$ V), the electrolyte keeps layered structures at the interface. The peaks are more pronounced due to the accumulation of charge on the electrode surfaces compared with those at the null potential difference. Apart from these, segregations of the ionic species (Li^+ and TFSI^-) appear on both the negative (left) and positive (right) electrodes, which is generally at the origin of the overscreening effect in ionic liquid electrolytes (more details of this effect will be discussed later in this section). In particular, on the negative electrode, water molecules approach to the electrode together with the increasing number of lithium cations while part of TFSI anions are excluded from the interfacial layers. In the meantime, on the positive electrode, most of the lithium cations and water molecules are rejected to enter the interfacial layer due to the domination of TFSI anions.

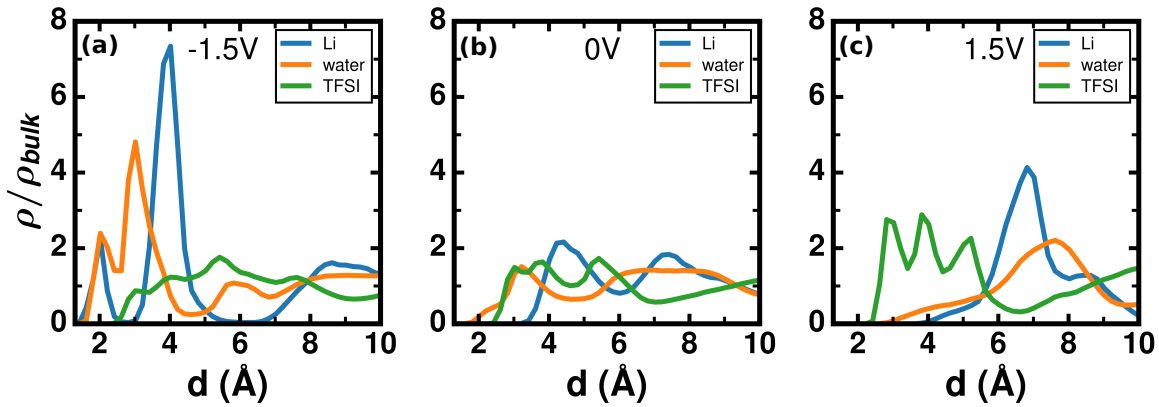


Figure 5-3: Normalized density profiles of Li cation, water molecule, and TFSI anion with respect to their bulk density, as a function of distance to the positive/negative electrode at applied potential $\Psi^- = -1.5$ V (a), $\Psi^\pm = 0$ V (b), and $\Psi^+ = 1.5$ V (c).

To have closer look at the structure of the interfacial layers, the number densities of ions and water molecules normalized by their corresponding bulk values are plotted

in Figure 5-3. They give results qualitatively similar to the one reported in previous work for a slightly different composition [81].

The most pronounced features of the ions and water density are observed within 6–8 Å, which correspond to ion and water partitioning in the interfacial layers. At null potential difference (Figure 5-3b), TFSI anions and water have similar peaks located at 3 Å, which is slightly higher than those in bulk. Though no lithium ion approaches the electrode surface closer than 3.4 Å, the first peak of Li cations appearing at 4.2 Å is the highest one observed in the interfacial layers. The overall peaks alternate between cations and anions indicating a typical picture of ionic liquid-like charge ordering at the interface.

Upon charging of the electrode up to $\Delta\Psi$ equals 3 V, i.e., 1.5 V and 1.5 V on the negative and positive electrodes, respectively, a significant increase of the cation (anion) and water adsorption at the interface is observed. On the negative electrode, the highest peaks of Li cations and water molecules increase up to values that are 7 and 5 times higher than their bulk ones, respectively (Figure 5-3a). The Li cations and water molecules have their first peaks located at the same distance to the electrode (2 Å), while different positions of their second peaks are observed (4 Å for Li and 3 Å for water). This indicates a change in the orientation of water molecules with respect to the electrode surface as reported by Vatamanu *et al.* [81]. On the positive electrode, the interfacial layers within 2–6 Å are dominated by TFSI anions with three observed peaks, while the water molecules and Li cations are screened from direct interaction with the electrode surface. Moreover, the highest peak within 6 Å is around 3 times higher than the bulk one for predominant species which is smaller than the ones on the negative electrode. The difference of the distributed features for all the species between negative and positive electrode surfaces has significant impact on the charge density distributions at interfacial layers.

In Figure 5-4, the charge density profiles are obtained by combining the contributions from both the electrodes and electrolytes, in which the relation $\rho_q = \sum \rho_\alpha \cdot q_\alpha$ (ρ_α and q_α are number density and charge for species α) is used to calculate the charge density of the electrolyte. Similarly to the number density profiles in Figure 5-

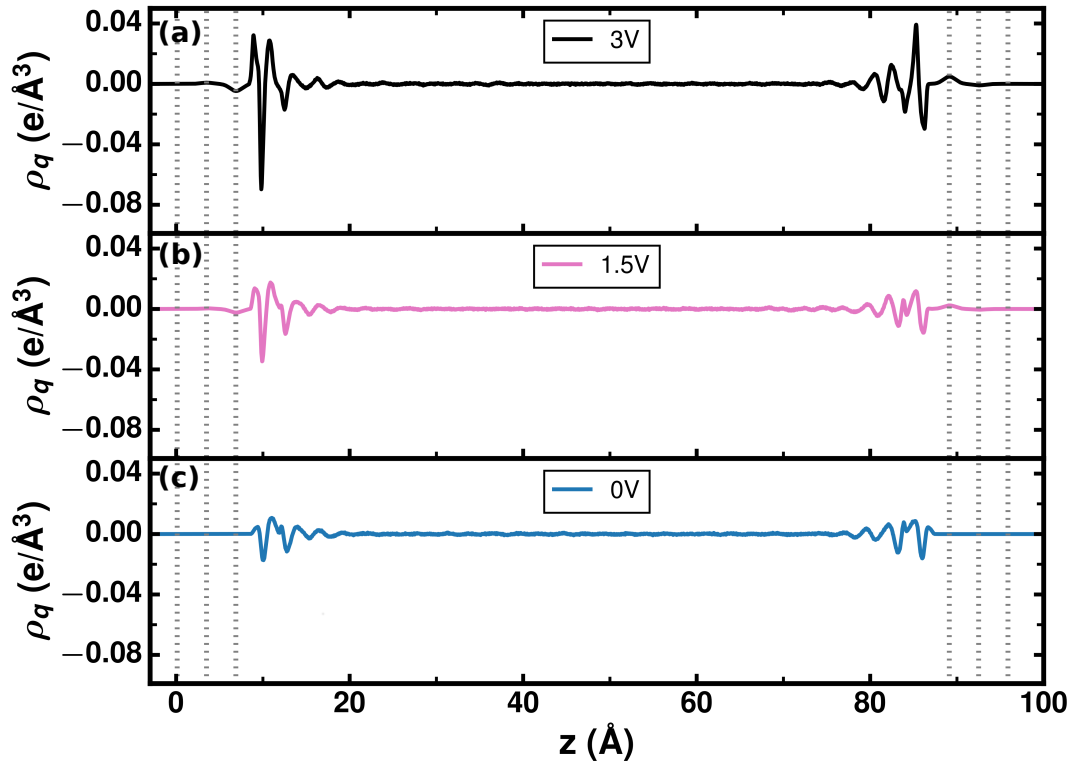


Figure 5-4: Charge density profiles across the simulation cell at applied potential difference $\Delta\Psi = 3$ V (a), 1.5 V (b), and 0 V (c).

2, bulk-like distributions are also observed for zero and non-zero applied potential differences in the cell center, confirming again the L_z length used in our simulations is long enough. At null potential difference (Figure 5-4c), a symmetric distribution of the charge density along the z direction is observed between negative and positive electrodes. However, the increase of the potential difference leads to an asymmetry between the two electrodes (Figure 5-4a and b), in which more pronounced peaks are observed at negative electrode surface compared to those at the positive electrode surface.

5.3 Calculation of integral capacitance from average surface charge

5.3.1 Average surface charge

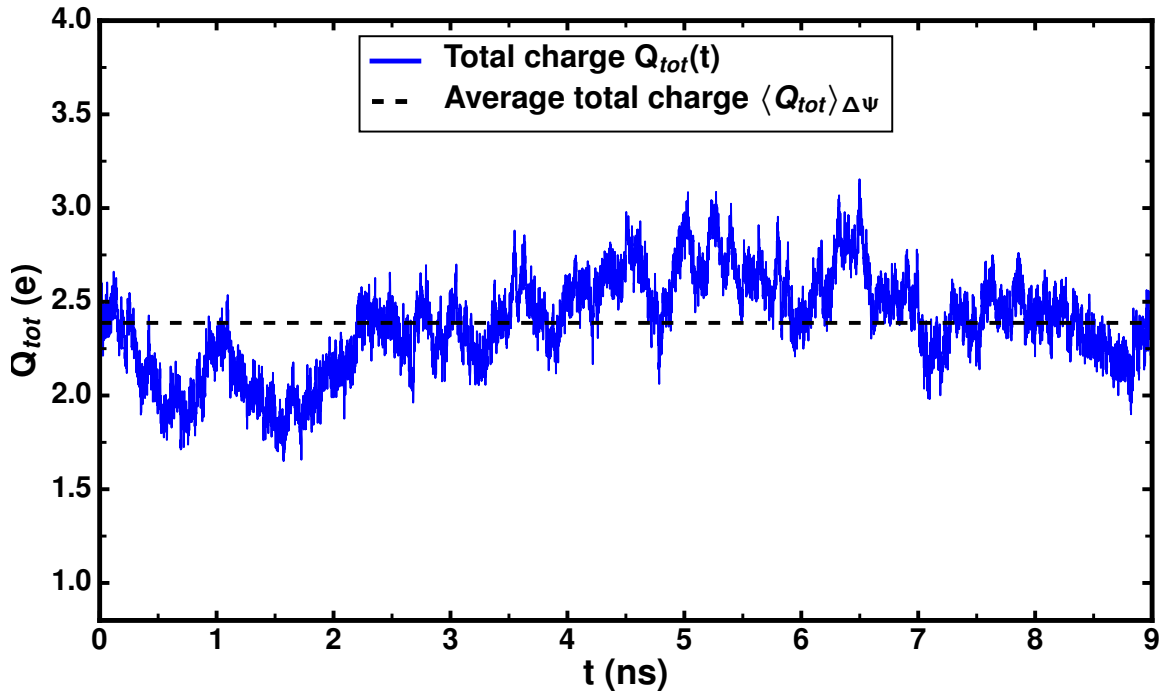


Figure 5-5: Total surface charge as a function of simulation time, the dashed line represents the average of the total surface charge.

The total surface charge on the negative/positive electrode is the sum of the charges of the individual electrode atoms, which is linked to the capacitive performance of supercapacitors. As shown in Figure 5-5, the total charge, $Q_{tot}(t)$, fluctuates with respect to the time in constant potential simulations. After a long equilibration for a fixed applied potential difference $\Delta\Psi$, the average total charge $\langle Q_{tot} \rangle_{\Delta\Psi}$ estimated from their fluctuations reaches a converged value. The latter can then be used to quantify the capacitance of a supercapacitor.

5.3.2 Integral capacitance of full electrochemical cell

The capacitance is one of the most important physical properties for the performance of EDLCs. However, one can define it in several ways. The integral capacitance of the full electrochemical cell, C_{int} , is defined as (for $\Delta\Psi \neq 0$):

$$C_{\text{int}}(\Delta\Psi) = \frac{\langle\sigma\rangle_{\Delta\Psi}}{\Delta\Psi} \quad (5.2)$$

where $\langle\sigma\rangle_{\Delta\Psi}$ is the average surface charge density of the positive electrode given by $\frac{\langle Q_{\text{tot}}\rangle_{\Delta\Psi}}{S}$ (with S the surface area). Note that most of the charge is accumulated on the two graphene planes located closer to the liquid, for example at the largest applied potential, the average charge within the three graphene layers are 0.21, -2.01 and 9.66 electrons, respectively. In the present work, the calculated C_{int} ranges from 3.5 to 4.3 $\mu\text{F}/\text{cm}^2$ depending on $\Delta\Psi$. This quantity is regularly used in applied studies to estimate the energy density of the EDLCs.

5.4 Calculation of differential capacitance of single electrode based on potential drop

5.4.1 Poisson potential

The electrostatic potential profile across the EDLC cell determines the potential drop for each interface, and is obtained by solving Poisson's equation:

$$\varphi(z) = \varphi_q(z_0) - \frac{1}{\epsilon_0} \int_{z_0}^z dz' \int_{-\infty}^{z'} dz'' \rho_q(z'') \quad (5.3)$$

where $\rho_q(z)$ is the average charge density profile across the cell, as shown in [Figure 5-4](#), and $\varphi(z_0)$ is an arbitrary integration constant with z_0 inside the left electrode, i.e. on the left $\varphi(z_0) = \Psi^-$ in our constant potential simulations. An illustration of the picture at $\Delta\Psi = 3$ V is shown in [Figure 5-6](#), the potential of the bulk Ψ_{bulk} , is determined as the average value of Poisson potential in the bulk region. The

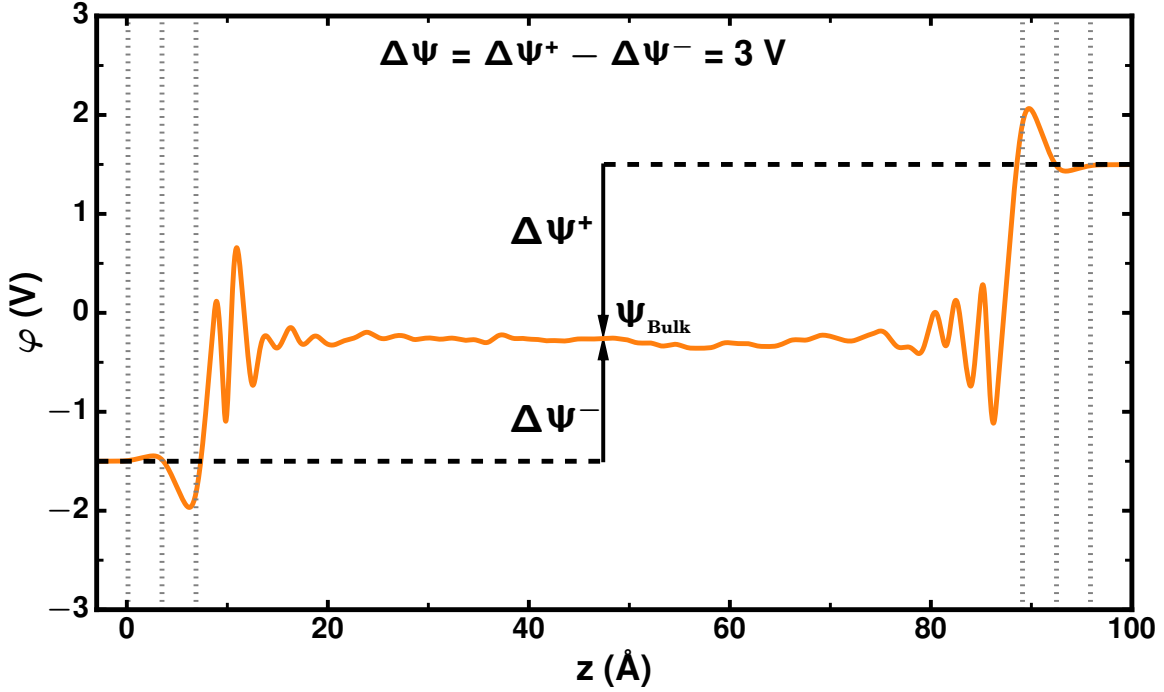


Figure 5-6: Poisson potential across the simulation cell calculated using Equation 5.3 at $\Delta\Psi = 3$ V.

potential drop across each interface is then given by $\Delta\Psi^\pm = \Psi^\pm - \Psi_{\text{bulk}}$ and is used to characterize the interfaces.

5.4.2 Differential capacitance of single electrode

The differential capacitance, C_{diff} , is defined by

$$C_{\text{diff}} = \frac{\partial \langle \sigma \rangle_{\Delta\Psi}}{\partial \Delta\Psi} \quad (5.4)$$

which measures the response of the average surface charge density to changes in the applied potential difference and provides much more information on the physico-chemical processes than the integral capacitance. The single electrode differential capacitances can also be defined by splitting the applied potential difference, $\Delta\Psi$, between the two electrodes into two potential drops, $\Delta\Psi^\pm$, at the electrode/electrolyte interface for both positive and negative electrodes.

