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Breaking the Scales: Electrolyte Modeling in Metal-Ion Batteries

by Ryan Jorn and Revati Kumar

The choice of electrolyte is literally at the center of lithium and sodium energy storage devices as it provides the pathway for metal ion transport between the electrodes during charge-discharge cycling. However, zoom in on the electrode interface during battery operation and it becomes clear that the electrolyte's role is not always to serve as a passive resistor. The organic solvent molecules used to dissolve metal salts in commercial batteries, namely cyclic and linear carbonates, frequently react with the electrified interfaces to form surface films that in turn effect device performance.¹ These films trap metal ions, preventing them from participating in the charge transfer reactions necessary to power an external circuit, and can grow to tens of nanometers in thickness while accumulating over the lifetime of the battery.² The quest to design a “better” electrolyte is thus complicated by potential degradation at the electrode surface weighed against transport properties tens of nanometers from the interface.³ In both cases, the manner in which metal ions are coordinated by solvent, co-solvent, additives, and counter-anions at the atomic level has been linked to the chemistry of the breakdown products as well as to trends in ionic conductivity in the bulk phase.^{4,5}

Connecting the molecular structure of the electrolyte with macroscopic charge cycling performance requires computational strategies that can span several orders of magnitude in spatial and temporal scales (see Fig. 1), from the solvation shell and diffusion of lithium (nanometers and nanoseconds) to the development of surface films (tens of nanometers and microseconds) and the effect of both on the lifetime and performance of the battery on the device-scale. Word-limit constraints on this article do not permit even a cursory examination of the wealth of experimental techniques that have been used to study electrolytes across these disparate spatial and time regimes in both half and full cell configurations (for excellent reviews, see Ref. 6 and 7). Even so, a simplified summary of these efforts points to common challenges in performing such experiments with sufficient spatial and temporal resolution in operando. As a result, many questions remain unanswered concerning the surface chemistry of electrolytes, the process of film formation, and the mechanism for ion transfer from the electrolyte to the electrode. Given the slow progress of various spectroscopic, microscopic, and surface imaging methods across decades of research, a natural question that arises is whether there is another approach that could lend complementary insights to the behavior of electrolytes in electrochemical energy storage devices and provide guidelines for their continued development.

In contrast to the early years of lithium-ion battery research, computational modeling is now contributing an important role in studying electrolyte properties and processes across a

wide range of length scales.⁸ The challenge for modeling electrolytes lies in the disparity between methods used at different length-scales: the basic physics included, level of parameterization, and the types of questions each method is capable of addressing pertaining to the electrochemistry of solvents and salts. Hence the same methods used to model chemical reactions at the electrode surface (based in quantum mechanics) cannot be readily applied to describe the evolution of the interface on the order of nanoseconds. Likewise, the appropriate simulations for describing longer time- and length-scales (classical molecular dynamics) do not readily incorporate reactive events and normally cannot be used to predict chemical dynamics. From the perspective of the state-of-the-art in computational modeling, lithium and sodium ion electrolytes provide an exciting new frontier for developing novel approaches that connect the quantum and classical worlds while offering significant motivation to meet global challenges in energy storage and sustainability. In what follows, the current impact of modeling on electrolyte research is briefly assessed with particular emphasis placed on efforts to bridge orders of magnitude in length- and time- scales. Two case studies will be discussed to demonstrate the utility of force-matching as a specific means of connecting quantum and classical approaches to model electrolytes for energy storage.

