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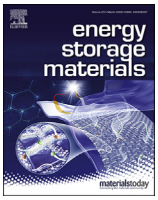

Ionic liquids as electrolytes for energy storage applications – A modelling perspective

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ABSTRACT

Ionic liquids as electrolytes for energy storage devices is a promising field. Here, the various approaches of how ionic liquids can be modelled are discussed along with how the modelling connects to experimental results. Recent theoretical developments are highlighted along with extended discussion of what molecular dynamics simulation options are now available and what key results can be extracted. Ab initio work is also discussed, this includes some of the spectral properties, both of ionic liquids and their electrolyte formulations.

1. Introduction

Ionic liquids (ILs) are salts that have uncommonly low melting points, below 100°C, usually liquid at room temperature. Since the discovery of the first IL in 1914, $[N(C_2H_5)H_3][NO_3]$, they have been intriguing systems to study. In modern times they have been popularised due to their inherent compositional flexibility, since the structural motifs can be endlessly varied as they are simple salts – an anion and cation. But why are these salts liquids at such low temperatures? IL molecular structures have in general the combination of a bulky organic cation and an inorganic anion, which means that the crystal packing is challenging. Many structural motifs have been tried – Fig. 1 shows a tiny subset/selection [1].

As the compositional flexibility spans a vast chemical space, ILs are often called “designer solvents”, due to the possibilities in tuning their physicochemical properties. They have found use in organic synthesis, lubrication and other fields. However, they are also fundamentally interesting for the field of electrochemical energy storage. As ILs are composed of ions, they are intrinsically conductive. For energy storage purposes, ILs have other commonly stated features: high thermal stability; non-toxicity; wide electrochemical stability window; tunable properties due to the large number of cation/anion combinations possible. Thus depending on the exact anion/cation combination, they are considered to be safe, making them attractive as electrolytes for energy storage applications. Another factor is the low vapour pressure, due to the inherent strong electrostatic interactions, meaning that most ILs are fundamentally hard to ignite (very relevant for Li-ion batteries). This is despite drawbacks such as their currently high price (bad for industrial and consumer applications) and the high viscosity of the electrolytes (hinders transport of charge carrying species, reducing their usability for electrolytes). Furthermore, the transference number of Li^+ in ILs is very poor, thus limiting the Li-ion battery rate capability.

It must be noted that while there is a common feature of ILs, i.e. they are molten salts thus intrinsically ionically conductive, the other previously mentioned features do not necessarily hold true for all ILs. For example, it is possible to distill some ILs [2]. The usual bulky cation and inorganic anions can be replaced with their isoelectronic counterparts [3], $K[C_4C_1Cp]$ and $K[C_6C_1Cp]$ (the mirrors of $[C_4C_1im][Cl]$ and $[C_6C_1im][Cl]$) – giving a small metallic cation with a bulky anion.

As the name of the special virtual issue implies, there is a focus on work within Europe, thus the discussion will be more focussed on researchers located within Europe. Anyway, a single short perspective article can not hope to fully capture this vast field of research [4–7]. First, the motivation of using ILs in energy storage systems will be introduced. Secondly, the various approaches to modelling ILs will be discussed along with some of the technical issues, i.e. introduce the tools of the trade. Lastly, there will be a discussion of what modelling has revealed about ILs and their applications in energy storage systems.

2. Energy storage with ionic liquids

Currently there is considerable interest in ILs for commercial energy storage applications, but they have not found their niche in this field yet, despite having done so in other fields [8]. Nonetheless, they are close to

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commercial viability for supercapacitors and may also open up alternative battery chemistries to the standard Li-ion batteries, e.g. Li-metal or metal-air, which would be game changing technologies due to their higher energy capacity [9]. ILs can be used as electrolytes for both supercapacitors and batteries – key energy storage applications. These devices have overlapping requirements for their electrolytes, despite their different energy storage mechanisms. Supercapacitors store energy by separating charges, whilst batteries perform electrochemical reactions at electrodes (a simplified supercapacitor schematic is shown in Fig. 2 along with an illustration of the mechanism in Fig. 3). ILs can order themselves on the porous electrodes of supercapacitors, but can also transport the redox active species between electrodes (assuming that it is not the IL). For example, in Li-ion batteries (LIB), Li-salts can be dissolved in ILs to create an electrolyte. This electrolyte then allows the Li$^+$ ions to participate in their usual intercalation reaction at the anode/cathode in LIBs.