The average surface charge as a function of the potential drop across each interface

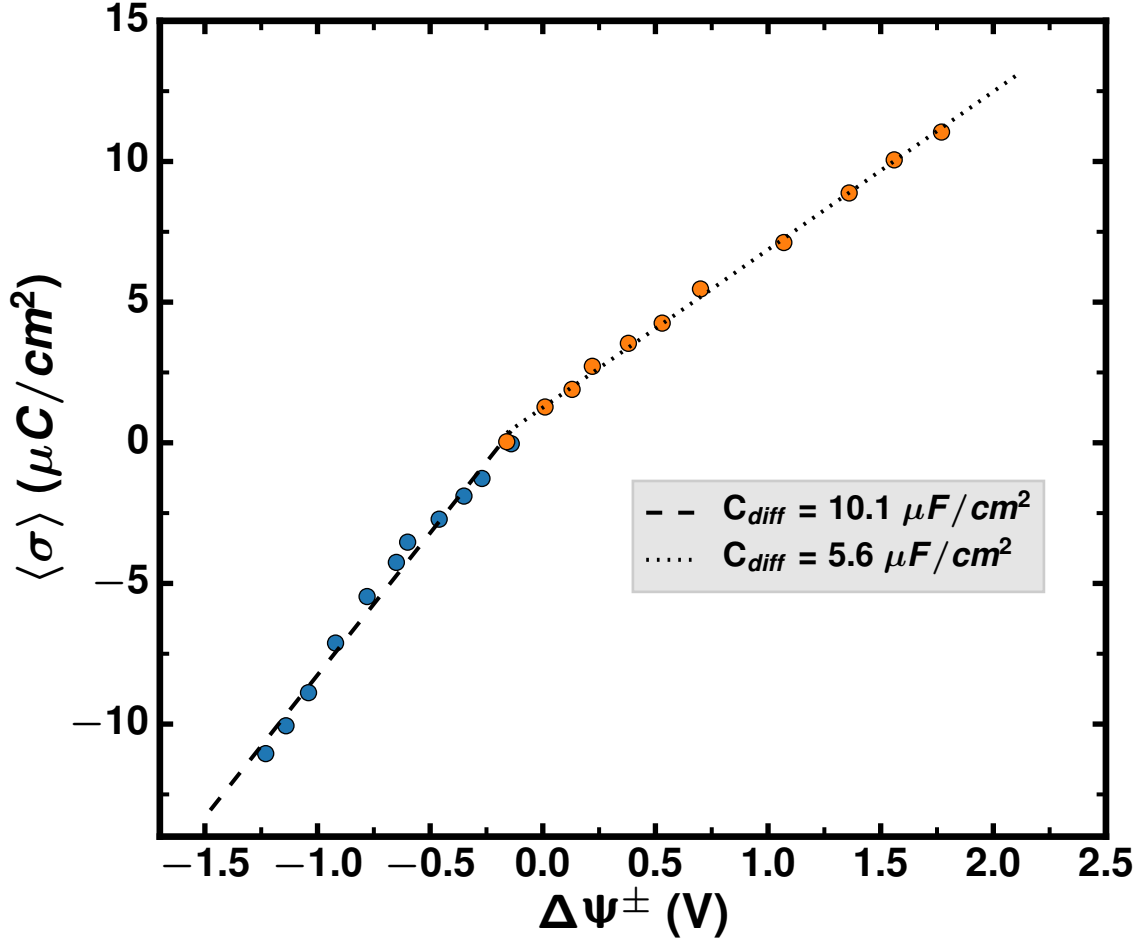


Figure 5-7: Surface charge density as a function of the potential drop across each interface. Linear fits are shown in dotted and dashed lines for negative ($\sigma < 0$) and positive electrodes ($\sigma > 0$), respectively. The corresponding differential capacitances are given by the slope of the two curves.

is represented in Figure 5-7 for various applied potentials. The average charge density $\langle \sigma \rangle = f(\Delta\Psi^\pm)$ plot differentiated at positive and negative surface charge with respect to $\Delta\Psi^\pm$, separately, provide the corresponding differential capacitances at positive and negative electrode through

$$C_{\text{diff}}^s = \frac{\partial \langle \sigma \rangle_{\Delta\Psi}}{\partial \Delta\Psi^\pm} \quad (5.5)$$

As shown in Figure 5-8, the curve may be fitted by many polynomial functions, leading to very different shapes for the capacitance. We therefore limit ourselves to two

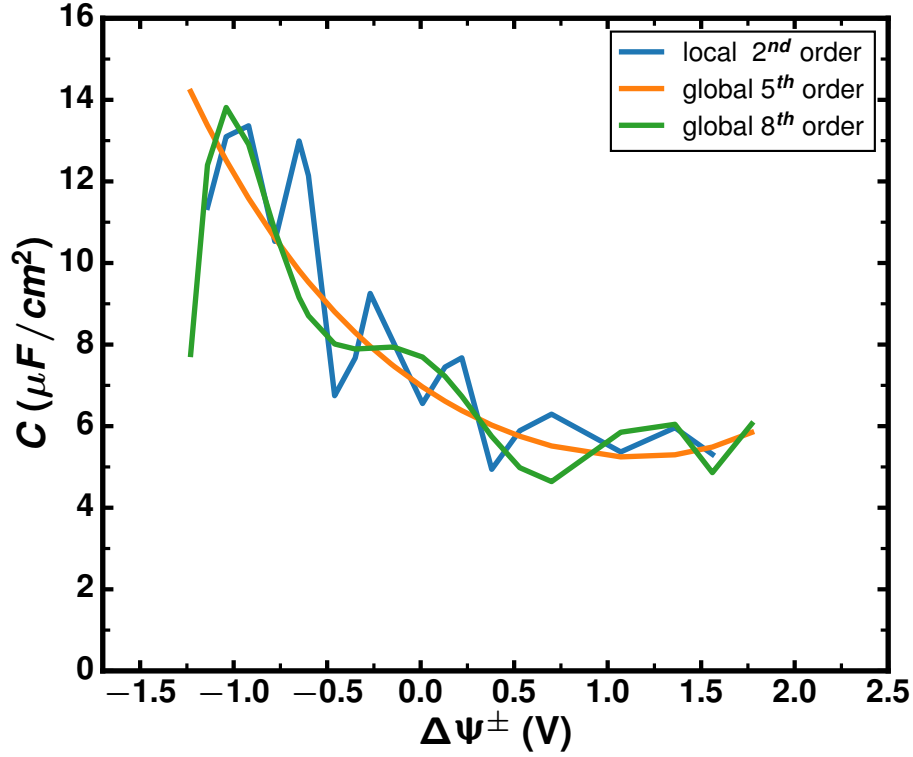


Figure 5-8: Fitted results of single electrode differential capacitance using different orders of polynomial fit. The $\langle\sigma\rangle = f(\Delta\Psi^\pm)$ plot in Figure 5-7 is fitted in different ways: first locally fits using 2nd order of polynomial for each three neighbored points; and then global fits using 5th and 8th orders of polynomial for the whole set of data. The differential capacitances are obtained by the derivative of each polynomial functions at specified potential drops.

linear fits, for $\Delta\Psi^\pm$ positive and negative, respectively. As shown in Figure 5-7, the negative electrode has a larger capacitance ($10.1 \mu\text{F}/\text{cm}^2$) than the positive electrode ($5.6 \mu\text{F}/\text{cm}^2$). Such a difference is in agreement with the results reported in planar graphite electrodes and pure RTILs [114, 142, 143], and it can be attributed to the different shapes or sizes of ions. The larger difference in capacitive behaviors between positive and negative electrodes compared with reported results in BMIM-PF₆ system ($3.9 \mu\text{F}/\text{cm}^2$ and $4.8 \mu\text{F}/\text{cm}^2$ for positive and negative electrode, respectively [142]) arises from the much larger asymmetry between the Li cation ($1.8 \text{ \AA}$ in radius) and the TFSI anion [144] (which has dimensions of $10.9 \times 5.1 \times 4.7 \text{ \AA}^3$).

5.5 Calculation of differential capacitance of full cell from fluctuation of surface charge

5.5.1 Fluctuation of surface charge

The differential capacitances can be computed more reliably using the importance sampling method [116, 118, 145, 146]. Compared to previous equation, single electrode capacitances cannot be obtained (the full cell one C_{diff} is calculated instead), but the method is much more converged statistically. This approach also allows studying microscopic properties, such as the number of ions close to the interface, as a continuous function of the applied potential difference. While for the standard approach these quantities are only available at the simulated potentials.

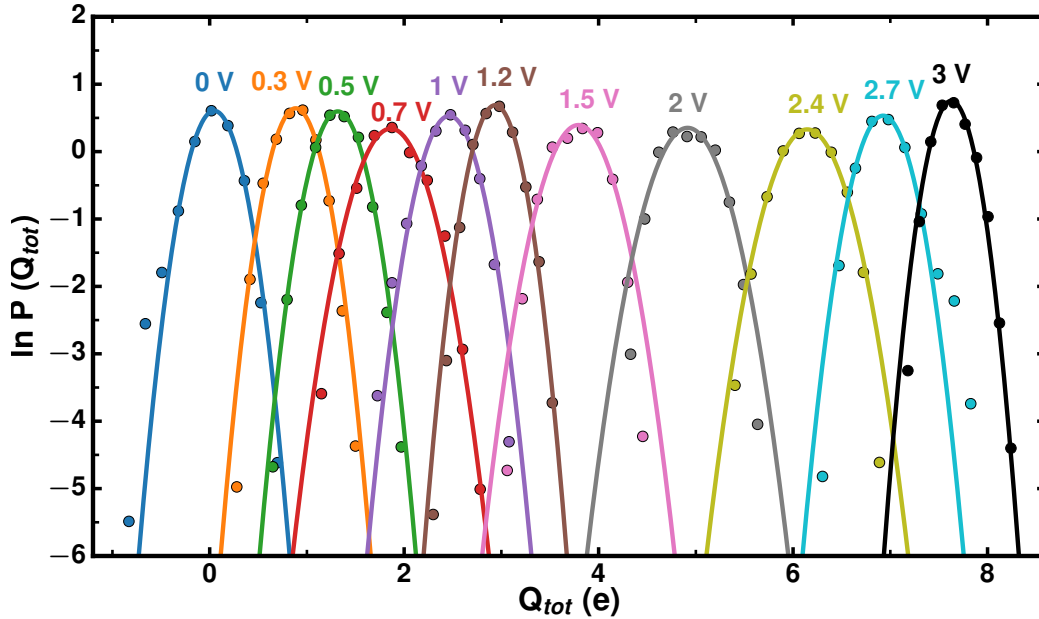


Figure 5-9: Distributions of total surface charge (Q_{tot}) at various applied potential difference, in which the distributions are shown in logarithmic scale. The points are the simulated results, and the corresponding line in same color represents the plot fitted by Gaussian distribution.

Here, the total charge Q_{tot} of the electrode is utilized to determine the weight of configurations at an arbitrarily applied potential by using the weighted histogram analysis method involved in importance sampling [147, 148]. As shown in Figure 5-9,

there is a good overlap between histograms of Q_{tot} obtained from the eleven performed simulations, which fulfills the requirement for correct histogram reweighting.

To obtain the probability distribution of any other property, A , as a function of $\Delta\Psi$, we just need to integrate Q_{tot} from the joint distribution of Q_{tot} and A as

$$P(A|\Delta\Psi) = \int dQ_{tot} P(Q_{tot}, A|\Delta\Psi) \quad (5.6)$$

Specifically, in this chapter, we consider below as the observables A : the surface charge density σ , the numbers of ions and water in the interfacial layers adsorbed on both negative and positive electrodes.

5.5.2 Distribution of surface charge and differential capacitance

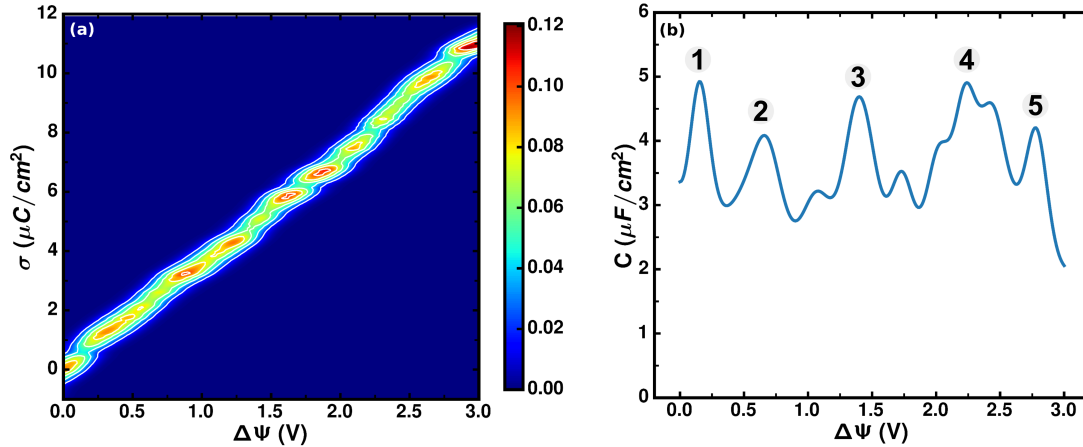


Figure 5-10: (a) Contour plot of the probability distribution of surface charge density on the electrodes. The probability is indicated by the color bar shown on the right. (b) Differential capacitance as a function of the applied potential difference.

The probability distribution $P(\sigma|\Delta\Psi)$ of electrode surface charge density at various $\Delta\Psi$ is represented by a contour plot in Figure 5-10a. The figure shows that the surface charge density monotonically increases with applied potential but experiences several nonlinear shifts in the probability distribution. In particular, there are several

more likely values of surface charge (red region), which are located at $\Delta\Psi \sim 0, 0.35, 0.9, 1.2, 1.6, 1.8, 2.6$, and 3 V. These applied potentials correspond to a more effective balance between the interfacial electrolyte and the surface charge on electrodes. The intermediate states between these points show large distributions of σ , which correspond to the large fluctuations regions where structural changes occur as we will discuss later.

In constant potential simulations, the differential capacitance (in Figure 5-10b) is proportional to the variation of surface charge density on the electrode as defined by

$$C_{\text{diff}} = \frac{S}{k_B T} \langle (\delta\sigma)^2 \rangle_{\Delta\Psi} \quad (5.7)$$

It can be obtained directly from the probability distribution of σ in Figure 5-10a. We recall here that the relation between the response to voltage and the equilibrium fluctuations of the surface charge is not limited to a typical linear response approximation [118, 149]. As discussed above the charge fluctuations are potential-dependent and therefore the differential capacitance shown in Figure 5-10b exhibits a strong dependence on the applied potential. It ranges from 2 to 5 $\mu\text{F}/\text{cm}^2$ with an average value of 3.67 $\mu\text{F}/\text{cm}^2$, which is in agreement with 3.6 $\mu\text{F}/\text{cm}^2$ computed from the single electrode capacitances as given by $1/C_{\text{tot}} = 1/C_- + 1/C_+$ (C_{tot} is the full cell differential capacitance corresponding to the values shown in Figure 5-10b). The minimum values of the differential capacitance correspond to the more likely distributions of surface charge at specific $\Delta\Psi$. Although some of the variations are quite small and may be due to finite-size effects, we observe five pronounced peaks at $\Delta\Psi \sim 0.15, 0.6, 1.3, 2.2$, and 2.8 V (labeled by ① – ⑤), that are more significant and are likely to correspond to intermediate states between two adjacent metastable basins (Figure 5-10a).

5.6 Effects of potential-driven structural changes on differential capacitance

The non-trivial features of the differential capacitance found in [Figure 5-10b](#) could be related to structural changes within the interfacial electrolytes. In order to investigate this possibility, the probability distributions ([Figure 5-11](#) and [Figure 5-12](#)) to find a given number of species in the interfacial layer of electrolyte are computed as a function of applied potential Ψ ($-\Delta\Psi/2$ or $+\Delta\Psi/2$ as defined in [Equation 5.1](#)). The interfacial layer is defined as the region within a distance of 6.6 Å from the negative (positive) electrode surface, this cutoff distance is extracted from the number and charge density profiles close to the interfaces at the studied potential range in order to account for the main adsorption peaks of lithium cations on the negative side and of TFSI anions on the positive side of the electrochemical cell (see [Figure 5-3](#)). The number of Li cations, O atoms of water, and O and F atoms of TFSI anions in the interfacial layers on the negative and positive electrodes are shown in [Figure 5-11](#) and [Figure 5-12](#), respectively.