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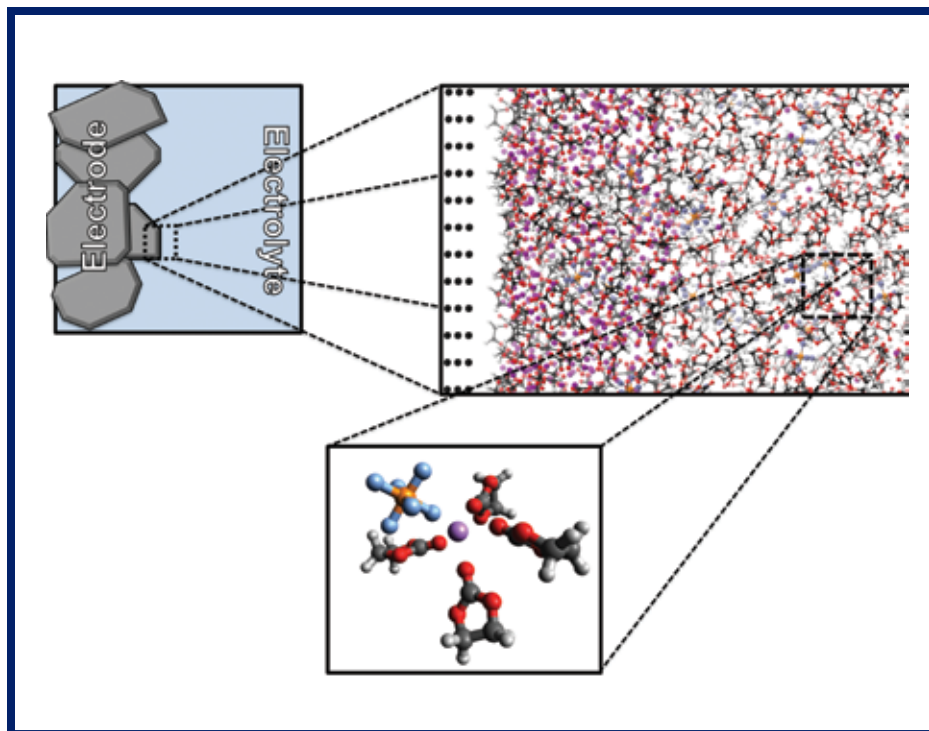


FIG. 1. An illustration of the multiscale nature of electrochemical systems—the properties at the microscale (indicated by the top leftmost panel) are effected by the formation of surface films and electrolyte structuring at the interface (indicated by the top right panel for an electrolyte comprised of ethylene carbonate and LiPF_6) and ultimately is reflective of the metal ion solvation shell (shown in the bottom panel for a single lithium ion).

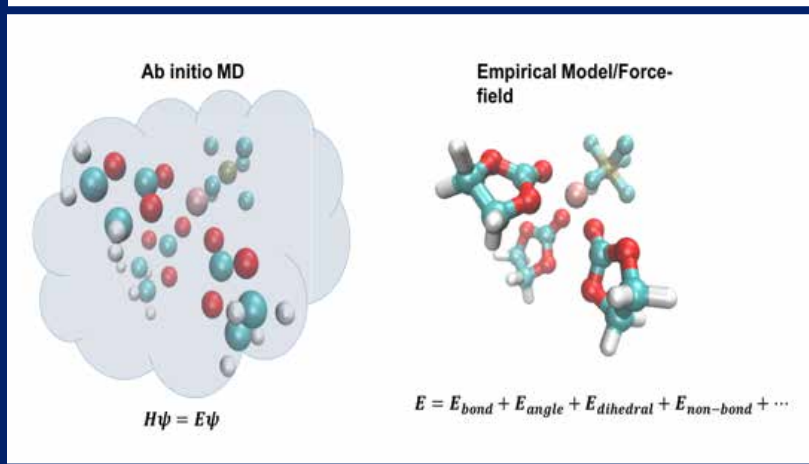


Fig. 2. (Left) Sketch of a snapshot from an AIMD simulation of LiPF_6 in ethylene carbonate. The colored spheres represent the nuclei and the bubble the electron cloud. (Right) A sketch of the same snapshot in a simulation using an empirical model. The atoms are represented by spheres and the bonds by cylinders.