The standard electrolyte for LIB is a mixture of two main components, a solvent mixture, ethylene carbonate and dimethyl carbonate, and the LiPF$_6$ salt [11–13]. However, this system is not very safe, as many fiery public displays of self-destructing mobile phones and laptops have shown. Furthermore, LiPF$_6$ can also hydrolyse and form HF, another unsafe chemical. Additionally, the limited thermal stability of the electrolyte means that ambient storage in high temperature countries will cause degradation of the battery. Thus the interest in an intrinsically safe

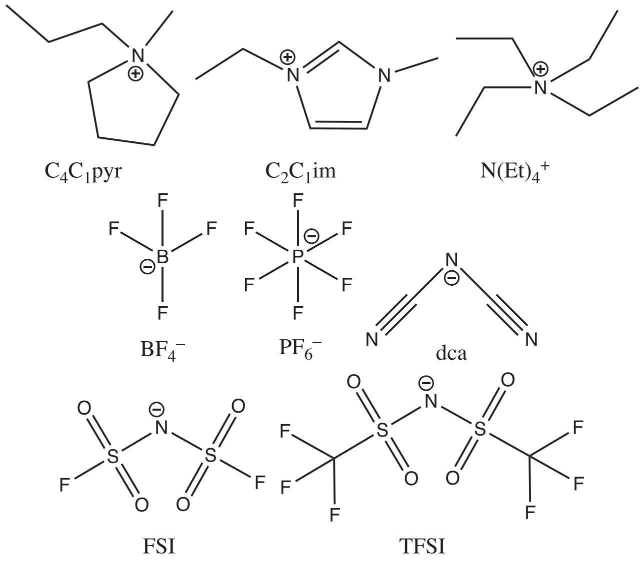

Fig. 1. A selection of ions used for ionic liquids along with their abbreviation (other notations are also used). Commonly used alkyl chains are shown for the cations.

Fig. 2. A simplified schematic of a supercapacitor. In both figures, the electrodes are black and the bulk electrolyte is purple. On the left is the supercapacitor in a state of discharge. On the right hand side, the bulk electrolyte (purple) has formed a double layer of anions (red) and cations (blue) on the surface of the electrodes. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

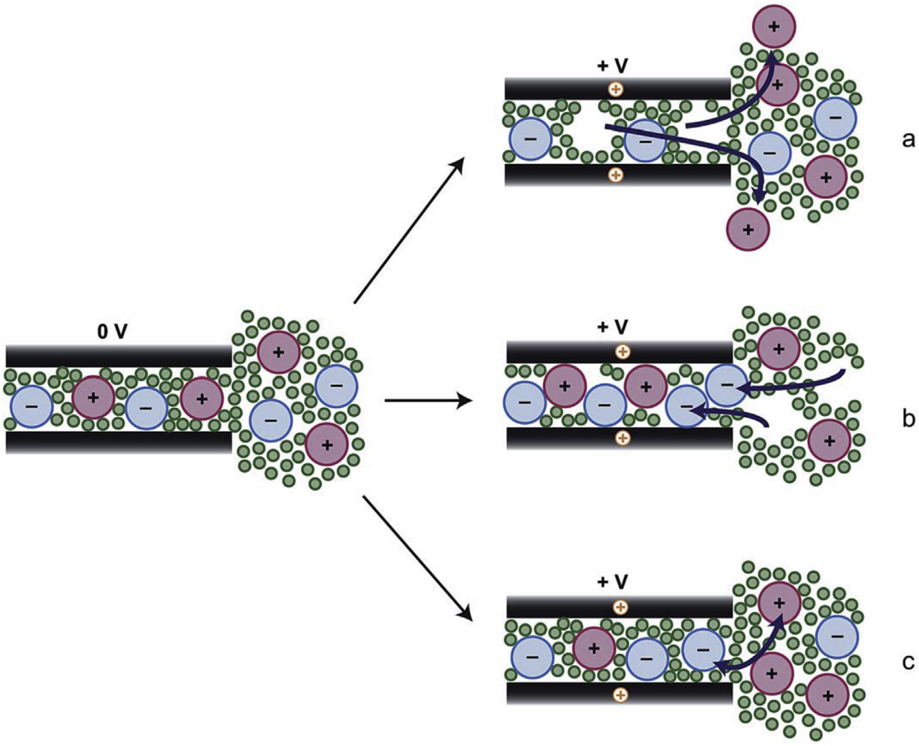

Fig. 3. Possible charging mechanisms of a carbon electrode charged to a positive potential, which are a) cation expulsion, b) anion adsorption and c) ion exchange. Reproduced from Ref. [10] with permission from The Royal Society of Chemistry.

electrolyte system, from both a thermal stability and flammability point of view. However, the electrochemical stability window requirements for LIB electrolytes are quite substantial, >4 V, due to the intrinsically high potential window between the graphite anode and the cathode, such as $LiCoO_2$. Fortunately, some ILs fullfill these requirements as per a recent review by Balducci [13].

Supercapacitors can also use ILs as their electrolyte as the electrochemical stability window of ILs will allow for a higher energy density [14]. The energy stored is related to the accessible voltage and the capacitance of the system, $E = CV^2/2$. By using these tailored solvents, the voltage window can be increased, but understanding the capacitance/behaviour of ILs at electrodes is a complex problem [15]. The full interactions between the charged molecules, electrodes and the applied electric potential are hard to untangle, but in order to rationally design a good electrolyte, they need to be understood. Modelling allows for a close look at each component separately as well as in combinations and can give phenomenological insights that are not necessarily accessible via normal experiments/instrumentation.