On the negative electrode, the number of Li cations increases with $|\Psi^-|$, and the probability distribution becomes narrower at large negative potential ([Figure 5-11a](#)). The number of water molecules smoothly increases together with Li cations at low negative potentials ([Figure 5-11b](#)), but fluctuates more at large negative potentials. This may be attributed to the overlap of the Li ion solvation shells competing to include the water molecules in the presence of a large number of Li cations, and also accompanied by the change in the number of O from TFSI ([Figure 5-11c](#)). The first notable change occurs at -0.075 V (dashed lines with label ①) where the most probable number of F ([Figure 5-11d](#)) drops while the one of O from TFSI increases ([Figure 5-11c](#)). This indicates a reorientation of the TFSI anions. At the same time, the probability distribution of the number of Li cations becomes different at this region. This structural change could be related to the first peak (label ①) of full cell differential capacitance in [Figure 5-10b](#) since the potential at negative electrode ($\Psi^- = -0.075$ V) exactly matches the potential difference, $\Delta\Psi$, at which the first peak

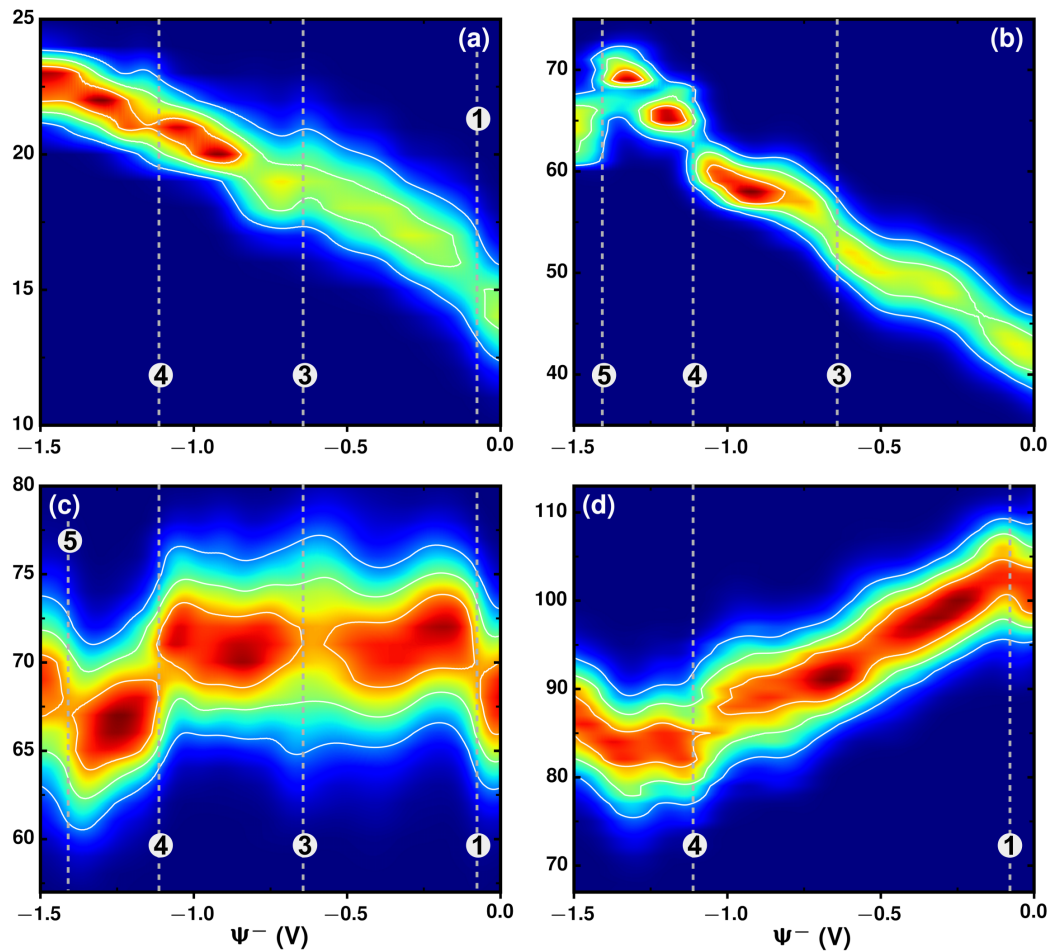


Figure 5-11: Number of ions in the interfacial layers on the negative electrode. Probability distribution of the number of Li cations (a), O (b) belonging to water molecules, O (c) and F (d) from TFSI anions, respectively, as a function of potential $\Psi^- = -\Delta\Psi/2$, as defined in Equation 5.1, for the negative electrode when the electrochemical cell is submitted to a voltage difference $\Delta\Psi$.

located ($\Delta\Psi = 0.15$ V). Different probability distributions around -0.65 V, labeled as ③ are found for Li cations, water molecules, and O atoms from TFSI (Figure 5-11a, b, and c), respectively, resulting in the third peak of capacitance in Figure 5-10b at $\Delta\Psi = 1.3$ V. The fourth peak in capacitance could be attributed to both the change of numbers and change of distributions for all species at $\Psi = -1.1$ V (labeled as ④), in which more Li cations approach the interfacial layer, along with more water molecules, and part of TFSI anions are forced to leave. Therefore, the interfacial structure strongly changes again.

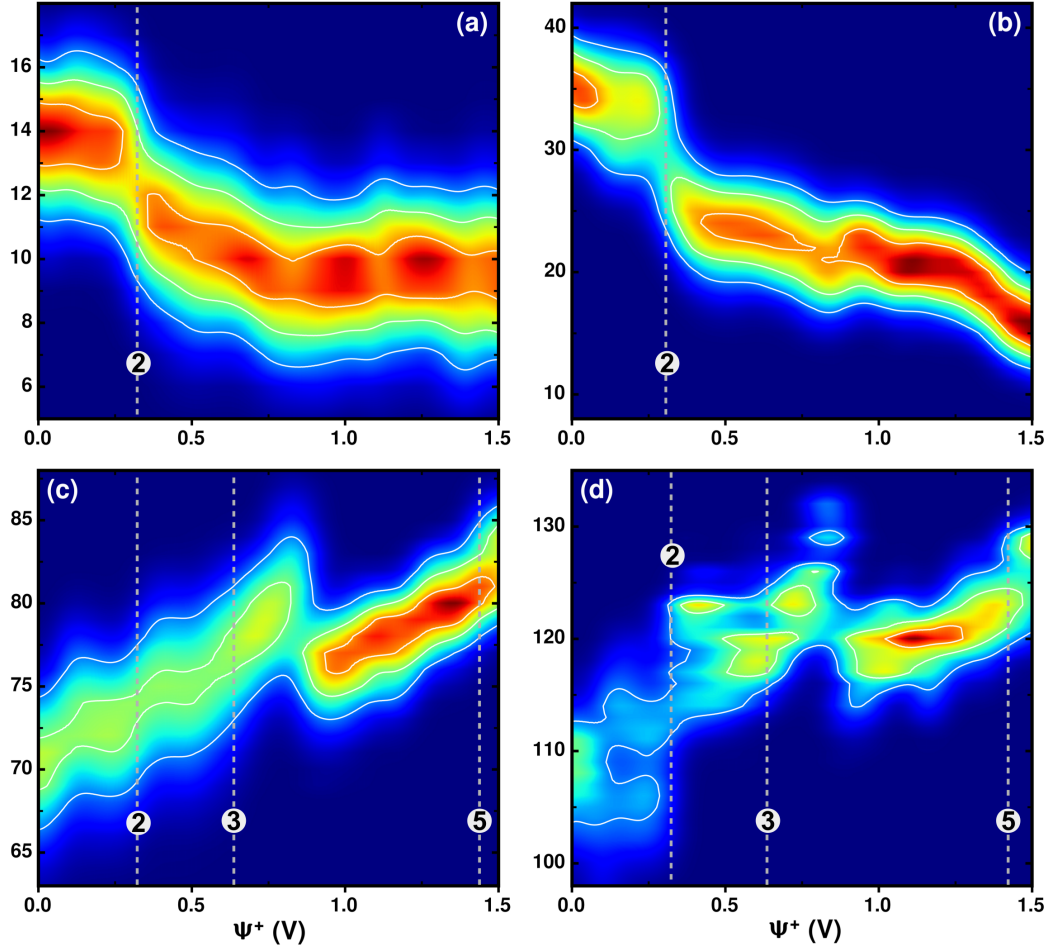


Figure 5-12: Number of ions in the interfacial layers on the positive electrode. Probability distribution of the number of Li cations (a), O (b) belonging to water molecules, O (c) and F (d) from TFSI anions, respectively, as a function of potential $\Psi^+ = \Delta\Psi/2$, as defined in Equation 5.1, for the positive electrode when the electrochemical cell is submitted to a voltage difference $\Delta\Psi$.

On the positive electrode the interfacial structure starts to change at $\Psi^+ = 0.3$ V as shown in Figure 5-12 (label ②). The desorption of Li cations (Figure 5-12a) together with water molecules (Figure 5-12b) starts at this potential while the number of TFSI anions keeps increasing (Figure 5-12c and d). These correspond to the second peak in the capacitance (Figure 5-10b) at $\Delta\Psi = 0.6$ V. At higher potential, $\Delta\Psi \approx 2.8$ V (with $\Psi^\pm \approx \pm 1.4$ V, labeled as ⑤), the distributions of number of O and F from TFSI become different on the positive electrode (Figure 5-12c and d), the number of O from TFSI (Figure 5-11c) increases again, along with decreasing number of water

molecules (Figure 5-11c) on negative electrode. This synergistic effect on the two electrodes leads to the fifth peak of capacitance located at 2.8 V.

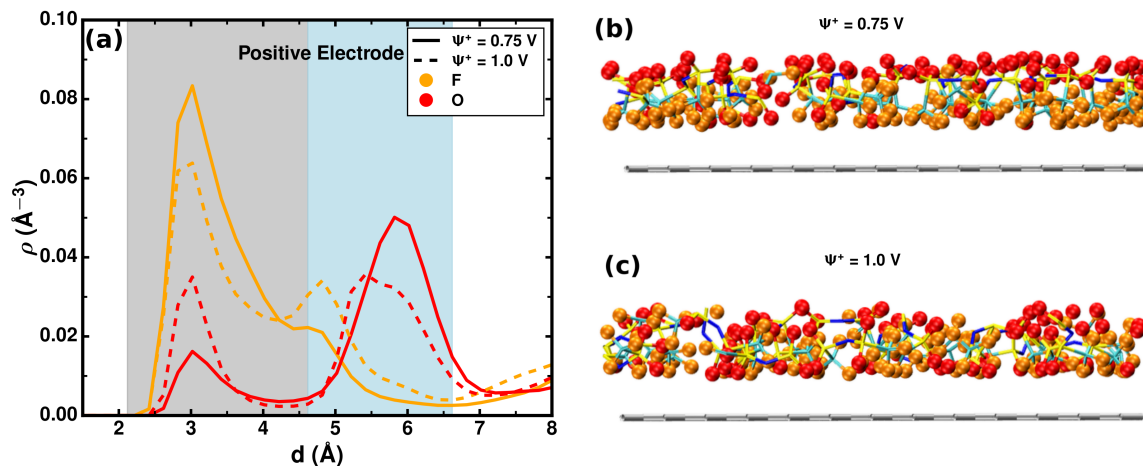


Figure 5-13: (a) Density profiles of O and F from TFSI anions as a function of distance from the positive electrode at $\Psi^+ = 0.75$ and 1.0 V ($\Delta\Psi = 1.5$ and 2 V). Grey and light-blue background represent the first and second adsorbed layers, respectively. (b) and (c) are the typical snapshots close to the positive electrode (grey slab on the bottom) from simulations at $\Psi^+ = 0.75$ and 1.0 V, respectively.

Apart from these structural changes associated with the capacitance peaks discussed above, we also observe a region between 0.75 V and 1 V, in which both the distributions and numbers of O and F from TFSI change on the positive electrode (Figure 5-12c and d). This reveals remarkable reorientations and rearrangements of TFSI anions at the interfacial layer on the positive electrode. We thus compare the number densities of O and F atoms from TFSI as a function of the distance from the positive electrode in this potential range. As shown in Figure 5-13a, the F atoms move from the first adsorbed layer (grey region) to the second layer (light-blue region) when Ψ^+ increases from 0.75 to 1 V, while the trend for O atoms is opposite. Considering that the O atom carries a larger negative charge than the F atom in our simulation cell, this change indicates that the TFSI anions rotate to approach more O atoms close to the electrode. This allows to compensate the growing surface charge on the positive electrode, as illustrated by two representative snapshots at 0.75 and 1 V, respectively, in Figure 5-13b and c. Such a structural change result in the rearrangement of not only TFSI anions but also the Li cations coordinated with these

TFSI anions, which could raise the fluctuation of differential capacitance.

5.7 Conclusions

In this chapter, the aim was to explore the capacitive performance of water-in-LiTFSI electrolyte in supercapacitors. We performed molecular dynamics simulations of 20 m LiTFSI placed between two planar graphite electrodes at various applied potentials ranging from 0 to 3 V. The integral capacitance of the full electrochemical cell, as well as the single electrode capacitances, were computed. Using importance sampling methods, the differential capacitance was investigated as a continuous function of the applied potential difference $\Delta\Psi$. The differential capacitance displays a number of non-trivial features which we explained by investigating the structural evolutions of the interfacial electrolytes. Contrarily to previous works on conventional aqueous or organic electrolytes [109, 150–154], the water molecules do not play a direct role on the variation of the capacitance because most of them are strongly bound inside the first hydration shell of the lithium ions, so that the capacitive behavior overall displays similar features as in the case of pure ionic liquids. This work is a first step toward understanding the capacitive behaviors of water-in-salt electrolyte in supercapacitors from simulations, in particular, the structural driven potential dependence of differential capacitance, which still requires more experimental explorations. The results could provide useful information for the understanding and development of new water-in-salts electrolytes and their applications in both supercapacitors and batteries.

General conclusions

The aim of this work was to investigate the water-in-salt electrolytes and their performance in supercapacitors. We performed molecular dynamics simulations for: i) bulk LiTFSI and water mixtures at various salt concentrations; and ii) interface of the LiTFSI-based water-in-salt electrolyte at high concentration in contact with planar graphite electrodes.

Firstly, the dynamic properties including viscosity, diffusion coefficient and conductivity were systemically investigated for systems of LiTFSI and water mixtures in a wide range of salt concentrations from 0.3 m to 20 m using a first parameterization of the force field (FF1). There is an apparent dependence of dynamic properties on salt concentrations. The system becomes viscous with increasing viscosity and decreasing diffusivity when switching from low to high concentration regime. The ionic conductivity first increases to a maximum (at 3.5 m) and then decreases at water-in-salt region. However, on the basis of Walden plot, where the molar conductivity is shown as a function of fluidity, the super-concentrated water-in-salt electrolytes exhibited even better performance as good-ionic solutions than those with smaller salt concentrations. Therefore, it seems that the conductivity of water-in-salt solutions at high concentration was decoupled from its viscosity, making it possible to be a promising electrolyte for both batteries and supercapacitors from the dynamic point of view.

Moreover, the dependence of diffusion coefficients on force field parameters, especially the ratio of water-to-lithium at super-concentrated water-in-salt electrolytes, are observed in our simulations, emphasizing the difficulty for precisely describing the water-in-salt electrolytes from simulations. Based on the modification of the parame-

ters from FF1, we re-computed the dynamics properties using four different force field and compared the results with experimental measurements. An optimized force field was ultimately proposed, which can be able to reproduce all the dynamic properties with experiments.

Apart from the dynamics of LiTFSI and water mixtures, the structural properties of the system at a specific concentration, i.e., 15 m LiTFSI dissolved in water, were also studied to have a deep understanding of the microscopic pictures of water-in-salt electrolytes at super-concentrated states. On the one hand, the solvation property of lithium ions was investigated in terms of the coordination number, residence time of water and potential of mean force. From the speciation point of view, the water/lithium ratio becomes lower than 4 due to the insufficient amount of water at 15 m, which leads to the under-hydration of Li^+ that forms $\text{Li}(\text{H}_2\text{O})_3^+$ or even $\text{Li}(\text{H}_2\text{O})_2^+$. The missing water molecules are then replaced by oxygen atoms from TFSI anions, but the latter is much more loosely bound based on the potential of mean force analysis. The analysis of residence time of water and fraction of free water strongly associated with the potential of mean force and exhibited a high dependence on the choice of force field. Moreover, the formation of some lithium-lithium dimers was observed at short distances ($r_{\text{Li-Li}} < 3.8 \text{ \AA}$), which were mostly coordinated by sharing water molecules rather than TFSI anions. On the other hand, the analysis of the solvation property of water molecules indicated that the hydrophobic behavior of TFSI anions also depends on the choice of force field.

Secondly, the study of 20 m LiTFSI aqueous solutions placed between two planar graphite electrodes was performed, in order to explore the double-layer structure of water-in-salt electrolyte, and its consequence for the interfacial capacitance. The results showed that many structural changes occur in the layer of adsorbed liquid when the potential of the electrode is changed. Fluctuations in the two ions (Li^+ and TFSI^-) concentrations as well as in the water distributions are observed. We also see substantial reorientations of the anionic species. All these structural changes, which were studied using importance sampling methods, are linked to peaks in the differential capacitance, which shows that the free energy landscape of this system is

very rich.

In summary, the comprehensive studies of water-in-salt electrolyte and its applications in supercapacitors provided beneficial microscopic pictures and mechanisms at play at the interface, leading to better understanding of these systems and the development of new water-in-salt electrolytes for electrochemical storage systems.

As perspective, on the one hand, the ion correlations and collective dynamics [155] in current LiTFSI-based water-in-salt electrolytes will be studied soon to fully understand the conductive behaviors of these systems, which are important for tuning new similar electrolytes towards optimal performance in their numerous applications. On the other hand, the study of Li-based water-in-salt electrolytes with various anion components is also deserved for ascertaining the role of anions plays in such systems. Furthermore, extending of the study to other salts-based, such as Na^+ , K^+ , Mg^{2+} , Zn^{2+} , etc. water-in-salt systems would also be interesting.

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Appendix A: publications

1. **Li Z.**, Jeanmairet G., Mendez-Morales T., Rotenberg B., Salanne M.*, Capacitive performance of water-in-salt electrolyte in supercapacitors: a simulation study. *J. Phys. Chem. C.*, **2018**, DOI:10.1021/acs.jpcc.8b07557.
2. **Li Z.**, Mendez-Morales T., Salanne M.*, Computer simulation studies of nanoporous carbon-based electrochemical capacitors, *Current Opinion in Electrochemistry*, **2018**, 9, 81-86.
3. **Li Z.**, Jeanmairet G., Mendez-Morales T., Burbano M., Haefele M., Salanne M.*, Confinement effects on an electron transfer reaction in nanoporous carbon electrodes, *J. Phys. Chem. Lett.*, **2017**, 8, 1925-1931.

Note: This work was done during the first year of my Ph.D., and it was not included in the thesis but as a appendix because the topic is quite different. The full paper could be found in appendix B.