Introduction to Computational Modeling

Because the term “computational modeling” has different meanings to different researchers, it is pertinent to clarify the different regimes of simulation used to study electrochemistry in metal-ion batteries (see Fig. 2). Starting at the smallest length scale, the time-independent Schrödinger equation provides a complete quantum mechanical description of the solvent molecules and ions in the electrolyte, albeit with frozen nuclei (the limit of 0 Kelvin). To solve the Schrödinger equation for systems of practical interest, Density Functional Theory (DFT) has become the standard for predicting the equilibrium solvation structures of small clusters of molecules embedded in an implicit solvent,^{9,10} the solvation energies of salts,¹¹ the positions of the HOMO and LUMO of electrolyte species,¹² and the reaction pathways for reduction and oxidation of carbonates with commonly used salts^{13–17} such as lithium hexafluorophosphate (LiPF_6). By developing reliable protocols for calculating reduction potentials for solvent and salt combinations, DFT methods have been connected with high-performance computing resources to perform guided searches for new candidate electrolyte materials.^{12,18} While several “high-throughput” endeavors are currently being pursued to discover new electrolytes, it is important to note that they often neglect the role of the electrode surface to keep the calculations manageable. It is known that interactions between the electrolyte species and the electrode often produce multiple new reaction pathways and shift the energetic positions of molecular orbitals from their bulk electrolyte values.^{19,20} Protocols are advancing for lithium-ion batteries in which an initial screening in the absence of the electrode is supplemented with more detailed calculations to avoid such restrictions. Clearly, efforts that account for the effects of the surface without significantly compromising high throughput is an important priority for realizing new electrolyte materials.

By allowing the nuclei to move in response to electronic forces in a quantum simulation, greater sampling of reaction coordinates and molecular geometries is enabled in real time. Rather than propagate the full time-dependent Schrödinger equation, two assumptions are made: 1) the nuclei remain classical objects; and 2) the motion of the nuclei is much slower than that of the electrons such that they can be essentially de-coupled as represented by the Born-Oppenheimer approximation. Solving the electronic Schrödinger equation and propagating the nuclei as classical objects—also known as ab initio molecular dynamics (AIMD)—has been used extensively to model electrolyte reactions at the carbon anode and metal oxide cathode,²¹ the related electron

transfer processes,²² and to better understand the solvation of metal ions at normal operating temperatures.^{23,24} Recent reports have proven the effectiveness of the AIMD approach (at the DFT level and combined with efficient periodic boundary conditions software) to investigate the stability of the electrolyte breakdown products at the electrode surface after the initial reaction.²⁵ Results from these AIMD studies and from time-independent quantum calculations have provided greater insights into the role of one- and two-electron reductions as well as a rationale for lithium fluoride production due to electrolyte decomposition. The advantage of AIMD simulations is built on its independence of parameterization and hence significant predictive power for exploring chemistries that are difficult to probe experimentally. At the same time, a major drawback of these simulations is their computational expense, which restricts the length and time scales studied to the order of a nanometer and tens of picoseconds, respectively. On a more technical level, the results are also often DFT functional dependent (i.e., the map that provides the energy for a given electron density) and a judicious choice of functional is required that is often validated against experimental observables.

When attention is shifted from the reactivity at the electrodes to the bulk conductivity of the electrolyte, classical molecular dynamics becomes the method of choice since it can access sufficiently long timescales to follow diffusive motion. In contrast to AIMD, classical simulations rely on atomistic empirical models to provide the forces on the nuclei of the electrolyte in a given configuration rather than upon the solution of the Schrödinger equation. Empirical force models are developed based on intuition for the energetics of chemical bonds, data from quantum calculations, and fitting parameters based on experimental observables such as density and heat of vaporization. In a sense, these models coarse-grain the electronic aspect of the system to represent the electrolyte by atomic particles that interact with each other as a function of geometric coordinates: Distances, angles, dihedral angles, etc. These models are typically non-reactive in that they do not allow for changes in bond topology and hence cannot be used to model chemical reactions.