ILs pose an interesting challenge for modellers and theoreticians alike. They have been described as “room temperature plasma” due to their charged internal structure with highly correlated motion. The high charge concentration means that commonly used theoretical models cannot be used, as they are based on dilute electrolyte theory. Furthermore, computational modelling of the charged molecules requires greater care, e.g. in density functional theory (DFT) most of the currently widely used functionals do not describe anions adequately due to the incorrect behaviour of the long-range interactions [16], while classical force fields used for molecular dynamics (MD) simulations do not readily deal with the partial charge transfer between anions and cations of an IL.

3. Modelling approaches

To model ILs a multitude of approaches can be used [17], spanning from first principles calculations or theoretical derivation of properties to large-scale simplified systems to explore emergent properties of the bulk system. These approaches include mathematical derivations of capacitance for highly charged systems [18], all-atom MD simulations to look at energetic barriers at electrodes [19], and looking at ion correlations within electrode layers with coarse grained models [20].

The modelling approaches span orders of magnitude in computational costs, so the question proposed by a researcher will choose the tools that are suitable for the work. At the same time, there is an extraordinary flexibility inherent to modelling, as the effect of individual parts of the IL systems can be probed in a manner that would not be possible in experiments. For example, what is the role of the relative size difference of the anion and cation? Is it due to the shape difference? What is the effect of the charge distribution in the cation? These are questions that can be studied by systematically changing the relevant parameters of the MD force fields to explore such effects.

Other applicable questions for energy storage systems that the various modelling options, e.g. DFT or classical MD, can look at include: What is the electrochemical stability window of the system? What are the transport properties of the electrolyte? Can ions or the redox species be transported readily through the system? What is the transport mechanism? What is the electrode layering behaviour in the system? This question has two clear follow-ups – depending on the system studied. For supercapacitors: how will that affect the capacitance? For batteries: will it affect the overpotential for the redox reactions?

3.1. Molecular dynamics

Molecular dynamics (MD) employ energy/force calculations to evolve systems over time. By using the right thermodynamic ensemble, e.g. NVT (constant number, volume and temperature) or NPT (constant number, pressure and temperature), one can look at the bulk properties of a system from its intra- and intermolecular interactions [21]. At every time step, the energy and forces are evaluated for all of the particles (or molecules) of the system, thus the calculation method chosen will greatly affect the complexity of the MD simulation. Should an ab intio method be chosen (AIMD), such as DFT, then the vast majority of the computational effort will be spent dealing with the electronic structure of the system, instead of using it to explore the phase space by running long MD trajectories. Thus AIMD is limited to small systems, i.e. tens of ion-pairs, as the scaling with respect to system size is not favorable. Hence the use of classical force fields for MD simulations as the scaling of classical MD simulations is $\approx O(N)$, in contrast to the scaling of AIMD (DFT) $\approx O(N^3)$.

Classical force fields have been created for MD simulations of ILs, with many different approaches used to create them. In each case, the researchers have to choose how to balance the accuracy and efficiency of their simulations. Depending on what questions their research poses, different design choices will be made. An example of that, charges are not uniquely defined, resulting in a number of different approaches to localise charges to an atom/moiety. This flexibility of designs can also be advantageous, e.g. creating non-physical models to explore the importance of structural features which would be impossible to do physically [22].

ILs are viscous, thus MD simulations have to contend with slow dynamics. The phase space of the system is sampled slowly, resulting in a slow convergence of the thermodynamic averages studied. Thus there is a strong incentive for force field designers to maximise the time step of MD simulations, but this cannot be done without taking into account the particulars of bonding. For classical force fields, bonds involving hydrogen atoms limit the time step, usually to 1 fs, while MD trajectories (the output of MD simulations) are usually on the order of ns. Depending on the design of the force field, this can be compensated for, for example the CL&P force field can use a fixed bond length between C and H (a commonly used approximation), thus a time step of 2 fs is feasible. Classical models that do not incorporate all atom approaches, e.g. coarse graining (CG), can of course use even larger time steps.

One of the first MD works on ILs [23,24] was on imidazolium cations (dimethyl and methyl ethyl, C_1C_1im and C_2C_1im, respectively) with Cl^- and $PF_6{}^-$ anions. Therein, both All Atom (AA) and United Atom (UA) approximations were tested, giving similar results for the structure. However, using the UA model alters the dynamics of the system noticeably (both diffusion constant and molecular reorientation rates), thus implying that future research should use AA models despite the increased simulation time. The work was followed up by studying $[C_1C_1\text{im}][Cl]$ with small solute molecules [25] along with looking at the role of water in the $[C_1C_1\text{im}][Cl]$ and $[C_1C_1\text{im}][PF_6]$ systems [26].

An inherent issue in IL simulation work is the highly charged nature of the liquid. This means that the electrostatics need to be thought of carefully. Thus size effects due to the periodic nature of the simulation boxes used can appear as image charge effects. This implies that IL simulations have a strict minimum box size requirement to prevent this issue. To get accurate results, a good number of ion-pairs need to be included: Gabl et al. [27] found that for $[C_2C_1\text{im}][CF_3SO_2]$ at least 50 ion-pairs are needed to get a reasonable structure but 500 are needed for dynamics. They also noted that consistent results for the dynamics required simulations spanning 20–30 ns (assuming the system is large enough). There is also prior work (not specific to IL modelling) that allows for the correct treatment of electrostatics in a slab system [28], e.g. an IL confined between electrodes. Due to the long-range interactions typically seen in IL systems, nanoscale structuring can been seen [29], thus any simulations are required to treat long-range forces correctly.

