RATIONAL MATERIALS DESIGN THROUGH THEORY AND MODELING

The rational design of novel electrical energy storage (EES) systems with high energy and power density will require the development of a full suite of computational techniques to calculate all the properties of electroactive materials and the microstructures in which they are embedded. A revolutionary advance, for example, would be the ability to design stable materials that can exchange multiple electrons per redox couple and to predict their structural stability during charge-discharge cycling. Compared with related areas of electrochemistry (including batteries), the theory of electrochemical capacitors (ECs) is largely undeveloped. Many opportunities exist to develop and apply new continuum, statistical-mechanical, atomistic, and quantum-mechanical models. Although this effort can benefit from progress in related fields, ECs present many unique modeling challenges, such as ultra-fast, nonlinear, and nonuniform double layer charging; anomalous transport, molecular structure, and wetting characteristics in nanopores; new nonpolar electrode materials and nonaqueous electrolytes; pseudocapacitance combining redox reactions with charge screening; and widely disparate length and time scales. To achieve the ideal of rational design of EES materials, microstructures, and systems, it will be necessary to develop fundamentally new theories and modeling tools that can also have broader impacts in physics, chemistry, biology, and applied mathematics.

Background

Advances in theory and modeling capabilities will be critical for obtaining atomic- and molecular-level insight into the myriad processes that occur in EES and for modeling new materials and architectures needed for future technology breakthroughs. Although chemical energy storage (batteries) and ECs share common components such as electrodes and electrolytes, the physical and chemical processes in these two systems are quite distinct. Therefore the research directions for each are presented separately.

Chemical Energy Storage

Storage of electrical charge through electrochemical means requires the reversible conversion and transport of ions, such as H^+, Li^+, Na^+, Mg^{2+}, OH^-, and O^{2-}, across large potential differences. These ions are shuttled from one electrode material through a composite electrode structure into the electrolyte and ultimately are stored in the other electrode. The design of EES systems with high energy and power and long lifetimes requires accommodating a large number of ions, and their charge-compensating electrons, at either electrode without inducing irreversible changes in the structure of the active material, the electrode-electrolyte interfaces, or the electrode microstructure. The rational design of electrodes requires the parallel development of computational techniques, from ab initio to the mesoscale and continuum scale, and a strategy to integrate them into a predictive tool. Specific examples include both bottom-up and top-down modeling. For example, high-throughput atomistic simulations can be scaled up to select real, often composite materials to produce novel electrochemistries, and scaled down from the device level to predict possible damage from structural loads to battery constituents.

Distinct mechanisms exist to accommodate ions on an electrode. Ions can be stored in interstitial sites of intercalation compounds while their charge-compensating electrons reduce

transition metal cations. Increasing energy density for such intercalation electrodes requires breaking through the one-electron-per-metal barrier and finding crystal (or noncrystalline) structures that can remain stable under a multivalence change of the redox center and a large concentration change of exchangeable cations. In conversion reactions, a compound chemically reacts or alloys with the incoming ions from the electrolyte and completely converts to other phases (e.g., $BiF_3 + 3Li \rightarrow Bi + 3\ LiF$).[1] Since such conversion reactions use all valence states of an ion up to the metallic state, they have the potential to radically increase the energy density of batteries. Whether ions are stored in intercalation compounds or through alloying reactions, the extreme degree of reversibility needed in applications (>1000 cycles) requires a fundamental understanding of what controls the kinetics of phase changes, interface creation and migration, and microstructure evolution. Finally, as active materials are typically embedded in complex multiphase, multicomponent microstructures, modeling at the mesoscale is needed to understand transport, deformation, and evolution of such microstructures.[2]

Enormous progress has already been made in the computational prediction of several important properties of electrochemical materials, including redox potential [3] and ion mobility. Mesoscale modeling has been advanced by simultaneous progress in applied mathematics and mechanics to allow simulation of transport and mechanics in complex architectures of packed agglomerates,[4] but a full predictive theory of chemical energy storage systems requires fundamental research and methodological developments in several areas listed below. Progress in these areas will enable computational modeling of performance, lifetime, and safety; drastically accelerate innovation in new materials; and catalyze new designs for higher energy and power at lower cost.