Classical force models, often referred to as force-fields, consist of an intramolecular component that includes energy terms for bonds, angles and dihedrals, and an intermolecular, or more properly a non-bonded, component. Most non-reactive empirical models, or force-fields, are broadly divided into two categories based on the types of non-bonded interactions: effective pair potentials and many-body models. The effective pair potentials are the most common and typically include Coulomb interactions between atomic sites that bear partial charges as well as Lennard-Jones type van der Waals interactions between atomic sites.²⁶ However, the real “quantum mechanical” potential energy consists of not only interactions between every pair of particles, but also higher order terms representing the response of the electrons on an atom to the electric field of its neighbors. Even though the two-body term is dominant, often up to 80% of the total energy, these many-body effects become especially important at interfaces. The many-body interactions can be included partially by using effective two-body models that are parameterized to experiment, accounting for some of the polarization effects in an implicit mean-field manner.²⁷

While a number of general force fields, such as OPLS-AA,²⁸ AMBER,²⁹ and COMPASS,³⁰ have been developed for organic compounds, transferability of these models to new types of molecules remains a concern. Often empirical models are developed specifically for the systems under study, or at least modified for the specific ions under consideration. On the other hand, models that include many-body effects, such as polarizable models, are inherently more transferable but come with additional computational cost. There has been significant effort made, specifically by Borodin and Smith, to develop highly accurate many-body polarizable force-fields for several organic electrolytes including carbonates, polymers, and ionic liquids that demonstrate greatly improved transport characteristics and solvation structures when compared with standard pair interaction models.^{31,32} Interestingly, a recent series of quantum calculations using a wavefunction embedding technique have hinted at the need to

consider not just dipoles for atomic sites, but also quadrupoles in the molecular response to accurately describe common solvent molecules such as dimethyl carbonate (DMC).³³

Building Bridges between Length and Time Scales: Multi-Scale Modeling

Surprisingly, given the individual successes of static quantum calculations, AIMD, and classical molecular dynamics, relatively little work has been pursued to connect these methodologies in a consistent manner. With regard to simulations of ion transport, progress has been made on integrating simulation cells containing multiple phases (i.e., electrode, surface film, and electrolyte) to calculate energy barriers to ion transfer and on bridging information from quantum simulations to describe mesoscale transport in surface films.³⁴ For an explicit connection of energetics from quantum and classical simulations, the work of Borodin and Smith stands apart as a tour de force of model development from extensive single point energy calculations using quantum calculations.^{31,32} Apart from these contributions, reports of extensive force field development for battery electrolytes have been sparse. As an alternative, others have also made use of the passage of information from classical models to quantum calculations by using empirical models to generate likely solvation structures that are used in static DFT calculations in order to enhance sampling.³⁵

An area that has received increasing attention has been the development of reactive classical molecular dynamics models to connect information on chemical reactions with surface film development on the nanometer length scale. Degradation of carbonates on lithium metal electrodes has been studied using the ReaxFF approach in which the bond order of atoms is used to update the force model “on-the-fly” and allow for chemical reactions to take place.^{36,37} Kinetic Monte Carlo has also been adapted to monitor film growth by using a classical molecular dynamics approach that randomly allows for bond breaking/formation events in a manner consistent with the underlying reaction rates.³⁸ Validation of these approaches with continued experiments remains critical to assessing their utility, but they provide first glimpses into the reactive nature of the electrode-electrolyte interface. In general, the pursuit of reactive force-fields remains a grand challenge in the field of simulations of soft matter systems and the studies mentioned here represent a growing aspect of electrolyte modeling – in particular at the electrode-electrolyte interface.