Another feature of ILs, that needs to be addressed in force field development, is the redistribution of charges that arises from the collective interactions between the ions. Classical force fields have fixed charges which does simplify their design significantly. Unfortunately, this neglect of the polarisation of the molecules does reduce the diffusion in the system, i.e. slow down the dynamics. One approach to compensate for this, is essentially to use non-integer charges for the cation-anion pairs in the force field. For example, using a charge of $0.7e^-$ [30] speeds up the dynamics of $[C_1C_1im][Cl]$ whilst perturbing the structure of the liquid in such a way that it is closer to AIMD results [31]. However, charge scaling must be done with due care to ensure that results remain meaningful, as changing this parameter to get diffusion constants closer to measured values will perturb other properties. Nonetheless, force fields can still correctly describe dynamics whilst using an integer charge, for example one developed by Köddermann and coworkers [32–34] (for $[C_nC_1im][TFSI]$, where nuclear magnetic resonance (NMR) relaxation times were used to fit force field parameters for the TFSI anion). These force fields can reproduce thermodynamic properties such as enthalpies of vaporization [33].

It would be impractical to create a new force field from scratch for each new IL, especially when researchers are often interested in exploring them systematically. The force field of Canongia Lopes and Pádua (CL&P) [35–41] was designed to tackle this problem. The CL&P force field has internal consistency, transferability and compatibility as key features. The internal consistency reflects the issue of anion/cation interactions and their need to be compatible. The transferability means that a series of ILs can be explored, e.g. $[C_nC_1im][TFSI]$, where $n = 1, \dots$ or a sequence of different anions like, PF_6^-, FSI and TFSI, for a specific cation. The compatibility requirement (here to the Optimised Potentials for Liquid Simulations All-Atom (OPLS-AA) force field [42]) allows for the use of other molecules in a simulation, like solutes. Thus by systematising this into a toolbox that allows for mixing and matching chemists can readily explore a large number of different combinations [43,44].

A more physical model would be to incorporate the instantaneous fluctuations of the charges into the force field itself, instead of approaching this phenomenon by averaging the interactions. Drude particles can be used, where point charges on springs are placed close to atoms. These particles then move around in space, constrained by the spring, and capture the polarisation of the electron cloud of the molecule. However, they require extra minimisation steps after each time step. Such polarisable force fields have started to appear more in the literature, however, as they are up to an order of magnitude more expensive to use than the standard classical force field, they are not without drawbacks. Nonetheless, they do bring significant advantages, for example polarisability affects the dynamics heavily allowing for a closer match to experimental results [45,46]. At the same time polarisability is not a cure-all for all IL simulations (even with the accumulation of 2 μs of dynamics), as a recent non-equilibrium MD study showed that polarisable force fields can have discrepancies in their response to electrostatic perturbations [47].

While polarisation can be approximated with charge scaling, the local interactions are poor [48], e.g. the local environment of imidazolium has issues due to the reduced interactions with the anions. Yet at the same time, larger scale features such as radial distribution functions (at higher r values) are not affected. Furthermore, the dielectric loss spectrum derived from these simulations of $[C_2C_1im][CF_3SO_3]$ agrees well with experiments, however, there is a frequency shift for the polarisable model, implying a faster rotational relaxation than for the charge scaled system.

Induced point-dipoles, another approach to include polarisation, have also been tested [49] for ILs. The electrostatics of Drude particles can be handled with standard techniques as they are point particles, while the induced point-dipole method requires that the MD simulation package has an electrostatic implementation that supports dipoles. Schmollngruber et al. looked at $[C_2C_1im][CF_3SO_3]$ with both CHARMM and AMBER MD program packages, using the former program's support for Drude particles and the latter's for induced point-dipoles. The authors found that the results were qualitatively equivalent, but there are nuances that become apparent at the highest levels of polarisability.

New force fields continue to be developed, for example Dommert et al. endeavoured to incorporate partial charges due to polarisation in a systematic manner to have a consistent force field for imidazolium-based ILs [50]. They derived an effective partial charge from the refractive index and designed their parametrisation scheme to be transferable to other cation and anion families. However, they do concede that proper treatment of polarisability would be of interest.

Atomic or molecular polarisabilities need to be carefully derived for force field applications [51,52]. It is tempting to simply incorporate them straight into previously derived force fields, however, some subcomponents of the polarisability are already incorporated into the Lennard-Jones potentials. Thus followup work [53] could use symmetry adapted perturbation theory to find different energy subcomponents – allowing for the derivation of LJ parameters that take into account that a subcomponent has been removed and placed into the Drude particle/dipole. Pádua looked [53] at three representative ILs, $[C_2C_1im][dca]$, $[C_4C_1im]$ [TFSI], $[C_4C_1pyr]$ [TFSI] – all low-viscosity systems. He noted, that while the computational time does increase, the speed-up in convergence of properties can actually compensate for it. Some systems will require great care in deriving the polarisability, for example the polyiodides with their variability in polarisability in the I_x^- (x = 1,3,5,7 and 9) family of structures [54].

