Theoretical Characterization of Correlated Redox Activity and Nanostructure in Hybrid Supercapacitors

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Jesse McDaniel

School of Chemistry and Biochemistry

Georgia Institute of Technology

Atlanta, GA, 30332

Supercapacitors (SCs) complement batteries as essential energy storage technologies, being unique in their exceptionally high power output and fast charging times. Recent progress for increasing the energy density of SCs has been enabled by utilizing highly nanoporous carbon electrode materials and/or introducing Faradaic or redox-active components to create hybrid/pseudo-capacitor devices. Incorporating both of these design paradigms in a synergistic manner can often be difficult, however, requiring a detailed understanding of the complex electrode/electrolyte chemistry and physics at the nanoscale. In this regard, it is vital to develop and apply computational techniques to better understand energy storage mechanisms in carbon-based supercapacitor (SC) devices. A major goal is to explore the synergy of the design principles of nano-structured electrodes and Faradaic activity for enhancing energy storage.

We have performed sophisticated computer simulations on a variety of supercapacitor systems chosen based on the broad goals of elucidating nanostructure and redox-functionalization improvements to energy storage.[1-7] Our simulations have targeted different electrode morphology and composition with a variety of electrolytes composed of different solvents, ions, and concentration. This exploration is guided and focused by previous experimental work that has shown certain electrode/electrolyte combinations to have particularly intriguing and/or important energy storage capabilities.

State-of-the-art supercapacitor electrodes often consist of highly nanoporous carbon materials such as activated carbon or carbide-derived carbon. Adsorbed electrolyte ions within these electrode materials are subject to a high degree of nanoconfinement that can significantly alter their physical properties and the resulting device performance. We have combined statistical mechanical theory with high-performance computer simulations to investigate the modulation of electrical double layer properties within highly nanoconfined carbon electrodes.[2] We have predicted an anomalous kinetic effect in which ion dynamics and diffusion rates exhibit a local maximum at several nanometer confinement distances for ionic liquid electrolytes. Utilizing

statistical mechanical linear-response theory, we rationalized this behavior in terms of electrostatic screening and ion correlation lengthscales within the EDL. We demonstrated that the EDL susceptibility and ion correlation increase non-monotonically as confinement constraints are relaxed, causing variation in ion dynamics.[2] This trend results from interference between opposite double layers as the confinement distance becomes smaller than the intrinsic electrostatic screening lengthscale of the electrolyte. These simulations were unique and novel in that microsecond timescales were achieved for fully polarizable, atomistic electrolyte force fields coupled with constant voltage MD, rendering a high-fidelity comparison of theory and simulation.

In another application, we have utilized computer simulations to predict capacitance profiles in carbon nanotube/graphene (CNT/G) composite electrodes coupled with organic electrolytes.[5] Our electrode models were inspired by experimental "layer-by-layer" synthesis, and the computer simulations attempt to elucidate paradigms of capacitance enhancement from nanoconfinement. We developed a novel algorithm for conducting fixed-voltage molecular dynamics simulations (FV-MD) on complex electrode architectures built from carbon nanotube/graphene composite. We conducted FV-MD simulations for five different electrode morphologies to investigate capacitance modulation from nanostructure and porosity. Several important design principles for enhancing energy storage in supercapacitors were found.[5] First, we observed "hot spots" at the contact points between nanotubes and graphene, in which ion separation was greatly enhanced through strong electrostatic interactions with electrode image charges. This indicates that the local capacitance at these contact points is significantly higher than at flat interfaces. In addition, one of the electrodes studied exhibited significantly higher specific capacitance than the others, due to nanoconfinement enhancement. By calculating the surface area of the nanoconfined region, we estimated a 3-4x local capacitance enhancement for this portion of the electrode.[5] Our simulations thus provided additional physical insight for designing nanoporous carbon electrodes with substantially enhanced capacitance.

This work complemented previous experimental findings that highly nanoporous carbon electrodes can demonstrate substantially enhanced energy storage. To realize maximum capacitance enhancement, such electrodes should contain pores of sub-nanometer dimension, so that ions are perfectly "size-matched" with the electrode pore and completely lose their solvation shell upon incorporation into the electrodes. However, optimizing both the *thermodynamic* (energy storage) and *kinetic* (power output) parameters of nanoporous electrodes is complicated by the fact that there may be intrinsic tradeoffs. For example, small nanopores which are "size-matched" to electrolyte ions (and thus optimal for capacitance), may exhibit substantial kinetic diffusion barriers for uptake/release of ions, the latter being detrimental to power output of a supercapacitor. Motivated by this consideration, we performed a systematic study of kinetic barriers for electrolyte ion diffusion through different sized pores in carbon electrolytes.[1] Using biased molecular dynamics simulations, we computed free energy barriers for diffusion of prototypical trimethylethylammonium (TMEA+), tetramethylammonium (TMA+), and tetrafluoroborate (BF4-) ions through systematically sized pores in model carbon electrodes. The electrolytes studied were