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Appendix B

Li Z., Jeanmairat G., Mendez-Morales T., Burbano M., Haefele M., Salanne M.*, Confinement effects on an electron transfer reaction in nanoporous carbon electrodes, *J. Phys. Chem. Lett.*, **2017**, 8, 1925-1931.

In this work, we have performed MD simulations of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple dissolved in 1-ethyl-3-methyl-imidazolium tetrafluoroborate (EMIM- BF_4) room-temperature ionic liquid (RTIL) in contact with carbide-derived carbon (CDC) nanoporous electrodes. We investigated the free energy properties of an electron transfer reaction in a nanoporous carbon electrode. The electrodes were maintained at a constant potential of 0 V by allowing the atomic charges on the carbon atoms to fluctuate during the simulations, and it is thus a polarizable electrode model.

The vertical energy gap between the redox species was used as the reaction coordinate, which enabled us to interpret the microscopic solvent fluctuation properties. The computed probability distribution of the vertical energy gaps and the equilibrium value of energy gaps do not follow the linear response approximation of standard Marcus theory. We demonstrated the strong influence of the nanoconfinement effect on the solvation shell of the iron cations, which is the main reason for this departure from Marcus theory. In particular, the Fe^{3+} cation, which is tetracoordinated in the bulk, admits two stable solvation states in the nanoporous material: tetracoordinated and hexacoordinated.

To account for this deviation, we used the Two-Gaussian solvation model, from which the free energy curves for all the redox species in their various solvation states were extracted. This allowed us to qualitatively analyse the effect of the confinement on the electron transfer reaction. The fluctuations in the structure of the solvation

shell of Fe^{3+} were shown to have a negligible effect from a thermodynamic point of view. Rather, it was shown that the activation energy of the associated electron transfer process is much higher for the hexacoordinated form. It is therefore likely that the stabilization of this solvation state will result in a slow down of the electron transfer reaction kinetic.

This work is a first step towards a deeper understanding of the influence of the confinement on the electron transfer in redox supercapacitor devices, which will be extended in future years to promising systems such as biredox RTILs. The techniques develop in this work could also provide useful information for the development of ionic liquids-based thermo-electrochemical cells.

Confinement Effects on an Electron Transfer Reaction in Nanoporous Carbon Electrodes

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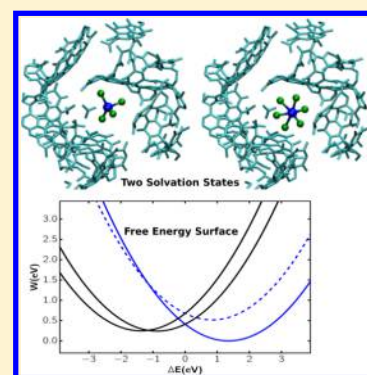
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Supporting Information

ABSTRACT: Nanoconfinement generally leads to a drastic effect on the physical and chemical properties of ionic liquids. Here we investigate how the electrochemical reactivity in such media may be impacted inside of nanoporous carbon electrodes. To this end, we study a simple electron transfer reaction using molecular dynamics simulations. The electrodes are held at constant electric potential by allowing the atomic charges on the carbon atoms to fluctuate. We show that the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple dissolved in an ionic liquid exhibits a deviation with respect to Marcus theory. This behavior is rationalized by the stabilization of a solvation state of the Fe^{3+} cation in the disordered nanoporous electrode that is not observed in the bulk. The simulation results are fitted with a recently proposed two solvation state model, which allows us to estimate the effect of such a deviation on the kinetics of electron transfer inside of nanoporous electrodes.



Nanoconfinement effects strongly impact many liquid properties, such as transport, diffusion coefficients, phase transitions, and solvation structures.^{1–4} They are particularly important for supercapacitors, which have emerged as a complementary energy storage solution to batteries.⁵ This is due to the fact that supercapacitors display faster charging times and consequently higher power deliveries than batteries while attaining longer life cycles. However, the energy density of batteries is higher. In supercapacitors, energy storage is realized through the adsorption of ions at the surface of two oppositely polarized electrodes, forming a so-called electrical double layer.⁶ Nanoconfinement has been observed to have a significant influence on the performance of supercapacitors, as has been demonstrated by experiments^{7,8} and simulations,^{9–12} where it was shown that the use of materials with subnanometric pores as electrodes greatly increases the capacitance of these devices.

Within the realm of electrochemical applications, room-temperature ionic liquids (RTILs) have attracted considerable attention.^{13,14} In principle, the properties of RTILs are tunable due to the wide variety of cations and anions from which they can be prepared. Because RTILs are solely made of charged species, it would have been expected that using them to replace standard electrolytes would increase the performance of supercapacitors. Yet, the interfacial capacitance of RTILs and acetonitrile-based electrolyte supercapacitors remains somewhat similar. This rather disappointing observation has been attributed to the more important correlations between ions in RTILs, which is due to the absence of electrostatic screening by the solvent.¹⁵

An alternative could be to take advantage of the tunability of RTILs to develop new storage concepts. Recently, Mourad et al. reported a large enhancement of the energy stored due to simultaneous capacitive and Faradaic processes when redox RTILs are used as electrolytes in a supercapacitor.¹⁶ Among the various questions raised by this study, the most important ones are the following: How is the electron transfer rate affected by confinement? Does the charging of such a supercapacitor remain dominated by the ionic diffusion?

From the theoretical point of view, electron transfer reactions in solution are usually studied in the framework of Marcus theory, which aims at accounting for the influence of solvent fluctuations on the rate of electron transfer.¹⁷ Marcus theory has been widely used to interpret experiments and simulations with undeniable success. However, some systems exhibiting a deviation from Marcus linear behavior have been reported.^{18,19} Several extensions to the theory were proposed to account for them.^{20,21} A reason why Marcus theory might fail arises from the fact that one of its key assumptions is that the fluctuations of the solvent around the reactant and the product are similar. Yet, if the solvation states of the two species are structurally different, this hypothesis can be wrong, as evidenced by the use of density functional theory-based molecular dynamics (MD) simulations of aqueous copper and silver ions.^{19,21} In experiments as well, introducing asymmetry in Marcus theory²² was necessary to fit

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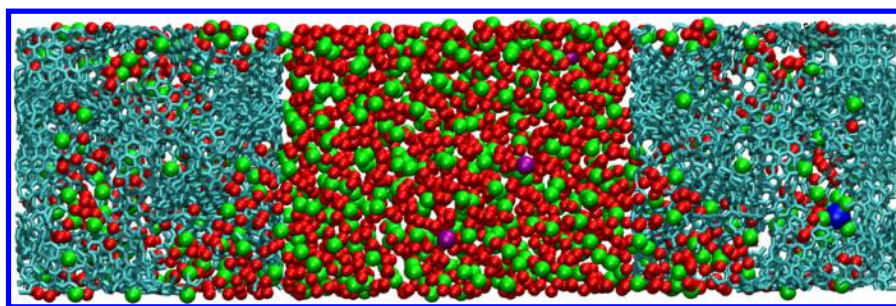


Figure 1. Simulation cell composed of two porous electrodes held at constant potential (cyan: C atoms). The electrolyte is composed of a FeCl_3 or FeCl_2 unit dissolved in EMIM- BF_4 , modeled using a coarse-grained force field³² (red: the three interaction sites of EMIM⁺; green: the single site of BF_4^- ; blue: Fe (III) cation; violet: Cl^- anions).

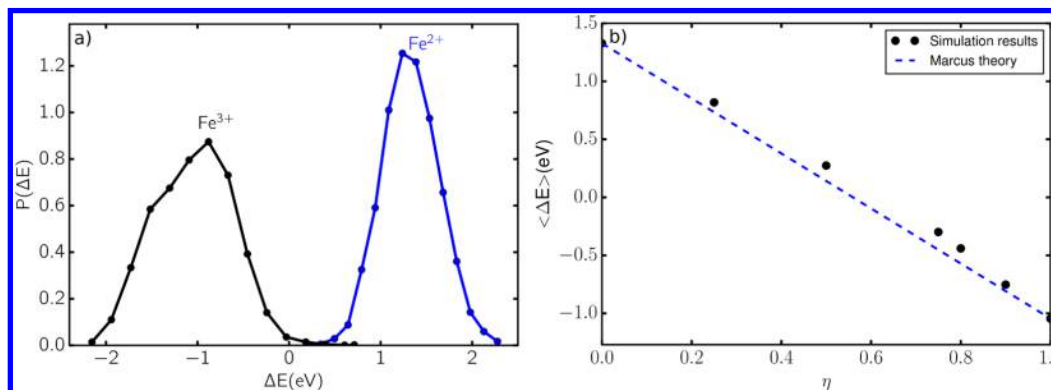


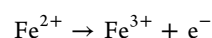
Figure 2. (a) Probability distribution of the vertical energy gap in reduced and oxidized states. (b) Average vertical energy gap for $\text{Fe}^{3+}/\text{Fe}^{2+}$ in RTILs with various coupling parameters η .

the voltammetric data of various RTILs.²³ Finally, in the case of interfacial systems, several studies have underlined the importance of field penetration into the metal and of solvent spatial correlations.^{24,25}

Confinement might have a drastic influence on the solvation shell of the adsorbed species.^{26,27} Thus, it is worth investigating this effect on the electron transfer rate.²⁸ We report here a MD study of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ electron transfer reaction, which has already been proposed in previous redox supercapacitor concepts.^{29,30} The experimental studies involve complex species, so that we focus on a simplified system in order to gain a first insight into electron transfer reactions in carbon nanopores. In particular, our study corresponds to infinite dilution because it is known that inorganic salts have low solubilities in imidazolium-based RTILs.³¹ The studied ionic liquid is 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM- BF_4), which is put in contact with model carbide-derived carbon (CDC) nanoporous electrodes. We show that the free-energy profiles for the electron transfer reaction strongly deviate from Marcus theory due to the presence of two solvation states for the Fe^{3+} species.

We build on previous work by using a simulation cell similar to the one that we used to investigate the origin of increased capacitance in nanoporous carbon-based supercapacitors (see Figure 1).¹⁰ We employ a coarse-grained model of EMIM- BF_4 with, respectively, 3 and 1 interaction sites for the cation and the anion,³³ to which we add one iron ion and the appropriate number of chloride counterions. We keep the electric potential inside of the electrodes constant and equal to 0 V by using the procedure developed by Siepmann and Sprik,³⁴ which allows the charge on the electrode to adjust in response to the local electric potential due to the electrolyte ions. Each electrode is represented by a model of CDC containing 3821 carbon

atoms.³⁵ To address the effect of the local environment experienced by the redox species, we run several simulations in which the initial position of the iron ion is set in different pores of the disordered carbon material. In order to study the following redox half-reaction



we perform simulations of the reduced species Fe^{2+} and of the oxidized one Fe^{3+} . It has been shown by Warshel^{36,37} that a relevant reaction coordinate to study the electron transfer reaction is the vertical energy gap ΔE , which is defined as

$$\Delta E(\{\mathbf{R}^N\}) = E_1(\{\mathbf{R}^N\}) - E_0(\{\mathbf{R}^N\}) \quad (1)$$

where E_1 and E_0 are the instantaneous potential energies of a system with either the reduced or the oxidized state of the redox-active species for a given microscopic configuration $\{\mathbf{R}^N\}$. We recall here that in the linear response assumption in Marcus theory,^{17,38} the distribution of the order parameter is Gaussian,³⁹ and in particular, the shape of the distribution of ΔE obtained by performing simulations with the Hamiltonian of the reactant or the product should be identical. As shown in Figure 2a, this is clearly not the case, the distribution for the Fe^{2+} being almost Gaussian while the one for the Fe^{3+} is not. This is a first indicator that this system does not follow a Marcus theory picture.

In order to increase the statistical accuracy, we use the free-energy perturbation method. This variant of umbrella sampling introduces a coupling parameter (η) between the reduced and oxidized states.⁴⁰ The simulations are then performed with an intermediate Hamiltonian associated with the potential energy surface E_η defined as the linear superposition

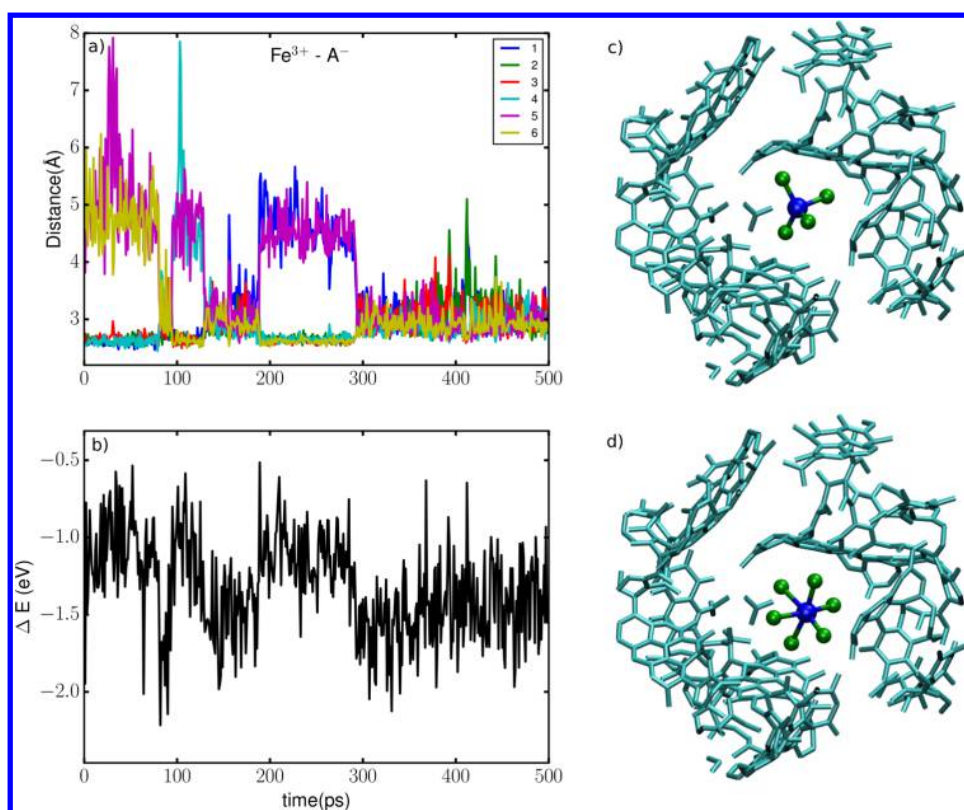


Figure 3. (a) Distance between Fe^{3+} and the six closest anions. (b) Vertical energy gaps of the oxidized state Fe^{3+} . (c,d) Snapshots of the two different solvation structures.

$$E_{\eta} = (1 - \eta)E_0 + \eta E_1 \quad (2)$$

A direct consequence of the linear assumption of Marcus theory is that E_{η} should vary linearly with η .⁴⁰ To test this, we carried out simulations with different values of the coupling parameter $\eta = 0, 0.25, 0.5, 0.75, 0.8, 0.9$, and 1.0 . It is clear for Figure 2b that the Marcus picture is violated because the corresponding vertical energy gaps do not follow the expected linear variation.

As pointed out in the introduction, discrepancy with Marcus theory often originates from strong changes in the solvation shell between the reduced and oxidized states. To investigate if that is indeed the case here, we examine the coordination number (CN) of the iron cation along the simulations. The radius of the first solvation shell is taken equal to the first minimum of the $\text{Fe}-\text{BF}_4^-$ radial distribution function in the absence of electrodes ($3.8 \text{ \AA}$). We observe that the CN of the Fe^{3+} cation fluctuates between values of 4 and 6 during the simulation. This is clearly an effect of the confinement because the cation remains close to the carbon electrode and the corresponding CN is 4 in the pure RTIL. In contrast, the Fe^{2+} cation has a CN that remains equal to 4 during the whole simulation, as shown in Figure S1.

The distances between Fe^{3+} and the six nearest anions along a representative trajectory are displayed in Figure 3a; the other simulations display similar variations. The alternation between two coordination environments is confirmed by the fact that during some parts of the simulations we detected that four anions are closely coordinated to the Fe^{3+} with a $\text{Fe}-\text{BF}_4$ distance of $2.8 \text{ \AA}$, the two remaining anions being located farther away from the iron with a distance greater than $4 \text{ \AA}$, while in other parts, the six anions are coordinated with Fe^{3+} with metal–ligand distances fluctuating between 2.6 and $3.8 \text{ \AA}$. Figure 3c,d shows representative snapshots of the two coordination states, which

appear to be tetrahedral and octahedral, respectively. The corresponding fluctuations of the vertical energy gap are shown in Figure 3b. Sudden changes occur concomitantly with the jumps in CN in Figure 3a, which shows that the confinement effect on the solvation of Fe^{3+} is at the origin of the departure from Marcus theory discussed above.

Among all models available in the literature to extend Marcus theory to nonlinear behavior,⁴¹ we use the one proposed by Vuilleumier et al.²¹ In particular, we employ their two-Gaussian solvation (TGS) state model, which allows the reactant and product to experience two different solvation states (S_0 and S_1). This leads to four (two pairs) diabatic free-energy parabolas instead of two in the case of Marcus theory. For each of the states S_0 or S_1 , the Landau free energy is assumed to be quadratic, which corresponds to a Gaussian probability distribution P_{η} . The authors also derived the necessary equations to compute the average energy gap $\langle \Delta E \rangle_{\eta}$ and the Landau free energies.