One interesting approach is to incorporate polarisability into a previously developed coarse grained model [55,56] such as $[C_4C_1im][PF_6]$ [57]. As the computational cost is greatly reduced, the authors note that this approach might be of great interest to researchers looking at interfaces such as vapour interfaces or of particular interest to readers of this journal, electrodes. These authors then generalized their approach to allow for arbitrary ILs [58], to give a multitude of polarisable CG IL models. As it is not a general force field, i.e. non-transferable models, but a strategy, it will hold promise for researchers requiring very large simulations.

3.2. Ab initio work

Calculations with ab initio methods on the condensed phase are common place in the literature, i.e. DFT calculations of crystals. Thus periodic boundary conditions are used extensively, however, the cells used for calculations are small. While the liquid state represents a disordered state which requires a far larger cell to ensure the correctness of the calculation setup – such calculations can quickly become prohibitively expensive to run. Hence ab initio work involving bulk ILs is not common, while gas phase work is used extensively. For example, the MD force fields discussed previously often use gas phase calculations to derive parameters.

High-level wave-function method calculations can also be used, though at a far greater cost than for DFT. Most prominent of these include MP2 (second order perturbation theory) and CCSD(T) (coupled cluster singles doubles and perturbative triples). The latter method, when combined with a suitably large basis set, is often referred to as being the 'gold standard' method of quantum chemistry. An example of their usage would be the description of the conformational ordering of $[C_4C_1im][Cl]$ [59]. Hunt and Gould showed that Cl^- has multiple stable position, including in plane and above it. The hydrogen bonding found in some ILs can pose issues for some ab initio methods. Due to the hydrogen bond's nature, it does require long range interactions that are not described correctly in all functionals used for DFT [60]. There is also the challenge of basis set choice, amongst others. For a more detailed description of this problem, along with suggested solutions, see the recent review by Hunt [61].

As IL ions interact at large distances, there is also the need to look at larger assemblies of ion-pairs/clusters. Koßmann et al. [62] noted cooperative effects in the calculations on $[C_1C_1im][Cl]$ ion-pairs. They constructed linear chains up to nine units long where properties approached asymptotically as a function chain length. To study the similar ion-ion interactions, a code was written by another group, to explore mindless configurations of clusters (up to 130 atoms) of $[C_2C_1im][BF_4]$, $[C_2C_1im][PF_6]$ and $[C_2C_1im]$ [TFSI] [63]. The DFT calculations used B3LYP/6-311+G* to optimise structures and calculate IR spectra – an asymptotic behaviour was seen w.r.t. increasing the number

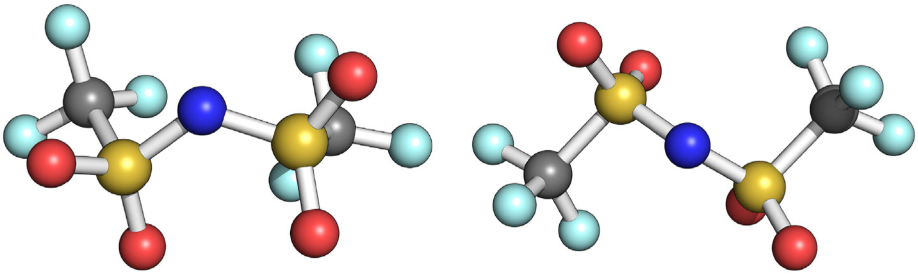

Fig. 4. Left: the C_1 conformer of TFSI, also known as cis. Right: the C_2 conformer of TFSI, also known as trans.

of ion-pairs. It must be noted, however, that DFT functionals will in general require dispersion correction to correct their long-range behaviour [64].

The electrochemical stability window has been studied for anions in LIB literature, with many anions common both to the Li-salt and IL. The study of the reductive limit of the electrolyte has focused on finding compatible molecular solvents for the graphite anode [65,66]. However, some ILs can have an unusal reductive behaviour, as the anion can be reduced ($[C_3C_1pyr][TFSI]$) [67,68]. The oxidative limit is determined by the anion, thus work has focussed on the electronic structure of the anion and its oxidised counterpart [69,70].

Ab initio methods can also be used to evaluate energies and forces for molecular dynamics, instead of biasing the results with the force field choice (for an introduction of AIMD see the book by Marx and Hutter [71]). Unfortunately, AIMD simulations are very time consuming, but as a tool for validation of force fields they are invaluable. They can also deal with situations that are hard to parameterise for, such as the conformational changes involved in evaporating an IL. Malberg et al. [72] studied $[C_2C_1im][C_2H_5SO_4]$, which is known to be distillable, and showed that a gas-phase ion-pair of this IL is distinct from its bulk phase ion-pair. Ingenmey et al. [73] looked at a protic IL, a mixture of C_1im and acetic acid (HOAc), for H_2 storage. As the diffusion mechanism relies on Grotthuss diffusion, the MD simulations need to allow for proton hopping.