Capacitive Energy Storage

Capacitive energy storage has received less attention from theorists than has chemical energy storage. The modeling of ECs is still in its infancy, so major technological advances may be expected from a long-term investment in fundamental research. The standard model consists of transmission-line equivalent circuits for the charging of cylindrical pores or networks of pores (Figure 16).[5] Although clearly oversimplified, such models provide useful analytical formulae to interpret experimental impedance spectra, for example, separating purely capacitive response (double layer charging) from pseudocapacitive response (simultaneous surface redox reactions).[6] By considering more complicated equivalent circuits of nested transmission lines, first attempts have also been made to understand and optimize the effect of microstructure on capacitive charging.[7] As simple as this approach may seem, it already suggests the possibility of radically improving power density and energy density through advanced structural design.

There are important distinctions between ECs and batteries that merit separate and focused research programs, in spite of some cross-cutting themes. Batteries use Faradaic reactions and bulk-phase transformations to achieve high energy density and high voltage at the expense of slow transport and limited cycle life. ECs use much faster interfacial transport in the electrolyte phase to achieve high power density and much longer cycle life, at the expense of lower energy density due to interfacial, rather than bulk, energy storage. The obvious route to increasing energy density is to increase the surface-to-volume ratio of the

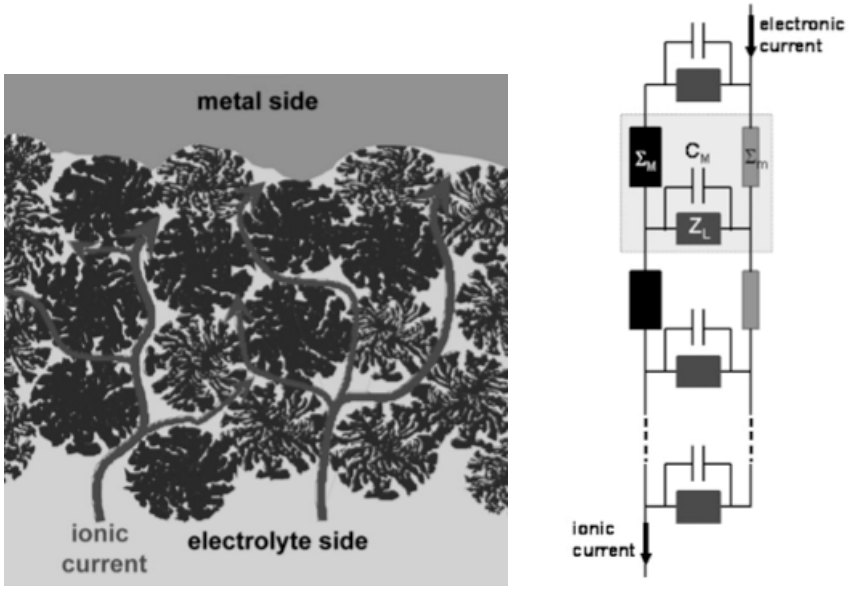

Figure 16. (Left) Sketch of a single electrode layer of a carbon-based EC illustrating the hierarchical pore structure with macropores between carbon agglomerates and micro-to-nanopores inside agglomerates. (Right) Transmission line model for the charging dynamics of the EC electrode, consisting of repeated blocks of resistors for bulk ionic current in the pores and electronic current in the carbon phase, connected by parallel impedance/capacitance elements to model double layer charging.[7]

electrode, but this raises fundamental scientific questions about potentially new physics and chemistry in nanostructured materials. There is little existing theory to predict, for example, the behavior of ions and solvents confined in nanopores or the nonlinear dynamics of charging in a complex electrified microstructure with vastly disparate length and time scales.

Unlike batteries, ECs also share some features with biological ion channels, but again, there are important differences and unique challenges. Biological ion channels exhibit highly selective, single-file diffusion of ions through protein pores in cell membranes that has been the subject of intense study in recent years.[8,9] Developing theoretical models based on continuum, statistical, and atomistic descriptions has been crucial to understanding size selectivity.[10]

Recent molecular dynamics (MD) simulations[11] and experiments[12] on nanoporous carbon, however, suggest that the structure of water and the solvation of ions are fundamentally different in nanopores from in the bulk. There is also tantalizing evidence that sub-nanometer carbon nanopores have a dramatic and anomalous increase in specific capacitance compared with larger nanopores and micropores.[13] The common wisdom is just the opposite—that pores smaller than the bulk solvation shell cannot contribute to charge storage. Clearly, there is a pressing need for better theories and MD simulations to explain and predict such anomalous behavior at the nanoscale, which could be exploited to boost dramatically the energy and power density of ECs.