Marcus theory involves only two parameters: ΔA measures the relative position of the two parabolas, while λ is the reorganization energy of the solvent, which fixes the curvature of the parabola and also the width of the Gaussian distribution of the reaction coordinate. In the TGS model, four parameters are required, one reorganization energy for each state λ_{S_0} and λ_{S_1} , and the relative positions of the two parabolas for each solvation state ΔA_{S_0} and ΔA_{S_1} . Moreover, a fifth parameter is necessary to set the relative position of the two pairs of parabolas, for instance, the difference in free energy between the two solvation states of the reduced species $\Delta_S A_0 = A_{S_1}^{\text{Fe}^{2+}} - A_{S_0}^{\text{Fe}^{2+}}$.

The effect of the confinement was not investigated by the authors of the TGS model because they only carried out simulations in bulk. However, it has been shown from simulation

studies of the $\text{Eu}^{3+}/\text{Eu}^{2+}$ redox couple in potassium chloride molten salt at a fcc metallic electrode that the reorganization energy strongly depends on the distance between the ion and the electrode.⁴² This reorganization energy is expected to decrease when the redox species get closer to the electrode. We mention that this behavior had previously been predicted theoretically by Marcus for perfect conductors,^{38,43} but this effect should decrease if the role of field penetration into the metal electrode was accounted for.^{24,25}

To quantify this effect in our system, we performed additional simulations with planar graphite electrodes. They confirm the dependency on the distance to the electrode of the reorganization energy, as shown in Figures S2–S4. In nanoporous electrodes, it is not possible to define a simple distance to the electrode; the fit of the TGS model should therefore yield an averaged contribution of all of the possible distances. However, we observed that the iron does not go into contact with the carbon during the entire simulation, regardless of the iron solvation state, the nature of the pore in which it is solvated, or its CN. For this reason and for the sake of simplicity, we made the additional assumption that the reorganization energies should be equal for both states, turning the original five-parameter model TGS into a four-parameter one. The different parameters obtained by fitting the simulation data are given in Table 1.

Table 1. TGS Model Parameters for $\text{Fe}^{3+}/\text{Fe}^{2+}$ Obtained by Fitting Simultaneously on $P_\eta(\Delta E)$ and $\langle\Delta E\rangle_\eta$

TGS parameters (eV)	λ_{S_0}	ΔA_{S_0}	λ_{S_1}	ΔA_{S_1}	$\Delta S A_0$
	1.11	0.24	1.11	−0.27	0.52

Figure 4 compares the results obtained by simulations to the TGS model with the parameters given in Table 1. The left-hand panel shows the probability distribution of the vertical energy gap for the simulations realized with different values of the η parameter. The fitted TGS model agrees well with the whole set of distributions. The right-hand panel reproduces the data of Figure 2, that is, the vertical energy gap as a function of η . While those data could not be well reproduced by assuming linear response, the use of the TGS model allows an almost perfect fit to the data.

The diabatic free-energy curves for the reduced and oxidized species in $\text{Fe}^{3+}/\text{Fe}^{2+}$ predicted by the TGS model with the parameters of Table 1 are plotted in Figure 5. The two parabolas

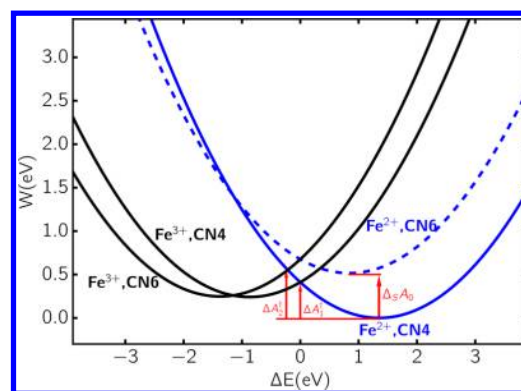


Figure 5. Diabatic free-energy curves of the reduced and oxidized species obtained by the TGS model with the parameters of Table 1. “CN4” and “CN6” labels refer to the tetra- and hexacoordinated solvation states and correspond to S_0 and S_1 , respectively.

for the reduced or oxidized state ($\eta = 0$ or 1) correspond to a given solvation state. The free-energy difference ($\Delta S A_0$) between the hexacoordinated and the tetraordinated forms of Fe^{2+} is large (0.52 eV) with respect to the thermal energy $k_B T$ (34.5 meV at $T = 400$ K). The hexacoordinated state is therefore very unlikely, which explains why it is never observed in our equilibrium simulations. On the other hand, the free energies of the two coordination states are very close to each other for Fe^{3+} .

The thermodynamic and kinetic information extracted from Figure 5 is summarized in a mechanistic diagram in Figure 6. We

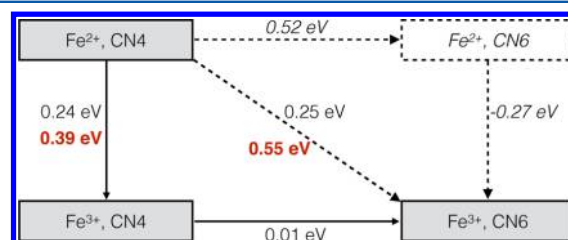


Figure 6. Mechanistic diagram of the electron transfer reaction under confinement. Black numbers: free-energy differences; red numbers: activation energies (labeled $\Delta A_1^\ddagger$ and $\Delta A_2^\ddagger$ in Figure 5).

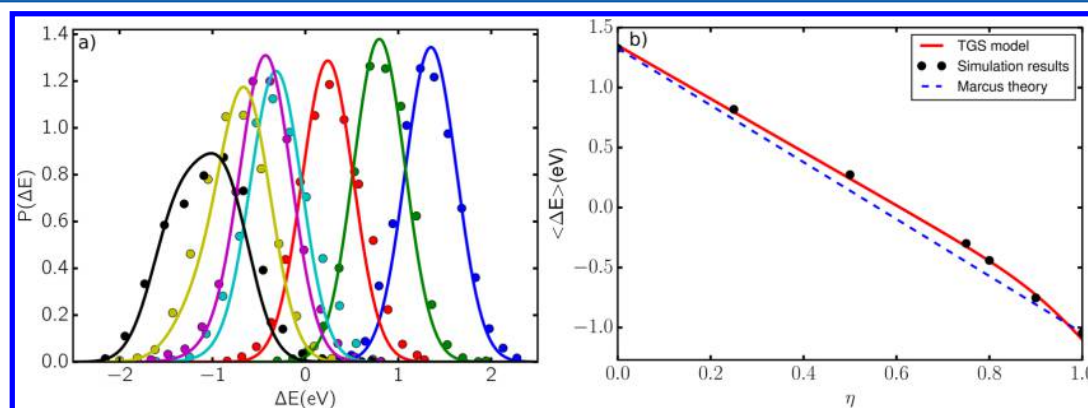


Figure 4. (a) Probability distribution of the vertical energy gap as a function of the coupling parameter η . Points are the simulation data, and lines are the TGS model with the parameters from Table 1. (b) Comparison between the simulated average vertical energy gap for $\text{Fe}^{3+}/\text{Fe}^{2+}$ in RTILs with various coupling parameters η (points) and the TGS model (red line).

can see that the electron transfer from tetracoordinated Fe^{2+} to hexacoordinated Fe^{3+} is as likely as the transfer to the tetracoordinated Fe^{3+} from a thermodynamic point of view because the corresponding free-energy differences are very similar, 0.25 and 0.24 eV, respectively. From a kinetic point of view, the picture is completely different because the corresponding activation energy, taken at the intersection between the two parabolas, is much higher (0.55 vs 0.39 eV). As a consequence, the effect of the confinement is likely to have a negative impact on the kinetic rate of the electron transfer reaction. Indeed, it allows for the existence of hexacoordinated Fe^{3+} , which is not stable in the bulk liquid in our simulations. The electron transfer from Fe^{2+} to this chemical species has a very large activation energy barrier, making such events unlikely to occur. This result contrasts with the observation of Remsing et al., who observed enhancement of the electron transfer due to the confinement⁴⁴ in a very different system. This is easily explained because in their work both the reduced and oxidized species were desolvated with respect to the bulk, while we observe the opposite behavior.

In conclusion, the aim of this work was to investigate the free-energy properties of an electron transfer reaction in a nanoporous carbon electrode. We performed MD simulations of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple dissolved in EMIM- BF_4 RTIL in contact with CDC electrodes. The latter were maintained at a constant potential of 0 V during the simulations. The vertical energy gap between the redox species was used as the reaction coordinate, which enabled us to interpret the microscopic solvent fluctuation properties. The computed probability distribution of the vertical energy gaps and the equilibrium value of energy gaps do not follow the linear response approximation of standard Marcus theory. We demonstrated the strong influence of the nanoconfinement effect on the solvation shell of the iron cations, which is the main reason for this departure from Marcus theory. In particular, the Fe^{3+} cation, which is tetracoordinated in the bulk, admits two stable solvation states in the nanoporous material: tetracoordinated and hexacoordinated. To account for this deviation, we used the TGS model,²¹ from which the free-energy curves for all of the redox species in their various solvation states were extracted. This allowed us to qualitatively analyze the effect of confinement on the electron transfer reaction. The fluctuations in the structure of the solvation shell of Fe^{3+} were shown to have a negligible effect from a thermodynamic point of view. Rather, it was shown that the activation energy of the associated electron transfer process is much higher for the hexacoordinated form. It is therefore likely that the stabilization of this solvation state will result in a slow down of the electron transfer reaction kinetics. This work is a first step toward a deeper understanding of the influence of the confinement on electron transfer in redox supercapacitor devices,²⁹ which will be extended in future years to promising systems such as biredox RTILs.¹⁶ To this end, it will be necessary to simulate more complex redox probes and to account systematically for the various complexation states. Another important aspect will be to decouple the contribution of the electron transfer event from the work term that controls the approach of the ion to the interface in nanoconfinement.²⁸ The techniques developed in this work could also provide useful information for the development of ionic-liquid-based thermo-electrochemical cells.⁴⁵

METHODS

We performed MD simulations of the present systems using coarse-grained force fields. The nonbonded interactions are

represented using Lennard-Jones and Coulomb potentials, and the corresponding parameters for carbon atoms and EMIM- BF_4 interaction sites that we used herein are obtained from our previous work.^{32,46} The parameters for the chloride and the iron ions are respectively taken from refs 47 and 48 (the chloride anions were added in order to maintain the electroneutrality of the simulation cell; however, their effect on the vertical energy gap was not studied because we focused on infinite dilution conditions). The simulations were conducted in the NVT ensemble, with the temperature set at 400 K using a Nosé–Hoover thermostat (relaxation time: 10 ps). The simulation cell was orthorhombic, with $x = y = 4.37$ nm and $z = 14.86$ nm, which reproduced the density of the RTILs compared with experimental results. Periodic boundary conditions were employed along x and y directions only through the use of a 2D Ewald summation.⁴⁹ For all of the simulations, the time step was 2 fs, and the time scales of production runs were over 500 ps after equilibration. The electrodes were maintained at a constant potential (0 V in our present study) during the production runs. The vertical energy gap was sampled every 1 ps during the simulation. Following our previous work, a constant was added to the energies calculated in the simulation to represent the (gas-phase) ionization potential of Fe^{2+} and the work function of the metal;⁴² in practice, the value (15.78 eV) was chosen to bring the calculated redox potential close to the typical experimental values for the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple in RTILs.⁵⁰

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.7b00458.

Distance between the anions and Fe^{2+} inside of the CDC electrode, snapshot of the simulated graphite-based electrochemical cell, potentials of mean force with respect to the distance to the graphite, and corresponding reorganization energies (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Alba-Simionesco, C.; Coasne, B.; Dosseh, G.; Dudziak, G.; Gubbins, K. E.; Radhakrishnan, R.; Sliwinski-Bartkowiak, M. Effects of Confinement on Freezing and Melting. *J. Phys.: Condens. Matter* **2006**, *18*, R15–R68.

- (2) Jiang, X.; Huang, J.; Sumpter, B. G.; Qiao, R. Electro-Induced Dewetting and Concomitant Ionic Current Avalanche in Nanopores. *J. Phys. Chem. Lett.* **2013**, *4*, 3120–3126.
- (3) Pean, C.; Daffos, B.; Rotenberg, B.; Levitz, P.; Haeefe, M.; Taberna, P. L.; Simon, P.; Salanne, M. Confinement, Desolvation, and Electro sorption Effects on the Diffusion of Ions in Nanoporous Carbon Electrodes. *J. Am. Chem. Soc.* **2015**, *137*, 12627–12632.
- (4) Agrawal, K. V.; Shimizu, S.; Drahushuk, L. W.; Kilcoyne, D.; Strano, M. S. Observation of Extreme Phase Transition Temperatures of Water Confined Inside Isolated Carbon Nanotubes. *Nat. Nanotechnol.* **2016**, *12*, 267–273.
- (5) Salanne, M.; Rotenberg, B.; Naoi, K.; Kaneko, K.; Taberna, P.-L.; Grey, C. P.; Dunn, B.; Simon, P. Efficient Storage Mechanisms for Building Better Supercapacitors. *Nat. Energy* **2016**, *1*, 16070.
- (6) Kornyshev, A. A. Double-layer in Ionic Liquids: Paradigm Change? *J. Phys. Chem. B* **2007**, *111*, 5545–5557.
- (7) Chmiola, J.; Yushin, G.; Gogotsi, Y.; Portet, C.; Simon, P.; Taberna, P. L. Anomalous Increase in Carbon Capacitance at Pore Sizes Less Than 1 Nanometer. *Science* **2006**, *313*, 1760–1763.
- (8) Raymundo-Piñero, E.; Kierzek, K.; Machnikowski, J.; Béguin, F. Relationship Between the Nanoporous Texture of Activated Carbons and Their Capacitance Properties in Different Electrolytes. *Carbon* **2006**, *44*, 2498–2507.
- (9) Kondrat, S.; Perez, C. R.; Presser, V.; Gogotsi, Y.; Kornyshev, A. A. Effect of Pore Size and Its Dispersity on the Energy Storage in Nanoporous Supercapacitors. *Energy Environ. Sci.* **2012**, *5*, 6474–6479.
- (10) Merlet, C.; Rotenberg, B.; Madden, P. A.; Taberna, P.-L.; Simon, P.; Gogotsi, Y.; Salanne, M. On the Molecular Origin of Supercapacitance in Nanoporous Carbon Electrodes. *Nat. Mater.* **2012**, *11*, 306–310.
- (11) He, Y.; Huang, J.; Sumpter, B. G.; Kornyshev, A. A.; Qiao, R. Dynamic Charge Storage in Ionic Liquids-filled Nanopores: Insight from a Computational Cyclic Voltammetry Study. *J. Phys. Chem. Lett.* **2015**, *6*, 22–30.
- (12) Vatamanu, J.; Bedrov, D. Capacitive Energy Storage: Current and Future Challenges. *J. Phys. Chem. Lett.* **2015**, *6*, 3594–3609.
- (13) Silvester, D. S.; Compton, R. G. Electrochemistry in Room Temperature Ionic Liquids: A Review and Some Possible Applications. *Z. Phys. Chem.* **2006**, *220*, 1247–1274.
- (14) 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*, 621–9.
- (15) Burt, R.; Breitsprecher, K.; Daffos, B.; Taberna, P.-L.; Simon, P.; Birkett, G.; Zhao, X. S.; Holm, C.; Salanne, M. Capacitance of Nanoporous Carbon-Based Supercapacitors Is a Trade-Off between the Concentration and the Separability of the Ions. *J. Phys. Chem. Lett.* **2016**, *7*, 4015–4021.
- (16) Mourad, E.; Coustan, L.; Lannelongue, P.; Zigah, D.; Mehdi, A.; Vioux, A.; Freunberger, S. A.; Favier, F.; Fontaine, O. Biredox Ionic Liquids with Solid-like Redox Density in the Liquid State for High-Energy Supercapacitors. *Nat. Mater.* **2017**, *16*, 446–453.
- (17) Marcus, R. A. On the Theory of Oxidation-Reduction Reactions Involving Electron Transfer. I. *J. Chem. Phys.* **1956**, *24*, 966–978.
- (18) Small, D. W.; Matyushov, D. V.; Voth, G. A. The Theory of Electron Transfer Reactions: What May Be Missing? *J. Am. Chem. Soc.* **2003**, *125*, 7470–7478.
- (19) Blumberger, J. $\text{Cu}_{\text{aq}}^+/\text{Cu}_{\text{aq}}^{2+}$ Redox Reaction Exhibits Strong Nonlinear Solvent Response Due to Change in Coordination Number. *J. Am. Chem. Soc.* **2008**, *130*, 16065–16068.
- (20) Matyushov, D. V.; Voth, G. A. Modeling the Free Energy Surfaces of Electron Transfer in Condensed Phases. *J. Chem. Phys.* **2000**, *113*, 5413–5424.
- (21) Vuilleumier, R.; Tay, K. A.; Jeanmairet, G.; Borgis, D.; Boutin, A. Extension of Marcus Picture for Electron Transfer Reactions with Large Solvation Changes. *J. Am. Chem. Soc.* **2012**, *134*, 2067–2074.
- (22) Laborda, E.; Henstridge, M. C.; Batchelor-McAuley, C.; Compton, R. G. Asymmetric Marcus-Hush Theory for Voltammetry. *Chem. Soc. Rev.* **2013**, *42*, 4894–4905.
- (23) Tanner, E. E. L.; Barnes, E. O.; Tickell, C. B.; Goodrich, P.; Hardacre, C.; Compton, R. G. Application of Asymmetric Marcus-Hush Theory to Voltammetry in Room-Temperature Ionic Liquids. *J. Phys. Chem. C* **2015**, *119*, 7360–7370.
- (24) Dzhabakhidze, P. G.; Kornyshev, A. A.; Krishtalik, L. I. Activation Energy of Electrode Reactions: the Non-Local Effects. *J. Electroanal. Chem. Interfacial Electrochem.* **1987**, *228*, 329–346.
- (25) Phelps, D. K.; Kornyshev, A. A.; Weaver, M. J. Nonlocal Electrostatic Effects on Electron-Transfer Activation Energies: Some Consequences for and Comparisons with Electrochemical and Homogeneous-Phase Kinetics. *J. Phys. Chem.* **1990**, *94*, 1454–1463.
- (26) Merlet, C.; Péan, C.; Rotenberg, B.; Madden, P. A.; Daffos, B.; Taberna, P.-L.; Simon, P.; Salanne, M. Highly Confined Ions Store Charge More Efficiently in Supercapacitors. *Nat. Commun.* **2013**, *4*, 2701.
- (27) Prehal, C.; Koczwar, C.; Jäckel, N.; Schreiber, A.; Burian, M.; Amenitsch, H.; Hartmann, M. A.; Presser, V.; Paris, O. Quantification of Ion Confinement and Desolvation in Nanoporous Carbon Supercapacitors with Modelling and in Situ X-ray Scattering. *Nat. Energy* **2017**, *2*, 16215.
- (28) Bai, P.; Bazant, M. Z. Charge Transfer Kinetics at the Solid-Solid Interface in Porous Electrodes. *Nat. Commun.* **2014**, *5*, 3585.
- (29) Akinwalemiwa, B.; Peng, C.; Chen, G. Z. Redox Electrolytes in Supercapacitors. *J. Electrochem. Soc.* **2015**, *162*, A5054–A5059.
- (30) Su, L.-H.; Zhang, X.-G.; Mi, C.-H.; Gao, B.; Liu, Y. Improvement of the Capacitive Performances for Co-Al Layered Double Hydroxide by Adding Hexacyanoferrate into the Electrolyte. *Phys. Chem. Chem. Phys.* **2009**, *11*, 2195–2202.
- (31) Pereiro, A. B.; Araújo, J. M. M.; Oliveira, F. S.; Esperança, J. M. S. S.; Canongia Lopes, J. N.; Marrucho, I. M.; Rebelo, L. P. N. Solubility of Inorganic Salts in Pure Ionic Liquids. *J. Chem. Thermodyn.* **2012**, *55*, 29–36.
- (32) Merlet, C.; Salanne, M.; Rotenberg, B. New Coarse-grained Models of Imidazolium Ionic Liquids for Bulk and Interfacial Molecular Simulations. *J. Phys. Chem. C* **2012**, *116*, 7687–7693.
- (33) Roy, D.; Maroncelli, M. An Improved Four-Site Ionic Liquid Model. *J. Phys. Chem. B* **2010**, *114*, 12629–12631.
- (34) Siepmann, J. I.; Sprik, M. Influence of Surface Topology and Electrostatic Potential on Water/Electrode Systems. *J. Chem. Phys.* **1995**, *102*, 511–524.
- (35) Palmer, J. C.; Llobet, A.; Yeon, S. H.; Fischer, J. E.; Shi, Y.; Gogotsi, Y.; Gubbins, K. E. Modeling the Structural Evolution of Carbide-derived Carbons Using Quenched Molecular Dynamics. *Carbon* **2010**, *48*, 1116–1123.
- (36) Warshel, A. Dynamics of Reactions in Polar Solvents. Semi-classical Trajectory Studies of Electron-transfer and Proton-transfer Reactions. *J. Phys. Chem.* **1982**, *86*, 2218–2224.
- (37) Hwang, J. K.; Warshel, A. Microscopic Examination of Free-energy Relationships for Electron Transfer in Polar Solvents. *J. Am. Chem. Soc.* **1987**, *109*, 715–720.
- (38) Marcus, R. A. On the Theory of Electron-Transfer Reactions. VI. Unified Treatment for Homogeneous and Electrode Reactions. *J. Chem. Phys.* **1965**, *43*, 679–701.
- (39) Georgievskii, Y.; Hsu, C.-P.; Marcus, R. A. Linear Response in Theory of Electron Transfer Reactions as an Alternative to the Molecular Harmonic Oscillator Model. *J. Chem. Phys.* **1999**, *110*, 5307–5317.
- (40) King, G.; Warshel, A. Investigation of the Free Energy Functions for Electron Transfer Reactions. *J. Chem. Phys.* **1990**, *93*, 8682–8692.
- (41) Blumberger, J. Recent Advances in the Theory and Molecular Simulation of Biological Electron Transfer Reactions. *Chem. Rev.* **2015**, *115*, 11191–11238.
- (42) Pounds, M. A.; Salanne, M.; Madden, P. A. Molecular Aspects of the $\text{Eu}^{3+}/\text{Eu}^{2+}$ Redox Reaction at the Interface Between a Molten Salt and a Metallic Electrode. *Mol. Phys.* **2015**, *113*, 2451–2462.
- (43) Marcus, R. A. Reorganization Free Energy for Electron Transfers at Liquid-liquid and Dielectric Semiconductor-liquid Interfaces. *J. Phys. Chem.* **1990**, *94*, 1050–1055.