3.3. Theory

Simple mental models, that many a chemist may think of when they think of electrolytes, start to break down when they leave the dilute electrolyte regime. For ILs, the solution itself is entirely composed of a salt, i.e. not dilute. Thus a model built assuming an aqueous 0.1 M KCl solution could have big issues when dealing with a system with Coulomb interactions between all molecules, some of which may have large complex shapes. Thus considerable efforts have gone into expanding theoretical tools to deal with ILs. A recent review by Fedorov and Kornyshev [15] gives an overview of the theoretical discussions regarding ILs on electrodes/electrified surfaces.

A key insight that is worth mentioning is the role of the ion size and how that will affect ion concentration at the electrodes [18]. As IL ions are not point particles, their size becomes important as ions pack onto electrodes as the system is polarised. Thus “lattice saturation” can take place and impose restrictions on the electric double layer. This results in an unusual capacitance curve, instead of the standard U-shape of Gouy-Chapman theory, both a camel and a bell shape can be observed (depending on lattice saturation). This work was followed up with further theoretical developments, including a proposed superionic state, along with Monte Carlo simulations [74–77].

Charged electrodes in ILs will have layers of ions on the surface. At these high concentrations, overscreening of the electrode can happen, i.e. there is an overabundance of the countercharge of the electrode in the first layer. The successive layers are then layered as a decaying response to the structured electrolyte layer of the electrode. However, as a recent report [78] points out, there is also the phenomenon of underscreening, where the ions of the electrolyte are not able to screen the full charge of the electrode. Recent work has been done to understand the origin of this effect, though this does touch upon the thornier topic of the nature of the solution [79–81]. Can ILs be considered to be dilute electrolyte solutions? As there are clearly aggregates in the system, so do they count as dissociated? While the work has been more experimental in nature [78, 82–85], it has clearly inspired work both on the bulk [86] and on the electrode case [87].

4. Applications

To understand what role ILs can play in energy storage devices, the combination of modelling with experiments has already revealed some of the details. Starting with alkali-ion electrolytes where the local environment of Alk^+ is important for the transport properties of the electrolyte. Vibrational spectroscopy, both infra-red and Raman, is capable of capturing the bonding information of this local environment. However, to understand the origin of all of the vibrational modes of the system, ab initio calculations can be invaluable. For example the interesting case of the two conformers of TFSI, C_1 and C_2 (Fig. 4). The effect of the two conformers can be seen both in crystalline LiTFSI systems [88] and also in IL systems such as $[C_2C_1im]$ [TFSI] [89]. In both these papers the spectral assignment was supported with DFT calculations. The spectral fingerprint of lithium coordination was then exploited to look at the ion transporting species in a number of imidazolium based ILs, $[C_2C_1im]$ [TFSI], $[C_4C_1im]$ [TFSI] and $[C_4C_1C_1im]$ [TFSI] (1-butyl-2, 3-di-methylimidazolium bis(trifluoromethylsulfonyl)imide). At lower LiTFSI concentrations a solvating cage of $[Li(TFSI)_2]^-$ was identified. At higher LiTFSI concentrations, the ratio of TFSI to lithium goes down as aggregate networks may form. A similar feature was observed for NaTFSI salts in $[C_2C_1im]$ [TFSI] and $[C_4C_1im]$ [TFSI]. According to a combination of spectroscopy and DFT calculations, the solvation complex does involve $[Na(TFSI)_3]^{2-}$ [90] instead of $[Na(TFSI)_2]^-$ (as might be expected from the previous LiTFSI results).

Other battery electrolytes can also be studied with modelling and theory. For example, Mg-ion batteries are also being researched, thus the interaction between Mg^{2+} and ILs is also of interest [91]. For more fundamental research of ILs, the combination of DFT and vibrational spectroscopy was used to assign C-H vibrations in imidazolium based ILs [92,93]. The Kirchner group has used both AIMD [94] and classical MD [95] to look at the solvation behaviour of ILs containing TFSI. Their focus was on how protic ILs would interact with TFSI in the presence of lithium. As they note, the Li^+ concentration affects the transport properties due to its interactions with TFSI which can create long lived cages [95]. These protic ILs would be cheaper to synthesize, which is one of the issues preventing the adoption of ILs in industry.

The solvating cage concept has been explored further with mixed anions, starting with the minimal ion triplet. This was initially done on systems of $LiAn_1An_2^-$, where cluster volumes were correlated with electrolyte properties [96], thus a tunable parameter. A follow up study from a different group [97] looked at ion triplets in $[C_2C_1im][X]$, where $X = B(CN_4)^-$, $PF_6{}^-$, $BF_4{}^-$, FSI or TFSI. This was a mixed ion study, utilising a combination of quantum chemistry and classical MD simulation, to see what transport mechanisms can occur. They noted that BF_4^- had the strongest binding, while $B(CN)_4^-$ had the weakest. They noted that polarisable continuum models (implicit solvation models) seemed to work fairly well, though absolute values may be off. Furthermore, dynamic interactions may differ from the static calculations.