Research Directions

Chemical Energy Storage

Predictive kinetics of phase changes. Electrode materials with high energy density undergo large chemical, dimensional, and morphological changes during charge and discharge. If these changes are irreversible, they can cause capacity degradation with repeated charge-discharge cycles. Although ab initio methods can accurately screen compounds for their energy density and redox potential, no quantitative predictions can be made for stability, a key requirement for electrode materials. For intercalation compounds, predictive modeling of the kinetics of phase transformations is needed to design compounds that can tolerate large changes in ion and electron concentration. To rationally design conversion electrodes, coarse-graining approaches are needed to predict which phases form upon alloying and dealloying of the active ions from the electrode and to understand the cause of hysteresis, as it significantly decreases the energy storage efficiency of these reactions.

Rational design and performance evaluation of electrode microstructures. Currently, macroscopic models that allow the prediction of battery behavior from fundamental materials properties incorporate a limited amount of microscopic detail. A classic example is the incorporation of intercalation processes in battery electrodes via the use of a pseudo-two-dimensional architecture. Here, the composite electrode is coarse grained across the spatial dimension, while the intercalation inside the particle is incorporated by coarse graining across a particle. The two scales are then combined to form the electrode model. While powerful, this coarse graining across the particle dimension eliminates detailed description of many of the complexities that are known to be important in batteries, especially the structural details of the various battery materials. A grand challenge in performance and lifetime modeling is being able to accurately incorporate the actual structural information in macroscopic models to provide an effective means of correlating material-specific information to performance. This would enable the prediction of electrode behavior in both spatial and temporal dimensions during high charge rates and the tracking of microstructure and materials evolution during cycling.

Formation, structure, and charge transfer across reaction interfaces. The phase that forms as a reaction layer between the electrode and electrolyte (the solid electrolyte interphase, or SEI) is critical to the performance, life, and safety of batteries. This complex interface is very poorly understood and even more poorly described in mathematical models for performance. The picture is complicated by the changes that the SEI undergoes during cycling, including cracking, spalling, and reformation. As new materials that perform at higher voltages are developed, and new additives identified, the interface will become more complex, necessitating methods to describe the formation and growth of these layers. The grand challenge lies in predicting the structure of the electrochemically formed reaction layers between the electrode and electrolyte under large variations in potentials and then quantifying electron and/or ion transport through them. MD methods that can include electric field effects and chemical reactivity may be particularly well suited to addressing this problem. Efforts to model the SEI layer must rely heavily on results from novel in situ characterization tools to establish their accuracy and relevance. When integrated with the mechanical modeling of electrode structures, SEI models are expected to result in a very detailed description of interfacial processes and to connect changes at the interface to

changes in performance through the life of an electrochemical cell. The result will be an ability to rapidly evaluate new combinations of materials and electrolytes and gauge their usefulness.

Modeling the electrochemistry of nanoscale materials and surfaces. Nanoscale materials offer great opportunity for energy storage. Chemistry and structure have been the dominant domains across which materials optimization has been performed. Reducing the particle size to the scale where the kinetics and thermodynamics become significantly different from those of the bulk can bring an extra dimension to this design space and generate materials that are fundamentally different from their bulk equivalents.

Modeling should address to what extent the thermodynamics and kinetics of ion reactions with nanomaterials are different from those with bulk materials and characterize the effects of surfaces on the intrinsic electrochemical properties and performance. Ab initio methods are good at modeling very small particles (< 2 nm) and infinite systems (with periodic boundary conditions); however, novel ideas are needed to deal with nanomaterials at the technologically relevant length scale from 10 to 150 nm.