Variational force-matching provides an algorithm that has been successful in constructing empirical “pair potentials” for a number of soft condensed matter systems, including organic electrolytes for batteries.^{39,40} The principle behind this method is to parameterize a classical model to reproduce the forces on select sites from a higher-resolution approach, hence the term force-matching. For example, one can carry out a DFT-based *ab initio* molecular dynamics simulation of the system of interest, in principle containing all of the information on the forces and responses, and then develop a simpler atomistic model by modifying parameters in the expressions for the atomic forces to reproduce the AIMD results. The fitting process can be iterated using dynamically uncorrelated snapshots taken from the DFT simulation to minimize the differences between the model forces and the actual forces present in the quantum simulation for a variety of configurations. In this manner certain degrees of freedom (electronic degrees in the above example) are coarse-grained out to develop a cheaper representation of the system that nonetheless retains key information encoded in the forces. As previously mentioned

in the context of other classical force fields, parameterization does create uncertainty about the transferability of the optimized model to other species. Technically, one is also restricted to using the model to simulate the system under the same conditions as the reference trajectory (temperature, concentration, etc.); however the results can be surprisingly robust as discussed below.

Force-Matching Lithium and Sodium Ion Electrolyte Systems

We have previously used the force-matching algorithm to develop atomistic empirical models from DFT-based AIMD simulations for two very different electrolytes: A carbonate-based electrolyte with Li^+ as the charge transport species and an ether-based electrolyte with a sodium salt.^{39,40} In both cases, improvements in the representation of the solvation shell around the metal ion were noted and contrasted with previous work using generic force-field models as well as AIMD. Classical simulations for the system consisting of 1.5 M LiPF_6 in ethylene carbonate (EC) revealed that on average, the coordination around the Li^+ ion was a little less than five with around 0.5 anion equivalents (PF_6^-) in the first solvation shell and showed improved agreement with the AIMD results. The solvation shell structure agreed well with previous many-body potential simulations, having the oxygen of the carbonyl group in the EC tightly coordinated to the cation and a diffusion coefficient in agreement with previous calculations. However, it was noted that an over coordination of the ion persists and likely requires fitting three-body interaction terms to capture more of the many-body polarizability. In contrast to the simulation of lithium ions in solution, our work with sodium triflate dissolved in diglyme showed that at the same concentration, the triflate is more strongly bound to the sodium ion with a large fraction existing in contact ion pairs with an average coordination of one triflate equivalent per sodium ion at a concentration of 1.5 M salt solution. Even at very low concentrations (0.5 M) contact ion pairs are formed, unlike in the case of lithium ions in EC. In Fig. 3, sample solvation structures

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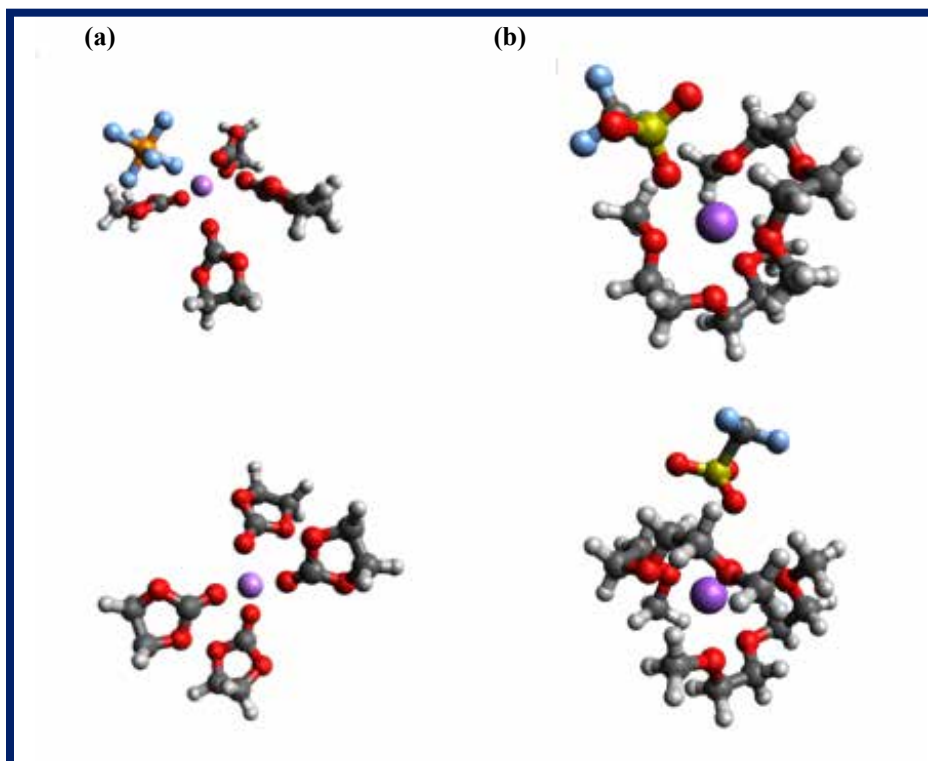