the corresponding salt (either TMEA/BF4 or TMA/TMEA/BF4) dissolved in acetonitrile or 1,2-dichloroethane, which are prototypical choices for supercapacitor electrolytes. The overarching conclusion of this investigation was that sub-nanometer sized pores of 0.75-1nm in diameter are optimal for energy storage and lie exactly at the limit of thermal diffusion accessibility.[1] For example, diffusion barriers through 0.75nm pores for the smaller BF4- anions were calculated to be ~14 kcal/mol, with reduction to ~ 5-6 kcal/mol as pore sizes are expanded to 1nm in diameter. A very interesting observation was that in the lower dielectric 1,2-dichloroethane solvent, barriers are dictated by diffusion of ion pairs rather than single ions, which is an important consideration when matching electrolyte/electrode combination. The primary physical origin for these diffusion barriers is desolvation of the ion within the confined pore, with this effect being more substantial for small, strongly coordinating ions. Overall, our work provided important design principles illustrating how not only the energy storage, but also the power output of supercapacitors depends sensitively on precise nanostructure of carbon electrodes.

In addition to the electrode, tuning the electrolyte can be an important strategy to enhance the performance of supercapacitors. In this regard, room-temperature ionic liquid electrolytes have many desirable properties, particularly their large electrochemical stability windows. However, the capacitance behavior of ionic liquids at electrode interfaces is not-well understood, fundamentally due to the fact that the liquid is composed of pure ions and no dipolar solvent molecules, which renders standard double-layer theories (e.g. Gouy-Chapman-Stern) inapplicable. In a collection of manuscripts,[3, 4, 7] we have utilized sophisticated molecular dynamics simulations to better understand the voltage-dependence of the capacitance profiles of ionic liquid electrolytes. A major goal was to understand the origin of the "camel-shape" capacitance profile, which has been experimentally observed for many different ionic liquid systems, but is not rationalized by standard double-layer models. Specifically, experiments show "camel-shaped" capacitance profile for ionic liquids that exhibit a minimum presumably at the potential of zero charge (PZC), and two maxima on either side of the PZC at positive and negative polarization. We performed extensive FV-MD simulations of two different ionic liquids BMIM/BF4 and BMIM/TFSI, and their mixtures with acetonitrile and 1,2-dichloroethane solvent. Our simulations predicted minima in the differential capacitance profiles of these systems, with semi- quantitative agreement to experiment. We were then able to rationalize that the physical reason for the existence of this surprising minima was strong "solvophobic interactions" between functional groups on the electrolyte molecules and the carbon electrode.[4] We computed electrolyte density profiles at different applied voltages, and showed that hydrophobic alkyl groups of the cation and -CF3 groups of the anion were "attracted" to the carbon electrode at the PZC. As the voltage is changed from the PZC to either positive/negative polarization, the hydrophobic groups are expelled from the electrode surface, replaced by polar and charged functional groups of the molecular ions. This effectively shifts the charge density of the electrolyte closer to the electrode surface, better screening the external electric field and thus increasing capacitance.

Our work on ionic liquid capacitance profiles has led us to develop a general model that can describe capacitance profiles of concentrated electrolytes, spanning aqueous, organic, or pure

ionic liquid systems. This model is based on the well-known Helmholtz model, but incorporates atomistic detail of the electrical double layer. For example, we allow both the dielectric constant "ε", and inner layer thickness "L" to vary with Voltage, due to the atomistic response of the double layer to the electric field. The voltage dependence of the capacitance profile C(V) then results from the combined voltage dependence of ε(V) and L(V), with the latter computed from accurate molecular dynamics simulations that incorporate full atomistic detail. This model has the success of rationalizing the previously unexplained "camel shape" profiles of ionic liquid electrolytes; the camel shape results from the superposition of a bell-shaped response ε(V) resulting from dielectric saturation, and a voltage-dependence of L(V) arising from electrostriction of the atomistic inner layer. We believe that this "generalized Helmholtz model" of ionic liquid double layers is much more physically interpretable than prior theories proposed in the literature.

While the main goal of our double-layer work was to investigate capacitance profiles of ionic liquid and organic electrolytes, we have also investigated concentrated aqueous electrolytes in order to demonstrate the applicability of our generalized Helmholtz model for these systems.[6] This demonstration would significant, as it would imply that the generalized Helmholtz model would be widely applicable for describing capacitance profiles of concentrated electrolytes, spanning aqueous, organic, or pure ionic liquid systems. We have conducted extensive FV-MD simulations of Au(100)/aqueous NaCl electrolyte interfaces as a function of ion concentration, voltage, and utilizing both polarizable and nonpolarizable force fields.[6] By computing capacitance-voltage curves and comparing the dielectric constant of the Stern water layer as a function of voltage, we were able to confirm the generalized Helmholtz model description in which the capacitance is proportional to the voltage-dependent, dielectric constant, ε(V). We showed that the structure and dielectric constant of the Stern layer is insensitive to ion concentration, so that the inner capacitance is largely determined by properties of the Au/water interface in absence of ions. An additional conclusion is that explicitly polarizable force fields are essential for correctly predicting the voltage-dependence of the double layer, as nonpolarizable force fields predict an unphysical ion distribution at positive polarization.