Transport modeling. Charge transport (ionic and electronic) is particularly important for chemical energy storage. While many materials and systems can, in principle, be used to exchange charge, many of them do not have the proper rate capability to function in storage devices at room temperature. To ultimately predict the rate at which chemical systems can charge and discharge, the development of models at multiple length scales, from crystal structures to microstructures, is required. Models need to be significantly complex to capture ion and electron transport in multicomponent electrolytes and complex multiphase microstructures. As many active materials are strongly anisotropic in their transport properties, mesoscale models of composite electrodes may need to take that into account. For nanosystems in which sizes approach the screening lengths and for high rate potential changes, models may have to remove the common constraint of local electroneutrality.[14] Poor electron conductors may be of particular interest as electrode materials because they are often strongly bonded, giving them good stability and safety characteristics. Methods to model mixed conduction in these systems need to go beyond mean field theory to explain the effect of the strong coupling between localized polarons and ions on the overall transport characteristics. Such transport models will need to be informed by electronic structure methods beyond common density functional theory (DFT) to properly capture electron localization.[15]

Inverse and high-throughput materials design. Materials for EES are likely to see the first benefits of large-scale computational materials science, which can be applied to calculating many of the required properties. One question is whether high-throughput search methods can be implemented with predictive modeling tools to scan large numbers of compositions, structures, particle sizes, etc., to find new electrode materials. New computational tools and analysis methods need to be developed to enable such large computational searches. In "inverse design," one tries to invert this problem and, rather than calculate properties for a well-defined composition or structure, to design materials or microstructures that have very

specific properties. Mathematical techniques that enable such inverse design, starting either from key physical insights or from large amounts of data, are particularly needed.

Capacitive Energy Storage

New predictive models for capacitive energy storage systems need to be developed at all length and time scales, ranging from quantum (<nanometer, <picosecond) to atomistic (<10 nm, <1 ns), to micro-continuum (>nanometer, >nanosecond), to macro-continuum (>millimeter, >microsecond) for relevant materials and geometries. Such models could enable rational selection of electrolyte and electrode materials, design and optimization of electrode architectures, and discovery of new physical or chemical phenomena. To achieve these goals, fundamental new understanding is needed through close interplay among theory, computation, and experiment based on simple model systems.

Can we systematically predict the nonlinear charging dynamics and energy density of an EC from first principles given only the chemical species and electrode microstructure? This vision would require accurate models to be developed at each scale and new methods to derive effective parameters at the next higher scale from analytical or simulation results at a smaller scale. For example, classical continuum models of ion transport (Poisson-Nernst-Planck, or PNP, equations) could be analyzed in suddenly electrified pore geometries to derive equivalent circuit models for linear and nonlinear responses. The continuum equations could then be modified to account for discrete effects coming from atomistic simulations, such as steric constraints, chemical potentials, and electrostatic correlations. Going down in scale, interatomic potentials for familiar materials (such as certain aqueous electrolytes and carbon) may need to be adjusted for new settings, and potentials will also need to be developed and validated for many new materials (such as complex organic solvents). In each of these cases, new models must be validated and calibrated using simple experiments to ensure their predictive power.

There are many open questions regarding the anomalous behavior of solvents and ions in nanostructures that must be answered for a fundamental understanding of ECs, especially as the surface-to-volume ratio increases to improve energy density. How and under what conditions will an electrolyte enter and wet a pore? What is the equilibrium structure of ions and solvents in a particular confined geometry? What are the effects of surface functional groups or bulk impurities? Do ions lose solvation under the influence of large fields and/or confined spaces? Do different ions in multicomponent electrolytes segregate upon insertion into a complex nanostructure? Is there any significant hydrodyamic slip or electro-osmotic flow? How does ion transport in a nanopore fundamentally differ from tangential “surface conduction” in a flat double layer? To answer such questions, the challenge will be to develop new and more accurate atomistic and quantum-mechanical modeling tools tailored for unique EC materials. Below, several different types of modeling tools are discussed in the context of EC systems.