For new anions, such as 2,5,8,11-tetraoxatridecan-13-oate (TOTO), quantum chemistry can reveal how they interact with cations such as Li^+, Na^+ and K^+. Eilmes and Kubisiak [98] showed with Møller-Plesset theory that the size of the alkali ion affects the complexation energy, i.e. the energies are in the order Li > Na > K. They also ran MD simulations of these systems, though only the NaTOTO had experimental values for the diffusion constant. Their simulated value was one sixth of the experimental value, however, they were not using polarisable force fields, which they suggest as a future avenue of research.

The ion transport results of MD simulations can be coupled to a number of NMR techniques. For example Bolimowska et al. [99] used NMR techniques both to reveals dynamical (pulsed field gradient) and structural ($\{^7Li–^1H\}$ HOESY) information. They studied a 1 M LiTFSI solution in a mixture of $[C_6C_1im]$ [TFSI] and vinylene carbonate (a commonly used additive for LIB electrolytes). They showed that the vinylene carbonate would participate in the transport of Li^+ in the system.

The transport of Li^+ is crucial for lithium-ion batteries, unfortunately, one of the key short-comings of ILs for LIB electrolytes is a very poor Li^+ transference number. The mechanisms that have been identified for transport of Li^+ are vehicular and structural diffusion. The first involves the motion of the entire solvation complex around Li^+, the latter involves structural rearrangement of the solvation structure to enable Li^+ hopping. Interestingly, systems having an overall slower diffusion can still give a higher Li^+ transference number, as seen in $[C_3C_1pyr]$ [TFSI] as compared to C_2C_1im [TFSI] [100]. MD simulations have shown that the solvating cages shown earlier reduce the motion of Li^+ in ILs. These anion cages around Li^+ have been observed for Li-salts in $[C_4C_1Im]$[TFSI], $[C_4C_1im][PF_6]$ and $[C_4C_1Im][BF_4]$. Furthermore, the same phenomenom was seen for $NaPF_6$ in $[C_4C_1im][PF_6]$ [101]. The protic IL $[N(C_2H_5)H_3][NO_3]$ had caged Li^+ in an extended nanostructure [102], implying that the caging of alkali cations is common in ILs.

Perturbing these ion cages to enable faster transport is clearly a goal for future work. One approach tested was to explore a mixture of two cations, C_2C_1im and Li^+, and two anions, FSI and TFSI [103]. This gave rise to a lithium dimer bridged by TFSI, i.e. Li^+-TFSI-Li^+, structures which had surprisingly long lifetimes according to the MD simulations. Another way to improve LIB electrolytes is simply to use ILs as an additive. For example, using 10% $[C_4C_1pyr]$[TFSI] with ethylene and dimethyl carbonate (the standard solvents for LIB) [104] proved beneficial for thermal and electrochemical stability. This work did look at the full range between using a pure IL to a pure molecular solvent.

Polymer electrolytes can also incorporate ILs in addition to their lithium salt. Ternary systems composed of $[C_3C_1pyr]$[TFSI], LiTFSI and poly(ethylene) oxide (PEO) have been studied in detail [105–107]. By using a transport model to identify transport mechanisms, the authors were able to rule out that lithium transport had been decoupled from the motion of the PEO chain. Instead, as the IL has a plasticizing effect which enhances the polymer (where the lithium is coordinated) segmental motion, thus the dynamics of Li^+ were improved. Incorporating a functionalised pyrrolidinium cation with polyether moieties was tested recently by Diddens et al. [108] They decoupled the transport of lithium from the polymer and found a novel mechanism, coined as the shuttling mechanism. Another group has looked at LiTFSI in PEO with $[C_2C_1im]$ [TFSI] as the IL [109]. The group tested multiple different force fields and found a large variability in the results, highlighting the need for carefulness for such simulations.

For supercapacitors, the electrodes and the layering behaviour of the electrolyte needs to be studied together, especially as the electrode shape does affect how the electrolyte can interact and even penetrate the full three dimensional structure. Hence, to look at the charging mechanisms of supercapacitors [110], fairly complex models may need to be constructed. Thus quite large and porous electrode structures need to be created or derived from experiments, but confinement effects can become apparent [111]. Charging of the electrode can also induce structural changes, for example carbide derived carbon (modelled as graphene flakes) with $[C_2C_1im][BF_4]$ that works as an actuator [112]. Applying a constant potential will also drive organisation of the interfacial layer due to the correlations of the IL ions [113]. The application of constant potential methods with electrodes can also show details hidden by constant charge methods, for example the ion-ion correlations than can happen between layers of graphene sheets [20].

In some cases, simple models can still be really helpful to understand details of the mechanism. For example, Wang et al. [114], use DFT calculations of nucleus-independent chemical shifts around coronene to understand spectral details of in situ NMR data ($[N(C_2H_5)_4][BF_4]$ with deuterated acetonitrile). In other cases larger systems are required, such as a study of the storage mechanism in a MXene-based supercapacitor [115], $Ti_3C_2T_x$ ($T = -F, =O, -OH$) with $[C_2C_1im]$ [TFSI] as the electrolyte, which showed that there are two distinct mechanisms at work in the system – revealing the origin of opposing volumetric changes.