- (44) Remsing, R. C.; McKendry, I. G.; Strongin, D. R.; Klein, M. L.; Zdilla, M. J. Frustrated Solvation Structures Can Enhance Electron Transfer Rates. *J. Phys. Chem. Lett.* **2015**, *6*, 4804–4808.
- (45) Abraham, T. J.; MacFarlane, D. R.; Pringle, J. M. Seebeck Coefficients in Ionic Liquids -prospects for Thermo-electrochemical Cells. *Chem. Commun.* **2011**, *47*, 6260–6262.
- (46) Merlet, C.; Péan, C.; Rotenberg, B.; Madden, P. A.; Simon, P.; Salanne, M. Simulating Supercapacitors: Can We Model Electrodes As Constant Charge Surfaces? *J. Phys. Chem. Lett.* **2013**, *4*, 264–268.
- (47) Dang, L. X. Mechanism and Thermodynamics of Ion Selectivity in Aqueous Solutions of 18-Crown-6 Ether: A Molecular Dynamics Study. *J. Am. Chem. Soc.* **1995**, *117*, 6954–6960.
- (48) Ando, K. Solvent Nuclear Quantum Effects in Electron Transfer Reactions. III. Metal Ions in Water. Solute Size and Ligand Effects. *J. Chem. Phys.* **2001**, *114*, 9470–9477.
- (49) Reed, S. K.; Lanning, O. J.; Madden, P. A. Electrochemical Interface Between an Ionic Liquid and a Model Metallic Electrode. *J. Chem. Phys.* **2007**, *126*, 084704.
- (50) Yamato, Y.; Katayama, Y.; Miura, T. Effects of the Interaction Between Ionic Liquids and Redox Couples on Their Reaction Entropies. *J. Electrochem. Soc.* **2013**, *160*, H309–H314.

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Bibliography

- [1] Douglas R MacFarlane, Maria Forsyth, Patrick C Howlett, Mega Kar, Stefano Passerini, Jennifer M Pringle, Hiroyuki Ohno, Masayoshi Watanabe, Feng Yan, Wenjun Zheng, Shiguo Zhang, and Jie Zhang. Ionic liquids and their solid-state analogues as materials for energy generation and storage. *Nat. Rev. Mater.*, 1:15005, 2016.
- [2] Liumin Suo, Yong-Sheng Hu, Hong Li, Michel Armand, and Liquan Chen. A new class of Solvent-in-Salt electrolyte for high-energy rechargeable metallic lithium batteries. *Nat. Commun.*, 4:1481, 2013.
- [3] Yuki Yamada, Makoto Yaegashi, Takeshi Abe, Atsuo Yamada, G. L. Henriksen, T. R. Jow, M. Ishikawa, M. Ishikawa, B. Denis, P. Juric, P. Aghakian, and J. R. Dahn. A superconcentrated ether electrolyte for fast-charging Li-ion batteries. *Chem. Commun.*, 49(95):11194, 2013.
- [4] Dennis W. McOwen, Daniel M. Seo, Oleg Borodin, Jenel Vatamanu, Paul D. Boyle, and Wesley A. Henderson. Concentrated electrolytes: decrypting electrolyte properties and reassessing Al corrosion mechanisms. *Energy Environ. Sci.*, 7(1):416–426, 2014.
- [5] Yuki Yamada, Kenji Usui, Ching Hua Chiang, Keisuke Kikuchi, Keizo Furukawa, and Atsuo Yamada. General Observation of Lithium Intercalation into Graphite in Ethylene-Carbonate-Free Superconcentrated Electrolytes. *ACS Appl. Mater. Interfaces*, 6(14):10892–10899, 2014.
- [6] Keitaro Sodeyama, Yuki Yamada, Koharu Aikawa, Atsuo Yamada, and Yoshitaka Tateyama. Sacrificial Anion Reduction Mechanism for Electrochemical Stability Improvement in Highly Concentrated Li-Salt Electrolyte. *J. Phys. Chem. C*, 118:14091, 2014.
- [7] Yuki Yamada, Ching Hua Chiang, Keitaro Sodeyama, Jianhui Wang, Yoshitaka Tateyama, and Atsuo Yamada. Corrosion Prevention Mechanism of Aluminum Metal in Superconcentrated Electrolytes. *ChemElectroChem*, 2(11):1687–1694, 2015.
- [8] R. Petibon, C. P. Aiken, L. Ma, D. Xiong, and J. R. Dahn. The use of ethyl acetate as a sole solvent in highly concentrated electrolyte for Li-ion batteries. *Electrochim. Acta*, 154:287–293, 2015.

- [9] Yuki Yamada and Atsuo Yamada. Review Superconcentrated Electrolytes for Lithium Batteries. *J. Electrochem. Soc.*, 162(14):A2406–A2423, 2015.
- [10] Mingfu He, Kah Chun Lau, Xiaodi Ren, Neng Xiao, William D. McCulloch, Larry A. Curtiss, and Yiyang Wu. Concentrated Electrolyte for the Sodium Oxygen Battery: Solvation Structure and Improved Cycle Life. *Angew. Chemie - Int. Ed.*, 55(49):15310–15314, 2016.
- [11] Jianhui Wang, Yuki Yamada, Keitaro Sodeyama, Ching Hua Chiang, Yoshitaka Tateyama, and Atsuo Yamada. Superconcentrated electrolytes for a high-voltage lithium-ion battery. *Nat. Commun.*, 7:12032, 2016.
- [12] Jaegi Lee, Yongwon Lee, Jeongmin Lee, Sang Min Lee, Jeong Hee Choi, Hyungsub Kim, Mi Sook Kwon, Kisuk Kang, Kyu Tae Lee, and Nam Soon Choi. Ultraconcentrated sodium bis(fluorosulfonyl)imide-based electrolytes for high-performance sodium metal batteries. *ACS Appl. Mater. Interfaces*, 9(4):3723–3732, 2017.
- [13] Jianhui Wang, Yuki Yamada, Keitaro Sodeyama, Eriko Watanabe, Koji Takada, Yoshitaka Tateyama, and Atsuo Yamada. Fire-extinguishing organic electrolytes for safe batteries. *Nat. Energy*, 3:22–29, 2017.
- [14] Yuki Yamada and Atsuo Yamada. Superconcentrated electrolytes to create new interfacial chemistry in non-aqueous and aqueous rechargeable batteries. *Chem. Lett.*, 46:170284, 2017.
- [15] Koji Takada, Yuki Yamada, Eriko Watanabe, Jianhui Wang, Keitaro Sodeyama, Yoshitaka Tateyama, Kazuhisa Hirata, Takeo Kawase, and Atsuo Yamada. Unusual Passivation Ability of Superconcentrated Electrolytes toward Hard Carbon Negative Electrodes in Sodium-Ion Batteries. *ACS Appl. Mater. Interfaces*, 9(39):33802–33809, 2017.
- [16] Dongping Lu, Jinhui Tao, Pengfei Yan, Wesley A. Henderson, Qiuyan Li, Yuyan Shao, Monte L. Helm, Oleg Borodin, Gordon L. Graff, Bryant Polzin, Chong Min Wang, Mark Engelhard, Ji Guang Zhang, James J. De Yoreo, Jun Liu, and Jie Xiao. Formation of Reversible Solid Electrolyte Interface on Graphite Surface from Concentrated Electrolytes. *Nano Lett.*, 17(3):1602–1609, 2017.
- [17] T. Zhang, M. Marinescu, S. Walus, P. Kovacic, and G. J. Offer. What Limits the Rate Capability of Li-S Batteries during Discharge: Charge Transfer or Mass Transfer? *J. Electrochem. Soc.*, 165(1):A6001–A6004, 2018.
- [18] Jianming Zheng, Shuru Chen, Wengao Zhao, Junhua Song, Mark H. Engelhard, and Ji Guang Zhang. Extremely Stable Sodium Metal Batteries Enabled by Localized High-Concentration Electrolytes. *ACS Energy Lett.*, 3(2):315–321, 2018.

- [19] Tomooki Hosaka, Kei Kubota, Haruka Kojima, and Shinichi Komaba. Highly concentrated electrolyte solutions for 4 V class potassium-ion batteries. *Chem. Commun.*, 54:8387–8390, 2018.
- [20] Ziqi Zeng, Vijayakumar Murugesan, Kee Sung Han, Xiaoyu Jiang, Yuliang Cao, Lifan Xiao, Xinping Ai, Hanxi Yang, Ji-Guang Zhang, Maria L. Sushko, and Jun Liu. Non-flammable electrolytes with high salt-to-solvent ratios for Li-ion and Li-metal batteries. *Nat. Energy*, 3:674681, 2018.
- [21] Shuru Chen, Jianming Zheng, Lu Yu, Xiaodi Ren, Mark H. Engelhard, Chaojiang Niu, Hongkyung Lee, Wu Xu, Jie Xiao, Jun Liu, and Ji Guang Zhang. High-Efficiency Lithium Metal Batteries with Fire-Retardant Electrolytes. *Joule*, 2:1548–1558, 2018.
- [22] Viktor Nilsson, Reza Younesi, Daniel Brandell, Kristina Edström, and Patrik Johansson. Critical evaluation of the stability of highly concentrated LiTFSI - Acetonitrile electrolytes vs. graphite, lithium metal and LiFePO₄ electrodes. *J. Power Sources*, 384:334–341, 2018.
- [23] Pengcheng Shi, Hao Zheng, Xin Liang, Yi Sun, Sheng Cheng, Chunhua Chen, and Hongfa Xiang. A highly concentrated phosphate-based electrolyte for high-safety rechargeable lithium batteries. *Chem. Commun.*, 2018.
- [24] Norio Takenaka, Takuya Fujie, Amine Bouibes, Yuki Yamada, Atsuo Yamada, and Masataka Nagaoka. Microscopic Formation Mechanism of Solid Electrolyte Interphase Film in Lithium-Ion Batteries with Highly Concentrated Electrolyte. *J. Phys. Chem. C*, 122(5):2564–2571, 2018.
- [25] Jun Ming, Zhen Cao, Wandu Wahyudi, Mengliu Li, Pushpendra Kumar, Yingqiang Wu, Jang-Yeon Hwang, Mohamed N Hedhili, Luigi Cavallo, Yang-Kook Sun, and Lain-Jong Li. New Insights of Graphite Anode Stability in Rechargeable Batteries: Li-Ion Coordination Structures Prevail over Solid Electrolyte Interphases. *ACS Energy Lett.*, 2018.
- [26] Xiaodi Ren, Shuru Chen, Hongkyung Lee, Donghai Mei, Mark H Engelhard, Sarah D Burton, Wengao Zhao, Jianming Zheng, Qiuyan Li, Michael S Ding, Marshall Schroeder, Judith Alvarado, Kang Xu, Y Shirley Meng, Jun Liu, Ji-Guang Zhang, and Wu Xu. Localized high-concentration sulfone electrolytes for high-efficiency lithium-metal batteries. *Chem*, 4:1877–1892, 2018.
- [27] Liumin Suo, Oleg Borodin, Tao Gao, Marco Olguin, Janet Ho, Xiulin Fan, Chao Luo, Chunsheng Wang, and Kang Xu. "Water-in-salt" electrolyte enables high-voltage aqueous lithium-ion chemistries. *Science*, 350(6263):938–943, 2015.
- [28] Chongyin Yang, Ji Chen, Tingting Qing, Xiulin Fan, Wei Sun, Arthur von Cresce, Michael S. Ding, Oleg Borodin, Jenel Vatamanu, Marshall A. Schroeder, Nico Eidson, Chunsheng Wang, and Kang Xu. 4.0 V Aqueous Li-Ion Batteries. *Joule*, 1(1):122–132, 2017.