Continuum modeling. A natural direction at the level of continuum modeling would be to go beyond equivalent-circuit models that, by design, can only describe the linear response of the system to a small applied voltage, such as the impedance. Although impedance spectroscopy is a key tool for characterization, nonlinear dynamics at large applied voltages

is often more relevant for the practical operation of ECs. One goal, therefore, would be to systematically derive nonlinear generalizations of circuit models starting from the underlying transport equations. This derivation has been done recently for thin double layers by using mathematical methods of matched asymptotic expansions applied to the classical PNP equations. In the simplest case of a parallel-plate cell of blocking electrodes subjected to a sudden large voltage (Figure 17), the analysis shows that the classical RC circuit model breaks down as a result of adsorption of neutral salt in the double layer.[16] The latter depletes the bulk solution and triggers slow diffusive relaxation, which invalidates the assumption of Ohm's law in the bulk. Such effects have also been calculated recently for nonlinear charging of metal spheres and cylinders,[17] but the nonlinear propagation of charge through long nanopores or complex microstructures in ECs is an important open problem.

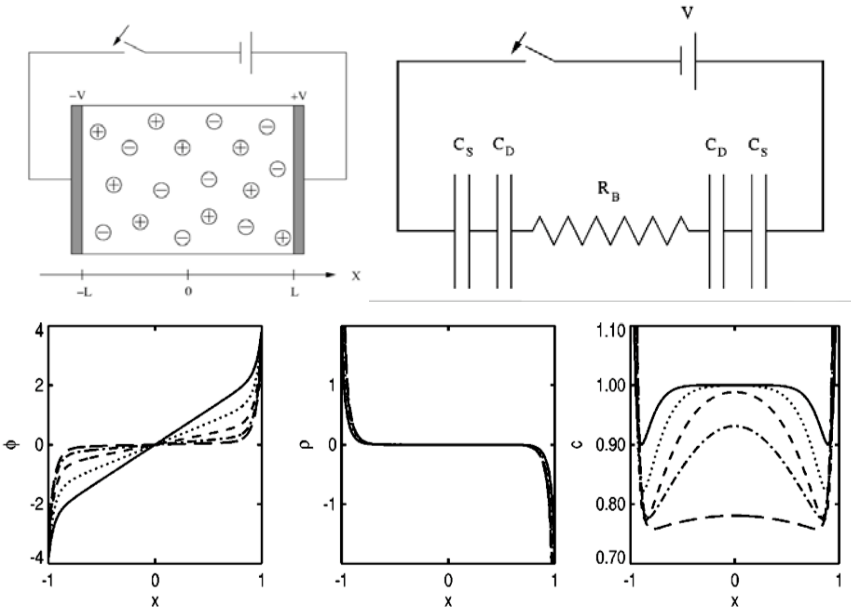

Figure 17. Breakdown of circuit models in nonlinear charging dynamics. (Top left) A suddenly applied large voltage across blocking electrodes. (Top right) Equivalent RC circuit. (Bottom) Solution to the Poisson-Nernst-Planck equations for the potential, charge density, and salt concentration profiles, from left to right, which shows that the double layers adsorb neutral salt upon charging, depleting the bulk electrolyte and leading to slow diffusive relaxation after the initial "RC" charging.[16]

The small dimensions of nanopores in ECs, as well as the large applied voltages, also call into question the validity of the classical PNP equations, including the Gouy-Chapman solution for a flat double layer in a binary electrolyte. There have been many attempts to derive "modified" Poisson-Boltzmann equations accounting for steric effects of finite ion size and electrostatic correlations in thermal equilibrium by applying statistical mechanical methods to the primitive model of a charged hard-sphere fluid. Recently this work has begun to be extended to charging dynamics via modified PNP equations with a simple description of steric effects.[18] It would be a great advance to derive and validate modified PNP equations for EC materials that can approximately describe the charging of nanopore arrays, including entrance effects from micropores.

Better continuum models can yield crucial analytical insights and efficient computational tools provided they can be validated against reliable atomistic simulations and experimental model systems. They also provide the ability to incorporate multiple physical processes occurring at the electrode or device scales. For example, the sudden insertion of ions into a nanoporous structure can cause it to swell, so it will be important to develop models coupling charge transport to the mechanical response of the composite material. Joule heating during EC charging can also be a serious concern, so the coupling of charging dynamics with heat transfer and energy dissipation will be another important long-term goal in continuum modeling of ECs.