The ions closest to the electrodes can adsorb/order on the surface, for example $[C_4C_1im][PF_6]$ on graphite [116]. Though charging the electrodes will induce a different structure on the double layer that is formed. Recent work from the Varela group has explored the structuring in great detail [117–120]. They looked carefully at the 3D structuring of $[C_4C_1im][BF_4]$ on graphite and the influence of co-solvents such as water, methanol and ethanol [120]. It was revealed that the charge asymmetry rather than the composition of the electrode seems to drive the lateral structuring of the IL from the surface. Mixtures of protic and aprotic ILs (alkyl ammonium nitrate and $[C_nC_1im][BF_4]$ ($n = 2,4$), respectively) on graphene surfaces has also been recently studied by the group [121]. They showed that in addition to the polar and non-polar domains previously reported, protic and aprotic dominated regions can be found. Thus the interface has a very complex heterogenous structure, requiring further work to understand fully.

Dielectric spectroscopy is commonly used in research on energy storage materials. Deriving such spectra from simulations is clearly viable now, though not common as there is the need for both a good description of the bulk liquid and also some of the electronic structure as the polarisation of the system is also important [122].

To allow for electrochemical reactions, the redox active species need to come close to the electrode surface, either to be deposited on the electrode or to be intercalated/alloyed with the electrode. One worrying issue of ILs, partly due to the screening effects discussed previously, is how large the barrier is for e.g. Li^+ to access the electrode. Méndez-Morales et al. [19] studied $[C_4C_1im][BF_4]$ by using MD simulations with fixed charge electrodes (see Fig. 5). They found large free energy barriers for both Li^+ and K^+ to access the electrode surface. They noted that high salt concentrations enabled some transport of alkali cations to the surface. Later work, showed that a protic IL, $[N(C_2H_5)H_3][NO_3]$, enabled easier access to the electrode surface (here for Li^+ and Mg^{2+}) via its hydrogen bonding network [123]. If these barriers can be reduced for the redox active species, that should help electrochemical applications.

As computational resources increase doing ab initio studies of ILs at interfaces becomes more practical. A recent study by Gómez-Gónzalez et al. [124] looked at the charge transfer between a graphene wall and Li^+/Mg^{2+} cations. Interestingly, they note that charge transfer can happen surprisingly far from the electrodes when exposed to an IL, $[C_4C_1im][BF_4]$. Other charge transfer work has actually combined ab initio results with X-ray techniques, i.e. near edge X-ray absorption fine structure (NEXAFS) [125,126]. This allowed the researchers to show charge transfer between cation and anion.

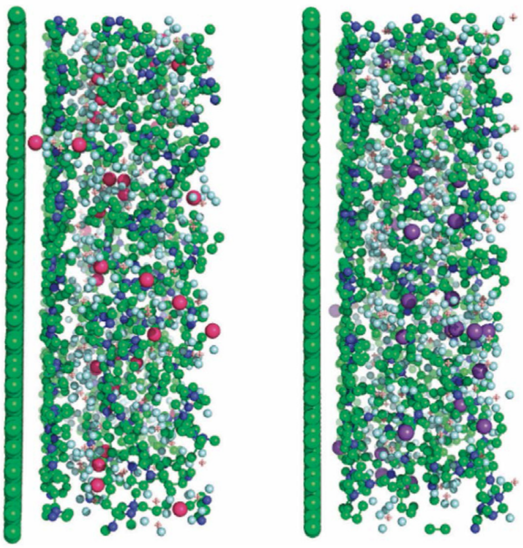

Fig. 5. Snapshots of the electric double layer formed on negatively charged graphene walls for simulations of 25% $LiBF_4$ (left) and 25% KBF_4 (right) in $[C_4C_1im][BF_4]$. Atom color coding is C:green, N:dark blue, F:light blue, B:light pink, Li:dark pink and K:violet. Reproduced from Ref. [19] with permission from the PCCP Owner Societies. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

5. Summary

ILs as electrolytes for energy storage are promising, but not quite there yet commercially. At the same time there is a lot of work being done to understand the implications of using these highly charged electrolytes. For example the role of over- and underscreening at the electrode interface, which may be barriers for electrochemical reactions taking place in batteries. Tuning these features can ensure that the kinetics of the redox chemistries are not hindered by the electrode screening.

To unravel spectroscopic details, e.g. deconvolute Raman spectra, ab initio methods have proven themselves to be invaluable. Calculations of the energetics of reactions are another key application of ab initio methods. Though it must be noted that size limitation do cause issues for larger simulations. Recently, there have been significant advances in quantum chemistry method development. This will allow for far larger IL clusters to be calculated and study some of their emergent bulk properties without having to parametrise as many force fields.

The force fields that have been developed for MD simulations of ILs are already well developed, as evidenced by the small selection of papers found in the Application section. For some applications standard force fields may have to be optimised further. Especially as generic polarisable force fields for ILs have not yet been fully developed/implemented, so for example dynamics will tend be slower. Yet at the same time practical MD force fields that incorporate the intrinsic polarisability of IL ion-pairs are now far more available, though not routine. The treatment of electrodes is often done with fixed charges, especially as many popular program packages do not yet have option to simulate fixed potential electrodes. Most of the modelling software packages used in the papers cited here are easily available and are able to deal with substantial systems.

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