- [29] R.-S. Kühnel, D. Reber, A. Remhof, R. Figi, D. Bleiner, and C. Battaglia. Water-in-salt electrolytes enable the use of cost-effective aluminum current collectors for aqueous high-voltage batteries. *Chem. Commun.*, 52(68):10435–10438, 2016.
- [30] Liumin Suo, Oleg Borodin, Wei Sun, Xiulin Fan, Chongyin Yang, Fei Wang, Tao Gao, Zhaohui Ma, Marshall Schroeder, Arthur von Cresce, Selena M. Russell, Michel Armand, Austen Angell, Kang Xu, and Chunsheng Wang. Advanced High-Voltage Aqueous Lithium-Ion Battery Enabled by Water-in-Bisalt Electrolyte. *Angew. Chemie Int. Ed.*, 55(25):7136–7141, 2016.
- [31] Yuki Yamada, Kenji Usui, Keitaro Sodeyama, Seongjae Ko, Yoshitaka Tateyama, and Atsuo Yamada. Hydrate-melt electrolytes for high-energy-density aqueous batteries. *Nat. Energy*, 1(10):16129, 2016.
- [32] Masahiro Yoshizawa, Wu Xu, and C Austen Angell. Ionic liquids by proton transfer: Vapor pressure, conductivity, and the relevance of δp_k a from aqueous solutions. *Journal of the American Chemical Society*, 125(50):15411–15419, 2003.
- [33] Jean-Philippe Belieres and C Austen Angell. Protic ionic liquids: preparation, characterization, and proton free energy level representation. *The Journal of Physical Chemistry B*, 111(18):4926–4937, 2007.
- [34] Oleg Borodin, Liumin Suo, Mallory Gobet, Xiaoming Ren, Fei Wang, Antonio Faraone, Jing Peng, Marco Olguin, Marshall Schroeder, Michael S. Ding, Eric Gobrogge, Arthur von Wald Cresce, Stephen Munoz, Joseph A. Dura, Steve Greenbaum, Chunsheng Wang, and Kang Xu. Liquid Structure with Nano-Heterogeneity Promotes Cationic Transport in Concentrated Electrolytes. *ACS Nano*, 11(10):10462–10471, 2017.
- [35] Wu Li, Jeff R Dahn, and David S Wainwright. Rechargeable lithium batteries with aqueous electrolytes. *Science*, 264(5162):1115–1118, 1994.
- [36] Yonggang Wang, Jin Yi, and Yongyao Xia. Recent progress in aqueous lithium-ion batteries. *Advanced Energy Materials*, 2(7):830–840, 2012.
- [37] Kang Xu. Electrolytes and interphases in Li-ion batteries and beyond. *Chem. Rev.*, 114(23):11503–11618, 2014.
- [38] S Liu, GL Pan, NF Yan, and XP Gao. Aqueous $\text{TiO}_2/\text{Ni(OH)}_2$ rechargeable battery with a high voltage based on proton and lithium insertion/extraction reactions. *Energy & Environmental Science*, 3(11):1732–1735, 2010.
- [39] Ali Eftekhari. High-Energy Aqueous Lithium Batteries. *Adv. Energy Mater.*, 8:1801156, 2018.

- [40] Duan Bin, Yunping Wen, Yonggang Wang, and Yongyao Xia. The development in aqueous lithium-ion batteries. *J. Energy Chem.*, DOI:10.1016/j.jechem.2018.06.004, 2018.
- [41] Rahul Malik. Aqueous Li-Ion Batteries: Now in Striking Distance. *Joule*, 1(1):17–19, 2017.
- [42] Liumin Suo, Fudong Han, Xiulin Fan, Huili Liu, Kang Xu, and Chunsheng Wang. Water-in-Salt electrolytes enable green and safe Li-ion batteries for large scale electric energy storage applications. *J. Mater. Chem. A*, 4(17):6639–6644, 2016.
- [43] Chongyin Yang, Liumin Suo, Oleg Borodin, Fei Wang, Wei Sun, Tao Gao, Xiulin Fan, Singyuk Hou, Zhaohui Ma, Khalil Amine, Kang Xu, and Chunsheng Wang. Unique aqueous Li-ion/sulfur chemistry with high energy density and reversibility. *Proc. Natl. Acad. Sci.*, 114(24):6197–6202, 2017.
- [44] Chongyin Yang, Xiao Ji, Xiulin Fan, Tao Gao, Liumin Suo, Fei Wang, Wei Sun, Ji Chen, Long Chen, Fudong Han, Ling Miao, Kang Xu, Konstantinos Gerasopoulos, and Chunsheng Wang. Flexible Aqueous Li-Ion Battery with High Energy and Power Densities. *Adv. Mater.*, 29:1701972, 2017.
- [45] Qi Dong, Xiahui Yao, Yanyan Zhao, Miao Qi, Xizi Zhang, Hongyu Sun, Yumin He, and Dunwei Wang. Cathodically Stable Li-O₂Battery Operations Using Water-in-Salt Electrolyte. *Chem*, 4:1345–1358, 2018.
- [46] Ruidong Yang, Yong Zhang, Kensuke Takechi, and Edward J. Maginn. Investigation of the relationship between solvation structure and battery performance in highly-concentrated aqueous nitroxyl radical catholyte. *J. Phys. Chem. C*, 122:13815–13826, 2018.
- [47] Maria R. R Lukatskaya, Jeremy Feldblyum, David G. Mackanic, Franziska Lissel, Dominik L. Michels, Yi Cui, and Zhenan Bao. Concentrated Mixed Cation Acetate Water-in-Salt Solutions as Green and Low Cost High Voltage Electrolytes for Aqueous Batteries. *Energy Environ. Sci.*, DOI: 10.1039/C8EE00833G, 2018.
- [48] Ruben-Simon Kühnel, David Reber, and Corsin Battaglia. A High-Voltage Aqueous Electrolyte for Sodium-Ion Batteries. *ACS Energy Lett.*, pages 2005–2006, 2017.
- [49] Wanfeng Li, Fang Zhang, Xingde Xiang, and Xiucheng Zhang. High-Efficiency Na-Storage Performance of a Nickel-Based Ferricyanide Cathode in High-Concentration Electrolytes for Aqueous Sodium-Ion Batteries. *ChemElectroChem*, 4(11):2870–2876, 2017.
- [50] Liumin Suo, Oleg Borodin, Yuesheng Wang, Xiaohui Rong, Wei Sun, Xiulin Fan, Shuyin Xu, Marshall A. Schroeder, Arthur V. Cresce, Fei Wang, Chongyin

- Yang, Yong-Sheng Hu, Kang Xu, and Chunsheng Wang. Water-in-Salt Electrolyte Makes Aqueous Sodium-Ion Battery Safe, Green, and Long-Lasting. *Adv. Energy Mater.*, 7:1701189, 2017.
- [51] Débora Ruiz-Martínez, Andras Kovacs, Roberto Gómez, S. M. Lee, J. H. Choi, H. Kim, M. S. Kwon, K. Kang, K. T. Lee, N. S. Choi, and H. Dai. Development of novel inorganic electrolytes for room temperature rechargeable sodium metal batteries. *Energy Environ. Sci.*, 10(9):1936–1941, 2017.
- [52] Andrew Basile, Shammi Akter Ferdousi, Faezeh Makhlooghiazad, Ruhamah Yunis, Matthias Hilder, Maria Forsyth, and Patrick C. Howlett. Beneficial effect of added water on sodium metal cycling in super concentrated ionic liquid sodium electrolytes. *J. Power Sources*, 379:344–349, 2018.
- [53] Huang Zhang, Sangsik Jeong, Bingsheng Qin, Diogo Carvalho, Daniel Buchholz, and Stefano Passerini. Towards High-Performance Aqueous Na-ion Batteries: Stabilizing the Solid/Liquid Interface for NASICON-Type $\text{Na}_2\text{VTi}(\text{PO}_4)_3$ via the Use of Concentrated Electrolytes. *ChemSusChem*, 11(8):1382–1389, 2018.
- [54] Daniel P. Leonard, Zhixuan Wei, Gang Chen, Fei Du, and Xiulei Ji. Water-in-Salt Electrolyte for Potassium-Ion Batteries. *ACS Energy Lett.*, 3(2):373–374, 2018.
- [55] Fei Wang, Xiulin Fan, Tao Gao, Wei Sun, Zhaohui Ma, Chongyin Yang, Fudong Han, Kang Xu, and Chunsheng Wang. High-Voltage Aqueous Magnesium Ion Batteries. *ACS Cent. Sci.*, 3(10):1121–1128, 2017.
- [56] Changhee Lee and Soon-Ki Jeong. Modulating the hydration number of calcium ions by varying the electrolyte concentration: Electrochemical performance in a Prussian blue electrode/aqueous electrolyte system for calcium-ion batteries. *Electrochim. Acta*, 265:430–436, 2018.
- [57] Ning Zhang, Fangyi Cheng, Yongchang Liu, Qing Zhao, Kaixiang Lei, Chengcheng Chen, Xiaosong Liu, and Jun Chen. Cation-Deficient Spinel ZnMn_2O_4 Cathode in $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ Electrolyte for Rechargeable Aqueous Zn-Ion Battery. *J. Am. Chem. Soc.*, 138(39):12894–12901, 2016.
- [58] Ping Hu, Mengyu Yan, Ting Zhu, Xuanpeng Wang, Xiujuan Wei, Jiantao Li, Liang Zhou, Zhaohuai Li, Lineng Chen, and Liqiang Mai. Zn/ V_2O_5 Aqueous Hybrid-Ion Battery with High Voltage Platform and Long Cycle Life. *ACS Appl. Mater. Interfaces*, 9(49):42717–42722, 2017.
- [59] Ning Zhang, Fangyi Cheng, Junxiang Liu, Liubin Wang, Xinghui Long, Xiaosong Liu, Fujun Li, and Jun Chen. Rechargeable aqueous zinc-manganese dioxide batteries with high energy and power densities. *Nat. Commun.*, 8(1):405, 2017.

- [60] Wei Li, Kangli Wang, Min Zhou, Houchao Zhan, Shijie Cheng, and Kai Jiang. Advanced Low-Cost, High-Voltage, Long-Life Aqueous Hybrid Sodium/Zinc Batteries Enabled by a Dendrite-Free Zinc Anode and Concentrated Electrolyte. *ACS Appl. Mater. Interfaces*, 10:22059–22066, 2018.
- [61] Jian Zhi, Koen Bertens, Alireza Zehtab Yazdi, and P. Chen. Acrylonitrile copolymer/graphene skinned cathode for long cycle life rechargeable hybrid aqueous batteries at high-temperature. *Electrochim. Acta*, 268:248–255, 2018.
- [62] Fang Wan, Linlin Zhang, Xi Dai, Xinyu Wang, Zhiqiang Niu, and Jun Chen. Aqueous rechargeable zinc/sodium vanadate batteries with enhanced performance from simultaneous insertion of dual carriers. *Nat. Commun.*, 9(1):1656, 2018.
- [63] Fei Wang, Oleg Borodin, Tao Gao, Xiulin Fan, Wei Sun, Fudong Han, Antonio Faraone, Joseph A Dura, Kang Xu, and Chunsheng Wang. Highly reversible zinc metal anode for aqueous batteries. *Nat. Mater.*, 17(6):543, 2018.
- [64] John J. Holoubek, Heng Jiang, Daniel Leonard, Yitong Qi, Galo C. Bustamante, and Xiulei Ji. Amorphous titanate acid electrode: its electrochemical storage of ammonium in a new water-in-salt electrolyte. *Chem. Commun.*, 54(70):9805–9808, 2018.
- [65] John R Miller and Patrice Simon. Electrochemical capacitors for energy management. *Science Magazine*, 321(5889):651–652, 2008.
- [66] P. Simon, Y. Gogotsi, and B. Dunn. Where Do Batteries End and Supercapacitors Begin? *Science*, 343(6176):1210–1211, 2014.
- [67] M. Salanne, B. Rotenberg, K. Naoi, K. Kaneko, P.-L. Taberna, C. P. Grey, B. Dunn, and P. Simon. Efficient storage mechanisms for building better supercapacitors. *Nat. Energy*, 1(6):16070, 2016.
- [68] Laura Coustan, Galyna Shul, and Daniel Bélanger. Electrochemical behavior of platinum, gold and glassy carbon electrodes in water-in-salt electrolyte. *Electrochem. commun.*, 77:89–92, 2017.
- [69] Axel Gambou-Bosca and Daniel Bélanger. Electrochemical characterization of MnO₂-based composite in the presence of salt-in-water and water-in-salt electrolytes as electrode for electrochemical capacitors. *J. Power Sources*, 326:595–603, 2016.
- [70] George Hasegawa, Kazuyoshi Kanamori, Tsutomu Kiyomura, Hiroki Kurata, Takeshi Abe, and Kazuki Nakanishi. Hierarchically Porous Carbon Monoliths Comprising Ordered Mesoporous Nanorod Assemblies for High-Voltage Aqueous Supercapacitors. *Chem. Mater.*, 28(11):3944–3950, 2016.

- [71] Zengying Tian, Wenjun Deng, Xusheng Wang, Chunyi Liu, Chang Li, Jitao Chen, Mianqi Xue, Rui Li, and Feng Pan. Superconcentrated aqueous electrolyte to enhance energy density for advanced supercapacitors. *Funct. Mater. Lett.*, 10(6):1750081, 2017.
- [72] David Reber, Ruben-Simon Kühnel, and Corsin Battaglia. High-voltage aqueous supercapacitors based on NaTFSI. *Sustain. Energy Fuels*, 1(10):2155–2161, 2017.
- [73] Cuihua An, Weiqin Li, Mengying Wang, Qibo Deng, and Yijing Wang. High energy density aqueous asymmetric supercapacitors based on MnO₂@C branch dendrite nanoarchitectures. *Electrochim. Acta*, 283:603–610, 2018.
- [74] Qingyun Dou, Shulai Lei, Dawei Wang, Qingnuan Zhang, Dewei Xiao, Hongwei Guo, Aiping Wang, Hui Yang, Yongle Li, Siqi Shi, and Xingbin Yan. Safe and high-rate supercapacitors based on acetonitrile/water in salt hybrid electrolyte. *Energy Environ. Sci.*, DOI: 10.1039/C8EE01040D, 2018.
- [75] Yadi Zhang, Ping Nie, Chengyang Xu, Guiyin Xu, Bing Ding, Hui Dou, and Xiaogang Zhang. High energy aqueous sodium-ion capacitor enabled by polyimide electrode and high-concentrated electrolyte. *Electrochim. Acta*, 268:512–519, 2018.
- [76] Laura Coustan, Karim Zaghib, and Daniel Bélanger. New insight in the electrochemical behaviour of stainless steel electrode in water-in-salt electrolyte. *J. Power Sources*, 399:299–303, 2018.
- [77] Yadi Zhang, Yufeng An, Jiangmin Jiang, Shengyang Dong, Langyuan Wu, Ruirui Fu, Hui Dou, and Xiaogang Zhang. High performance aqueous sodium-ion capacitors enabled by pseudocapacitance of layered mno₂. *Energy Technology*, 6:1–9, 2018.
- [78] Pierre Lannelongue, Roza Bouchal, Eléonore Mourad, Charlotte Bodin, Marco Olarte, Steven le Vot, Frédéric Favier, and Olivier Fontaine. Water-in-Salt for Supercapacitors: A Compromise between Voltage, Power Density, Energy Density and Stability. *J. Electrochem. Soc.*, 165(3):A657–A663, 2018.
- [79] Ming Zhang, Sho Makino, Dai Mochizuki, and Wataru Sugimoto. High-performance hybrid supercapacitors enabled by protected lithium negative electrode and water-in-salt electrolyte. *J. Power Sources*, 396:498–505, 2018.
- [80] Sungho Han. Dynamic features of water molecules in superconcentrated aqueous electrolytes. *Sci. Rep.*, 8(1):9347, 2018.
- [81] Jenel Vatamanu and Oleg Borodin. Ramifications of Water-in-Salt Interfacial Structure at Charged Electrodes for Electrolyte Electrochemical Stability. *J. Phys. Chem. Lett.*, 8:4362–4367, 2017.

- [82] Loup Verlet. Computer” experiments” on classical fluids. i. thermodynamical properties of lennard-jones molecules. *Physical review*, 159(1):98, 1967.
- [83] Michael P Allen and Dominic J Tildesley. *Computer simulation of liquids*. Oxford university press, 2017.
- [84] William G Hoover. Canonical dynamics: equilibrium phase-space distributions. *Physical review A*, 31(3):1695, 1985.
- [85] Simone Melchionna, Giovanni Ciccotti, and Brad Lee Holian. Hoover npt dynamics for systems varying in shape and size. *Molecular Physics*, 78(3):533–544, 1993.
- [86] Glenn J Martyna, Michael L Klein, and Mark Tuckerman. Nosé–hoover chains: The canonical ensemble via continuous dynamics. *The Journal of chemical physics*, 97(4):2635–2643, 1992.
- [87] Daan Frenkel and Berend Smit. *Understanding molecular simulation: from algorithms to applications*, volume 1. Elsevier, 2001.
- [88] William L Jorgensen, David S Maxwell, and Julian Tirado-Rives. Development and testing of the opls all-atom force field on conformational energetics and properties of organic liquids. *Journal of the American Chemical Society*, 118(45):11225–11236, 1996.
- [89] Scott J Weiner, Peter A Kollman, David A Case, U Chandra Singh, Caterina Ghio, Guliano Alagona, Salvatore Profeta, and Paul Weiner. A new force field for molecular mechanical simulation of nucleic acids and proteins. *Journal of the American Chemical Society*, 106(3):765–784, 1984.
- [90] Wendy D Cornell, Piotr Cieplak, Christopher I Bayly, Ian R Gould, Kenneth M Merz, David M Ferguson, David C Spellmeyer, Thomas Fox, James W Caldwell, and Peter A Kollman. A second generation force field for the simulation of proteins, nucleic acids, and organic molecules. *Journal of the American Chemical Society*, 117(19):5179–5197, 1995.
- [91] Carlos Pinilla, MG Del Pópolo, Jorge Kohanoff, and RM Lynden-Bell. Polarization relaxation in an ionic liquid confined between electrified walls. *The Journal of Physical Chemistry B*, 111(18):4877–4884, 2007.
- [92] Oliver J Lanning and Paul A Madden. Screening at a charged surface by a molten salt. *The Journal of Physical Chemistry B*, 108(30):11069–11072, 2004.
- [93] G Feng, JS Zhang, and R Qiao. Microstructure and capacitance of the electrical double layers at the interface of ionic liquids and planar electrodes. *The Journal of Physical Chemistry C*, 113(11):4549–4559, 2009.