Atomistic modeling. The simplest form of atomistic modeling involves statistical sampling of model discrete systems, such as the primitive model and its variants or Lennard-Jones potentials, via Monte Carlo simulations. This approach has been used extensively to understand equilibrium double layers in modified Poisson-Boltzmann theories[18] and applied to transport in biological ion channels.[9,10] In the setting of ECs, reverse Monte Carlo simulations have been used to reconstruct the typical atomic structure of solvent and ions that best fits experimental X-ray diffraction structure factors (Figure 18). Grand canonical Monte Carlo simulations have also been used to study the structure of water in nanopores and the effect of introducing functional groups on the walls.[19] Although Monte Carlo methods are not as effective in describing dynamical phenomena, they can efficiently reveal statistical structure with reasonable computational expense.

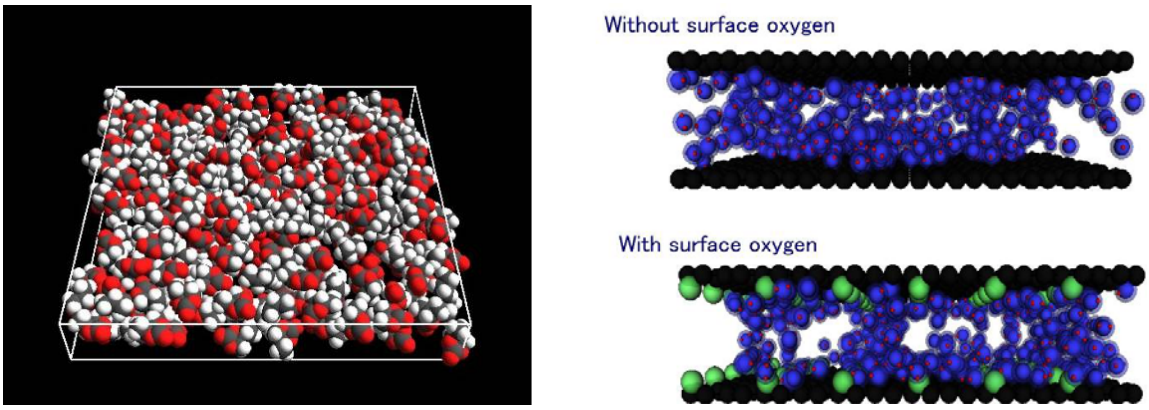

Figure 18. (Left) Atomic configuration of propylene carbonate in a carbon slit obtained by reverse Monte Carlo simulations from X-ray diffraction measurements on Maxsorb92-16 porous carbon with a surface area of 2440 m^2/g and a pore size of 1 nm (provided by K. Kaneka, unpublished, 2007). (Right) Grand canonical Monte Carlo simulations of water (TIP5 potential) confined in a flat slit of structureless carbon (10-4-3 potentials). The effect of surface oxygen is simulated by artificial functional groups described by a Lennard-Jones potential.[20]

Molecular dynamics simulations. MD simulations often provide the best balance between computational expense and accuracy in capturing atomic interactions. The method consists of integrating Newton's law for atoms described by point masses interacting through effective interatomic potentials (like balls and springs). It has been widely developed in many other fields, such as semiconductors and biophysics, but the greatest challenge for performing meaningful MD simulations is to derive accurate and reliable interatomic potentials,

validated against quantum-mechanical simulations (see below) or experiments, where possible. These validations must be done in the atomic environments of interest, such as the interior of a nanotube in contact with a particular organic solvent, because a potential often cannot be trusted to be transferable to a new set of configurations far from the domain where it was fitted.

To date, there have been no MD simulations of actual ECs, but some recent studies have begun to address fundamental issues arising from confinement in nanopores. For example, MD simulations have predicted anomalous solvation of ions and surprising water structures (such as hydrogen "wires") in carbon nanotubes.[11] A full-scale model of a carbon nanotube forest in an organic electrolyte has recently been studied to understand better new EC designs, including charging dynamics (Figure 19). Such simulations can provide crucial aid in the rational design of electrode and electrolyte materials for desired properties in ECs.