FIG. 3. Sample solvation structures are shown for the a) lithium ion in 1.5 M LiPF_6 in ethylene carbonate and b) sodium ion in 1.5 M sodium triflate in diglyme (sodium/lithium atoms represented as magenta spheres, oxygen as red spheres, sulfur as yellow, fluorine as cyan spheres, carbon as grey spheres and hydrogen as white spheres).

are shown for both the lithium ion (1.5 M LiPF₆ in EC) as well as the sodium ion (1.5 M sodium triflate in diglyme) that illustrates the above discussion. By using the force-matching procedure, we were able to construct simple pairwise models capable of accurately describing the coordination of metal ions in diverse electrolytes at a scale readily extended to the highly heterogeneous electrode interface.

While unraveling the nature of the molecular structure and charge transport in bulk electrolytes is important, the true power of molecular simulations lies in its ability to provide insight at the electrode-electrolyte interface. With a simple model in hand that can be readily connected to generic force-fields, simulations can now be built to describe the complex interface formed during electrolyte degradation. In the case of lithium-ion cell technologies, several components are known to build up at the electrode surface including lithium fluoride, lithium carbonate, and oligomers of carbonate subunits such as dilithium ethylenedicarbonate (Li₂EDC). Using our force-matched models, we have simulated the lithium ion electrolyte held between two graphitic electrodes with a voltage applied between the two electrode surfaces. Since these models are non-reactive, the set up more accurately describes a supercapacitor than a functioning battery. However, this approach does enable us to study the structure and dynamics of the interface in relation to the bulk, which may have implications for the solvation structures used in future reactive methods.

In the simulations of LiPF₆ in EC, we observed that the Li⁺ ion is not present in the first layer next to the negative electrode except at very high applied voltages, unlike the case of the counterion (PF₆⁻) that is present in the double layer at the positive electrode. Hence, it is the organic solvent that solvates both positive and negative electrodes rather than the salt ions. In addition to the pure electrode-electrolyte interface, the electrode-SEI-electrolyte interface was also considered. Interestingly, phase separation of the inorganic layer near the electrode surface and the organic layer closer to the electrolyte was observed in agreement with experiments pertaining to surface film composition. These studies are ongoing and have implications in the study of battery aging wherein layered SEI interfaces impact battery performance.

Outlook for Electrolyte Modeling

Computational modeling of electrolytes is currently developing along two complementary tracks: 1) searching for new combinations of solvents and salts enabled by 2) developing greater understanding of the basic electrochemistry of these species at the electrode interface. Continued progress in simulating the bulk properties of electrolytes as well as the electrode-electrolyte interface will advance both of these objectives, however this effort will require the development of new computational strategies to connect the microscopic structure to predictions of macroscopic performance. A few reports have been published recently towards this end, however there is still significant need to advance multi-scale methods capable of accurately capturing charge transport and chemical events in the context of the mesoscale morphology at the electrode surface. A substantial aspect of this challenge is the development of novel chemically reactive algorithms to model sufficient length- and time- scales to consider film formation and its impact on ion transport. Modeling efforts along these lines that institute a synergistic approach with experiments will result in a far deeper understanding of processes in electrolytes as well as at electrolyte interfaces. These types of investigations should result in the end-goal of developing predictive models that will accelerate the development of “designer” electrolytes with tailored properties. ■


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