- [94] Lu Yang, Brian H Fishbine, Albert Migliori, and Lawrence R Pratt. Molecular simulation of electric double-layer capacitors based on carbon nanotube forests. *Journal of the American Chemical Society*, 131(34):12373–12376, 2009.
- [95] Mathieu Salanne, Leonardo JA Siqueira, Ari P Seitsonen, Paul A Madden, and Barbara Kirchner. From molten salts to room temperature ionic liquids: Simulation studies on chloroaluminate systems. *Faraday discussions*, 154:171–188, 2012.
- [96] Federico Iori and Stefano Corni. Including image charge effects in the molecular dynamics simulations of molecules on metal surfaces. *Journal of computational chemistry*, 29(10):1656–1666, 2008.
- [97] Guillaume Lamoureux and Benoit Roux. Modeling induced polarization with classical drude oscillators: Theory and molecular dynamics simulation algorithm. *The Journal of chemical physics*, 119(6):3025–3039, 2003.
- [98] Alfonso S Pensado and Agílio AH Pádua. Solvation and stabilization of metallic nanoparticles in ionic liquids. *Angewandte Chemie International Edition*, 50(37):8683–8687, 2011.
- [99] Ajda Podgorsek, Alfonso S Pensado, Catherine C Santini, Margarida F Costa Gomes, and Agílio AH Padua. Interaction energies of ionic liquids with metallic nanoparticles: Solvation and stabilization effects. *The Journal of Physical Chemistry C*, 117(7):3537–3547, 2013.
- [100] Ana CF Mendonca, Agílio AH Padua, and Patrice Malfreyt. Nonequilibrium molecular simulations of new ionic lubricants at metallic surfaces: prediction of the friction. *Journal of chemical theory and computation*, 9(3):1600–1610, 2013.
- [101] Ana CF Mendonca, Patrice Malfreyt, and Agílio AH Padua. Interactions and ordering of ionic liquids at a metal surface. *Journal of chemical theory and computation*, 8(9):3348–3355, 2012.
- [102] J Ilja Siepmann and Michiel Sprik. Influence of surface topology and electrostatic potential on water/electrode systems. *The Journal of chemical physics*, 102(1):511–524, 1995.
- [103] Stewart K. Reed, Oliver J. Lanning, and Paul A. Madden. Electrochemical interface between an ionic liquid and a model metallic electrode. *J. Chem. Phys.*, 126(8):084704, 2007.
- [104] Stewart K. Reed, Paul A. Madden, and Aristides Papadopoulos. Electrochemical charge transfer at a metallic electrode: A simulation study. *J. Chem. Phys.*, 128(12):1–10, 2008.
- [105] Michael A Pounds, Mathieu Salanne, and Paul A Madden. Molecular aspects of the $\text{Eu}^{3+}/\text{Eu}^{2+}$ redox reaction at the interface between a molten salt and a metallic electrode. *Mol. Phys.*, 113(17-18):2451–2462, 2015.

- [106] Jenel Vatamanu, Oleg Borodin, and Grant D. Smith. Molecular insights into the potential and temperature dependences of the differential capacitance of a room-temperature ionic liquid at graphite electrodes. *J. Am. Chem. Soc.*, 132(42):14825–14833, 2010.
- [107] Jenel Vatamanu, Oleg Borodin, Dmitry Bedrov, and Grant D. Smith. Molecular Dynamics Simulation Study of the Interfacial Structure and Differential Capacitance of Alkylimidazolium Bis(trifluoromethanesulfonyl)imide [C_nmim][TFSI] Ionic Liquids at Graphite Electrodes. *J. Phys. Chem. C*, 116(14):7940–7951, 2012.
- [108] Jenel Vatamanu, Oleg Borodin, and Grant D. Smith. Molecular Simulations of the Electric Double Layer Structure, Differential Capacitance, and Charging Kinetics for N-Methyl-N-propylpyrrolidinium Bis(fluorosulfonyl)imide at Graphite Electrodes. *J. Phys. Chem. B*, 115(12):3073–3084, 2011.
- [109] Ryan Burt, Konrad Breitsprecher, Barbara Daffos, Pierre-Louis Taberna, Patrice Simon, Greg Birkett, X. S. Zhao, Christian Holm, and Mathieu Salanne. Capacitance of Nanoporous Carbon-Based Supercapacitors Is a Trade-Off between the Concentration and the Separability of the Ions. *J. Phys. Chem. Lett.*, 7(19):4015–4021, 2016.
- [110] Clarisse Pean, Barbara Daffos, Benjamin Rotenberg, Pierre Levitz, Matthieu Haefele, Pierre-Louis Taberna, Patrice Simon, and Mathieu Salanne. Confinement, Desolvation, And Electrosorption Effects on the Diffusion of Ions in Nanoporous Carbon Electrodes. *J. Am. Chem. Soc.*, 137(39):12627–12632, 2015.
- [111] C. Pean, B. Rotenberg, P. Simon, and M. Salanne. Multi-scale modelling of supercapacitors: From molecular simulations to a transmission line model. *J. Power Sources*, 326:680–685, 2016.
- [112] Céline Merlet, Benjamin Rotenberg, Paul A Madden, Pierre-Louis Taberna, Patrice Simon, Yury Gogotsi, and Mathieu Salanne. On the molecular origin of supercapacitance in nanoporous carbon electrodes. *Nat. Mater.*, 11(4):306–310, 2012.
- [113] Céline Merlet, Benjamin Rotenberg, Paul A Madden, and Mathieu Salanne. Computer simulations of ionic liquids at electrochemical interfaces. *Phys. Chem. Chem. Phys.*, 15(38):15781, 2013.
- [114] Céline Merlet, Mathieu Salanne, Benjamin Rotenberg, and Paul A. Madden. Influence of solvation on the structural and capacitive properties of electrical double layer capacitors. *Electrochim. Acta*, 101:262–271, 2013.
- [115] Céline Merlet, Clarisse Péan, Benjamin Rotenberg, Paul A. Madden, Patrice Simon, and Mathieu Salanne. Simulating supercapacitors: Can we model electrodes as constant charge surfaces? *J. Phys. Chem. Lett.*, 4(2):264–268, 2013.

- [116] Céline Merlet, David T. Limmer, Mathieu Salanne, René van Roij, Paul A. Madden, David Chandler, and Benjamin Rotenberg. The Electric Double Layer Has a Life of Its Own. *J. Phys. Chem. C*, 118(32):18291–18298, 2014.
- [117] Matt K Petersen, Revati Kumar, Henry S White, and Gregory A Voth. A computationally efficient treatment of polarizable electrochemical cells held at a constant potential. *The Journal of Physical Chemistry C*, 116(7):4903–4912, 2012.
- [118] David T. Limmer, Céline Merlet, Mathieu Salanne, David Chandler, Paul A. Madden, René van Roij, and Benjamin Rotenberg. Charge Fluctuations in Nanoscale Capacitors. *Phys. Rev. Lett.*, 111(10):106102, 2013.
- [119] Steve Plimpton. Fast Parallel Algorithms for Short-Range Molecular Dynamics. *J. Comput. Phys.*, 117(1):1–19, 1995.
- [120] H. J. C. Berendsen, J. R. Grigera, and T. P. Straatsma. The Missing Term in Effective Pair Potentials. *J. Phys. Chem.*, 91(24):6269–6271, 1987.
- [121] Marcelo J Monteiro, Fernanda F C Bazito, Leonardo J A Siqueira, Mauro C C Ribeiro, and Roberto M Torresi. Transport Coefficients, Raman Spectroscopy, and Computer Simulation of Lithium Salt Solutions in an Ionic Liquid. *J. Phys. Chem. B*, 112(7):2102–2109, 2008.
- [122] Mathieu Salanne, Christian Simon, Pierre Turq, and Paul A. Madden. Conductivity-viscosity-structure: Unpicking the relationship in an ionic liquid. *J. Phys. Chem. B*, 111(18):4678–4684, 2007.
- [123] Burkhard Dünweg and Kurt Kremer. Molecular dynamics simulation of a polymer chain in solution. *The Journal of chemical physics*, 99(9):6983–6997, 1993.
- [124] In-Chul Yeh and Gerhard Hummer. System-size dependence of diffusion coefficients and viscosities from molecular dynamics simulations with periodic boundary conditions. *The Journal of Physical Chemistry B*, 108(40):15873–15879, 2004.
- [125] José N. Canongia Lopes, Agílio A H Pádua, and Agílio A. H. Pádua*. Molecular force field for ionic liquids composed of triflate or bistriflylimide anions. *J. Phys. Chem. B*, 108(43):16893–16898, 2004.
- [126] Eran Rabani, J Daniel Gezelter, and B. J. Berne. Calculating the hopping rate for self-diffusion on rough potential energy surfaces: Cage correlations. *J. Chem. Phys.*, 107(17):6867–6876, 1997.
- [127] Daniel Spångberg, Rossend Rey, James T Hynes, and Kersti Hermansson. Rate and Mechanisms for Water Exchange around Li + (aq) from MD Simulations. *J. Phys. Chem. B*, 107(18):4470–4477, 2003.

- [128] Mathieu Salanne. Ionic Liquids for Supercapacitor Applications. *Top. Curr. Chem.*, 375(3):63, 2017.
- [129] Jenel Vatamanu and Dmitry Bedrov. Capacitive Energy Storage: Current and Future Challenges. *J. Phys. Chem. Lett.*, 6(18):3594–3609, 2015.
- [130] Jenel Vatamanu, Oleg Borodin, Marco Olguin, Gleb Yushin, and Dmitry Bedrov. Charge storage at the nanoscale: understanding the trends from the molecular scale perspective. *J. Mater. Chem. A*, 5(40):21049–21076, 2017.
- [131] J. Chmiola, G. Yushin, Y. Gogotsi, C. Portet, P. Simon, and P. L. Taberna. Anomalous Increase in Carbon Capacitance at Pore Sizes Less Than 1 Nanometer. *Science*, 313(5794):1760–1763, 2006.
- [132] Justin B. Haskins, James J. Wu, and John W. Lawson. Computational and Experimental Study of Li-Doped Ionic Liquids at Electrified Interfaces. *J. Phys. Chem. C*, 120(22):11993–12011, 2016.
- [133] C Merlet, C Péan, B Rotenberg, P a Madden, B Daffos, P. L. Taberna, P Simon, and M Salanne. Highly confined ions store charge more efficiently in supercapacitors. *Nat. Commun.*, 4:2701, 2013.
- [134] Jochen Friedl, Iulius I.E. Markovits, Max Herpich, Guang Feng, Alexei A. Kornyshev, and Ulrich Stimming. Interface between an Au(111) Surface and an Ionic Liquid: The Influence of Water on the Double-Layer Capacitance. *Chem-ElectroChem*, 4(1):216–220, 2017.
- [135] Yu-Zhuan Su, Yong-Chun Fu, Jia-Wei Yan, Zhao-Bin Chen, and Bing-Wei Mao. Double Layer of Au(100)/Ionic Liquid Interface and Its Stability in Imidazolium-Based Ionic Liquids. *Angew. Chemie*, 121(28):5250–5253, 2009.
- [136] Rui Wen, Björn Rahn, and Olaf M. Magnussen. Potential-dependent adlayer structure and dynamics at the ionic liquid/Au(111) interface: A molecular-scale in situ video-STM study. *Angew. Chemie - Int. Ed.*, 54(20):6062–6066, 2015.
- [137] David T. Limmer. Interfacial Ordering and Accompanying Divergent Capacitance at Ionic Liquid-Metal Interfaces. *Phys. Rev. Lett.*, 115(25):1–5, 2015.
- [138] Jia Le Ma, Qiangqiang Meng, and Jun Fan. Charge driven lateral structural evolution of ions in electric double layer capacitors strongly correlates with differential capacitance. *Phys. Chem. Chem. Phys.*, 20(12):8054–8063, 2018.
- [139] Oleg Borodin, Xiaoming Ren, Jenel Vatamanu, Arthur von Wald Cresce, Jaroslaw Knap, and Kang Xu. Modeling Insight into Battery Electrolyte Electrochemical Stability and Interfacial Structure. *Acc. Chem. Res.*, 50(12):2886–2894, 2017.

- [140] Fei Wang, Oleg Borodin, Michael S. Ding, Mallory Gobet, Jenel Vatamanu, Xiulin Fan, Tao Gao, Nico Edison, Yujia Liang, Wei Sun, Steve Greenbaum, Kang Xu, and Chunsheng Wang. Hybrid Aqueous/Non-aqueous Electrolyte for Safe and High-Energy Li-Ion Batteries. *Joule*, 2(5):927–937, 2018.
- [141] Zhenxing Wang, Yang Yang, David L. Olmsted, Mark Asta, and Brian B. Laird. Evaluation of the constant potential method in simulating electric double-layer capacitors. *J. Chem. Phys.*, 141(18):184102, 2014.
- [142] Celine Merlet, Mathieu Salanne, Benjamin Rotenberg, and Paul A Madden. Imidazolium Ionic Liquid Interfaces with Vapor and Graphite: Interfacial Tension and Capacitance from Coarse-Grained Molecular Simulations. *J. Phys. Chem. C*, 115(33):16613–16618, 2011.
- [143] Lidan Xing, Jenel Vatamanu, Oleg Borodin, Grant D. Smith, and Dmitry Bedrov. Electrode/Electrolyte Interface in Sulfolane-Based Electrolytes for Li Ion Batteries: A Molecular Dynamics Simulation Study. *J. Phys. Chem. C*, 116(45):23871–23881, 2012.
- [144] Ahmet Uysal, Hua Zhou, Guang Feng, Sang Soo Lee, Song Li, Paul Fenter, Peter T Cummings, Pasquale F Fulvio, Sheng Dai, John K McDonough, et al. Structural origins of potential dependent hysteresis at the electrified graphene/ionic liquid interface. *The Journal of Physical Chemistry C*, 118(1):569–574, 2013.
- [145] Betul Uralcan, Ilhan A. Aksay, Pablo G. Debenedetti, and David T. Limmer. Concentration Fluctuations and Capacitive Response in Dense Ionic Solutions. *J. Phys. Chem. Lett.*, 7(13):2333–2338, 2016.
- [146] Ushnish Ray, Garnet Kin-Lic Chan, and David T. Limmer. Importance sampling large deviations in nonequilibrium steady states. I. *J. Chem. Phys.*, 148(12):124120, 2018.
- [147] Alan M. Ferrenberg and Robert H. Swendsen. Optimized Monte Carlo data analysis. *Phys. Rev. Lett.*, 63(12):1195–1198, 1989.
- [148] Zhiqiang Tan, Emilio Gallicchio, Mauro Lapelosa, and Ronald M Levy. Theory of binless multi-state free energy estimation with applications to protein-ligand binding. *The Journal of chemical physics*, 136(14):144102, 2012.
- [149] Benjamin Rotenberg and Mathieu Salanne. Structural Transitions at Ionic Liquid Interfaces. *J. Phys. Chem. Lett.*, 6(24):4978–4985, 2015.
- [150] De-en Jiang, Zhehui Jin, Douglas Henderson, and Jianzhong Wu. Solvent effect on the pore-size dependence of an organic electrolyte supercapacitor. *The journal of physical chemistry letters*, 3(13):1727–1731, 2012.

-
- [151] De-en Jiang and Jianzhong Wu. Unusual effects of solvent polarity on capacitance for organic electrolytes in a nanoporous electrode. *Nanoscale*, 6(10):5545–5550, 2014.
- [152] Gengping Jiang, Chi Cheng, Dan Li, and Jefferson Zhe Liu. Molecular dynamics simulations of the electric double layer capacitance of graphene electrodes in mono-valent aqueous electrolytes. *Nano Research*, 9(1):174–186, 2016.
- [153] Huachao Yang, Xiaoliang Zhang, Jinyuan Yang, Zheng Bo, Ming Hu, Jianhua Yan, and Kefa Cen. Molecular Origin of Electric Double-Layer Capacitance at Multilayer Graphene Edges. *J. Phys. Chem. Lett.*, 8(1):153–160, 2017.
- [154] Zheng Bo, Changwen Li, Huachao Yang, Kostya Ostrikov, Jianhua Yan, and Kefa Cen. Design of Supercapacitor Electrodes Using Molecular Dynamics Simulations. *Nano-Micro Lett.*, 10(2):33, 2018.
- [155] Jesse Gatten McDaniel and Chang Yun Son. Ion Correlation and Collective Dynamics in BMIM/BF₄ Based Organic Electrolytes: From Dilute Solutions to the Ionic Liquid Limit. *J. Phys. Chem. B*, 122:7154–7169, 2018.