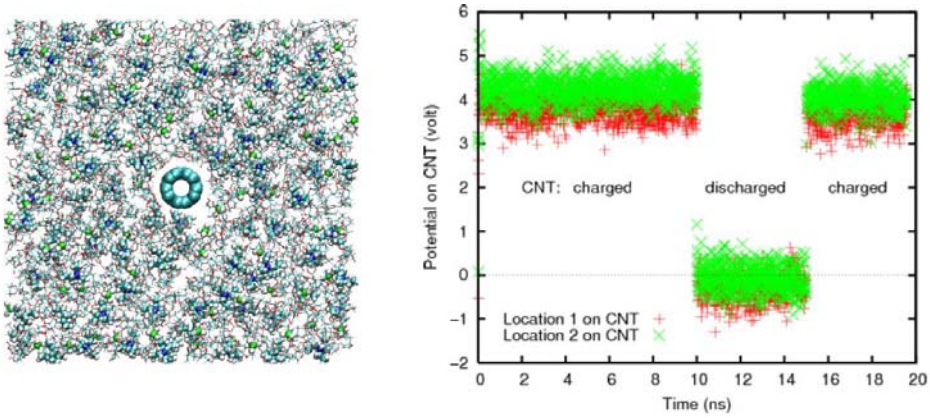

Figure 19. Molecular-dynamics simulations of an EC consisting of a periodic carbon nanotube forest in a common organic electrolyte (1 M TEA + BF4- in propylene carbonate). (Left) Initial molecular configuration. (Right) Time series of the carbon nanotube potential in response to a sudden change in surface charge, showing picosecond response. (Provided by L. Yang, B. Fishbine, and L. R. Pratt, unpublished, 2007.)

Finally, it will also be essential to develop ab initio quantum-mechanical simulations for ECs, since classical potentials cannot be expected to reliably predict interfacial forces, charge transfer (for pseudocapacitance), activation energy barriers for transport, desolvation or adsorption, etc. The challenge for ECs is in some ways much greater than for batteries, where ab initio methods based on DFT have had a major impact in predicting new lithium intercalation materials and bulk diffusion coefficients. The reason is that battery intercalation compounds, although complicated, have a regular bulk crystal structure that can be treated with periodic boundary conditions and a small number of atoms (<100). In contrast, disordered organic solvent molecules and ions in confined nanostructures require many more atoms and time dependence to evolve configurations for a proper description. Predictive quantum-mechanical simulations of such situations clearly present a long-term grand challenge for research. Perhaps the largest impact in the short term would be predicting the bulk properties of new candidate electrolytes to aid in their selection for use in ECs.

Modeling of Spectroscopic Methods

Novel characterization techniques can create complex signal outputs whose relation to the underlying structure or physical phenomena can benefit significantly from computational modeling. Electronic structure modeling has, for example, been particularly useful for interpreting nuclear magnetic resonance, infrared, Raman, or X-ray photoelectron spectroscopy spectra. It is expected that the novel spectroscopic methods that will be developed to characterize chemical systems with spatial and temporal resolution will push theoretical approaches to the limit and require the further development of more advanced approaches that treat more accurately the dynamical interaction between electrons (e.g., quantum Monte Carlo and other methods beyond DFT, such as the GW method, the Bethe-Salpeter equation, or dynamical mean field theory), and between the electrons and rapidly varying external potentials (e.g., time-dependent DFT).

Impact

Revolutionary advances in EES, which are needed to address future needs in energy storage, utilization, and regeneration, are not likely to occur without an aggressive investment in developing fundamental scientific understanding of the myriad processes that occur in these devices. There are tremendous opportunities for significant impact on this field from harnessing the powerful capabilities in modeling and theory. For example, with more accurate models, improved electrode nanostructures may be designed for attaining higher energy density without sacrificing power density. Fundamental new understanding at the atomistic level for highly charged double layers and transport in nanopores will also provide clues to improving the energy density or safety of EES by different (and sometimes unexpected) choices of electrode and electrolyte materials, as well as different choices of microstructured and nanostructured electrode architectures.