In carrying out the described research endeavors, we developed both new computational methods/algorithms, and software implementations, to enable the requisite computer simulations. All of our method/algorithm development has been implemented in state-of-the-art, high-performance, open-source software, so that it is accessible and may be used by the broader computational community. The two primary software packages that we have developed computational methods and algorithms for are: OpenMM, a versatile molecular dynamics package that is unparalleled in speed on graphics processing units (GPUs) and Psi4, a highly efficient quantum chemistry code with a versatile python API. Customized versions of these software packages that we have developed for the encompassed research are accessible on out Github webpage. The methods/software efforts that we have developed are described below.

Efficient Poisson Solver for Fixed-Voltage MD: Absolutely essential to computational characterization of electrochemical interfaces is an efficient method to fix the applied Voltage of the electrodes. The Voltage modulates the physics of the double layer, and it is very important to incorporate this effect within the simulations. While previous fixed-voltage or constant-potential molecular dynamics methods have been published, they suffer from very expensive algorithms and inefficient software implementations. We have thus developed and implement a general, efficient algorithm for fixed-voltage MD simulations that can be applied to a variety of electrode morphologies and is implemented on GPU software (OpenMM).[3, 5] This new software has enabled direct characterization of complex supercapacitor architectures with fixed-voltage molecular dynamics simulations, to explore how nanostructured electrodes modulate capacitance as a function of external voltage. We have developed and applied this method for flat electrode morphologies (graphite/graphene),[3] as well electrodes with well-defined curvature (carbon nanotube arrays).[5] This combination of software/method development enabled our broad computational investigation of a variety of supercapacitor systems with varying nanostructure, as was described above.

Functionalizing carbon electrode surfaces with redox-active moieties can give important energy storage enhancement. Because these redox events occur directly at the electrochemical interface, redox potentials and electron transfer rates may be significantly shifted from corresponding bulk-solvent properties. We have attempted to utilize first-principles computer simulations to predict standard-state redox potentials and electron transfer rates for important redox-active, functional groups attached to carbon electrode surfaces. Exploring Faradaic, redox-based energy storage mechanisms in SCs requires a computational approach for first-principles prediction of redox potentials and electron-transfer barriers at the electrochemical interface. To enable this, we have developed a novel Fixed-Voltage, quantum mechanics/molecular mechanics "QM/MM" approach that treats the redox-active species at the QM level (DFT) with embedded electrostatics from the full electrochemical cell incorporated through particle-mesh Ewald (PME) machinery. In our developed QM/MM/PME approach,[8] a QM/MM Kohn-Sham Hamiltonian is utilized that employs numerically exact, long-range electrostatic embedding based on particle-mesh Ewald algorithms. Combined with our Poisson solvers, this method enables explicit description of electron transfer energetics between the electrode and redox molecule, with electrons of the electrode modeled classically as image charges. This powerful approach thus enables energetic calculations of "outer-sphere" electron transfer events, in combination with thermodynamic integration schemes for free energy calculations, performed with the chemical potential of electrons fixed by the external Voltage.

A key goal was to understand how Faradaic energy storage mechanisms can be effectively incorporated into supercapacitors. Computational prediction/modeling of this chemistry requires accurately computing redox potentials in complex electrochemical environments with concentrated ionic solutions and at electrode interfaces. Historically, the majority of computational studies of redox chemistry have been done using implicit solvent models, which are simply not applicable in this case. We thus have undertaken a systematic benchmark study for redox potential prediction utilizing explicit, all-atom molecular dynamics simulations. We have benchmarked different force fields, polarizable and nonpolarizable, and different

approaches for computing solvation free energies including thermodynamic integration and linear response approximations. We have focused on concentrated organic electrolytes that are commonly utilized in supercapacitors, including BMIM/BF4 ionic liquid and mixtures with acetonitrile and 1,2-dichloroethane solvent. We focused on the ferrocene/ferrocenium (Fc/Fc$^+$) redox couple, which is a prototypical redox couple, and a large number of experimental benchmarks are available for comparison. We have found that ion pairing and ion correlation substantially modulates the Fc/Fc$^+$ redox potential over a 0.5-1.0 eV range for ion concentrations spanning from 0M (pure solvent) to the neat ionic liquid limit (pure ions). We find that this ion pairing and correlation is only well described using polarizable force fields, and long simulations (10's-100's ns) must be run to sample the ion correlation and minimize statistical uncertainty in the predicted redox potentials. We believe that this work provides an important benchmark for computational prediction of redox chemistry in concentrated organic electrolytes, with applications to better designing supercapacitor systems that incorporate Faradaic activity.

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