Many of the goals outlined are ambitious and will require sustained efforts in basic research to address. The stakes are high, however, because breakthroughs in the theoretical understanding of nanoscale phenomena and charging dynamics in EES systems can have an immediate and lasting impact, not only on EES technology through rational design and interpretation of experiments but also on the basic science of electrochemical systems and nanostructures. A century after the Gouy-Chapman-Stern model of the double layer was proposed, it is still by far the most widespread theoretical picture of the diffuse electrochemical double layer. If new research can develop more accurate, but still tractable, continuum models for nonlinear dynamics of double layer charging in the context of ECs, for example—taking into account steric, solvation, or correlation effects in confined spaces—then they would surely enter the base of knowledge in electrochemistry and permanently alter how the scientific community treats double layers and pores. Similarly, accurate atomistic models for MD of important new electrolytes or electrode materials would have lasting use. The same holds for quantum-mechanical methods, which may become more tractable and thus more widely applicable with advanced computers of the future.

References

1. M. Bervas et al., "Investigation of the lithiation and delithiation conversion mechanisms of bismuth fluoride nanocomposites," *Journal of the Electrochemical Society* **153**, A799–A808 (2006).
2. K. A. Striebel et al., "The effect of compression on natural graphite anode performance and matrix conductivity," *Journal of Power Sources* **134**(2), 241–251 (2004).
3. F. Zhou et al., "First-principles prediction of redox potentials in transition-metal compounds with LDA + U.," *Physical Review B* **70**, 235121 (2004).
4. C.-W. Wang, K. A. Cook, and A. M. Sastry, "Conduction in multiphase particulate fibrous networks simulations and experiments on Li-ion anodes," *Journal of the Electrochemical Society* **150**(3), A385–A397 (2003).
5. R. Kotz and M. Carlen, "Principles and applications of electrochemical capacitors," *Electrochimica Acta* **45**, 2483 (2000).
6. J. H. Jang, et al., "Complex capacitance analysis on leakage current appearing in electric double layer capacitor carbon electrode," *Journal of the Electrochemical Society* **152**, A1418 (2005).
7. M. Eikerling, A. A. Kornyshev, and E. Lust, "Optimized structure of nanoporous carbon-based double layer capacitors," *Journal of the Electrochemical Society* **152**, E24 (2005).
8. L. R. Pratt and A. Pohorille, "Modeling of aqueous solution interfaces in biophysics," *Chemical Reviews* (2002).
9. B. Nadler et al., "Diffusion through protein channels: From molecular description to continuum equations," *Nanotechnology* **3**, 439 (2003).
10. D. Gillespie and R. Roth, "Physics of size selectivity," *Physical Review Letters* **95**, 247801 (2005).
11. L. Yang, and G. Shekhar, "Modeling the selective partitioning of cations into negatively charged nanopores in water," *Journal of Chemical Physics* **126**, 084706 (2007).
12. C.-H. Yang, et al., "Nanowindow-regulated specific conductance of supercapacitor electrodes of single-wall carbon nanohorns," *Journal of the American Chemical Society Communications* **129**, 20 (2007).
13. J. Chmiola, et al., "Anomalous increase in carbon capacitance at pore sizes less than 1 nanometer," *Science* **313**, 1760 (2006).
14. K. T. Chu and M. Z. Bazant, "Electrochemical thin films at and above the classical limiting current," *Siam Journal on Applied Mathematics* **65**, 1485–1505 (2005).
15. T. Maxisch, F. Zhou, and G. Ceder, "Ab initio study of the migration of small polarons in olivine LixFePO4 and their association with lithium ions and vacancies," *Physical Review B* **73** (2006).
16. M. Z. Bazant, K. Thornton, and A. Ajdari, "Diffuse-charge dynamics in electrochemical systems," *Physical Review E* **70**, 021506 (2004).
17. K. T. Chu and M. Z. Bazant, "Nonlinear electrochemical relaxation around conductors," *Physical Review E* **74**, 011501 (2006).
18. M. S. Kilic, M. Z. Bazant, and A. Ajdari, "Steric effects on the dynamics of electrolytes at large applied voltages: I. Double layer capacitance," *Physical Review E* **75**, 021502 (2007).
19. T. Ohba, H. Kanoh, and K. Kaneko, "Structures and stability of water nanoclusters in hydrophobic nanospaces," *Nano Letters* **5**, 227–230 (2005).
20. T. Ohba and K. Kaneka, *Journal of Chemical Physics*, in press, 2007.