Large-Scale First-Principles Molecular Dynamics Simulations of Materials for Energy Conversion

Francois Gygi

University of California Davis, Davis, CA95616, USA

An accurate description of energy conversion mechanisms often requires atomic-scale models as well as the electronic structure of the materials under consideration. First-principles molecular dynamics (FPMD) provides a seamlessly coupled, consistent picture of both atomic structure and electronic structure. This approach is becoming increasingly popular for simulations of materials having complex structure, such as nanoparticles or interfaces. FPMD simulations are limited by the high computational cost of the underlying electronic structure computations, which are most often carried out using Density Functional Theory (DFT). In recent applications, the need for higher accuracy has motivated the use of hybrid-DFT approximations, which further increases the computational cost of simulations. We discuss the current limits and tradeoffs of feasible FPMD simulation, using examples of nanoparticles and solid-liquid interfaces relevant to solar energy conversion.

in situ Nanomechanics of Electrode Failure in Lithium-Ion Batteries

Ting Zhu, Shan Huang, Feifei Fan

Woodruff School of Mechanical Engineering Georgia Institute of Technology, Atlanta, GA 30332

Lithium-ion batteries revolutionize portable electronics and are key to next-generation electric vehicles. However, they usually suffer from the electrochemically induced mechanical degradation in high-capacity electrodes, resulting in quick capacity fading and poor cyclability. Using a unique nanobattery cell inside a transmission electron microscope, we made the in situ observations of reaction, deformation and fracture in individual nanowire and nanoparticle electrodes. A wide range of novel phenomena were discovered, including the size dependent fracture in silicon nanoparticles, anisotropic swelling in silicon nanowires, two-phase lithiation in amorphous silicon, nanoporosity formation in germanium nanowires, and cracking in the coating of tin oxide nanowires. We developed the continuum and atomistic models to reveal the mechanistic origin of stress generation and mechanical failure in these high-capacity electrode materials. The results provide insights into the microstructural evolution and mechanical degradation in nanobatteries. Our work has broad implications for designing durable electrodes in lithium-ion batteries.

A Multiscale Analysis of Ion Conductivity in Non-Equilibrium Environment

Jan Hamaekers, <u>Christian Neuen</u>

Fraunhofer SCAI, Germany

Batteries and (super-)capacitors function on the basis of ion migration between electrodes. Even today our society can hardly function without batteries as they enable the use of a variety of mobile electronic devices.

Despite many different approaches, there is still no full understanding of the contribution of counterions to the conductivity and transference numbers within the batteries cell. In particular, the electric voltage along the cell and its respective fluctuation move the system to a non-steady state.

For the prediction of material properties, we use molecular dynamics where the ensemble specifically takes into account the non-equilibrium state of the system induced by the presence of outer forces and treat the corresponding energy flow.

Even with the ensemble being able to handle a non-equilibrium ensemble, the normal evaluation of macroscopic properties cannot be trivially transferred from the equilibrium case and need to be adapted to account for the flux introduced.

The extended measurement of macroscopic variables then allows us to evaluate the performance on the cell level with an adaptive finite element solver to the time dependent, fully coupled Poisson-Nernst Planck equations in 2/3D. In this context special challenges appear with the strong non-linear coupling via the ions' electric field and the boundary conditions of both equation types.

We demonstrate results achieved with this method by predicting the ionic current flow in an alternating voltage setting in order to compute transference numbers.

Composition and catalytic activity of Au/Cu electrocatalytic nanoalloys in solution: A combination of DFT and accurate neural network potentials

Nongnuch Artrith, Alexie M. Kolpak

Department of Mechanical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139, USA

Heterogeneous catalytic chemical reactions are at the core of many energy and environment related challenges. The shape, size, and composition of catalyst nanoparticles can have a significant influence on catalytic activity. Understanding structure-reactivity relationship is crucial for the optimization of industrial catalysts and the design of novel catalysts with enhance properties. Recently, Shao-Horn, Hamand-Schifferli, et al. have shown that Au/Cu nanoparticles are stable and efficient electrocatalysts for the reduction of CO_2 [1]. We employ a combination of first-principles computations and large-scale Monte-Carlo simulations with highly accurate neural network (NN) potentials to study the equilibrium surface structure and composition of bimetallic Au/Cu nanoparticles (NPs), which have recently been of interest as stable and efficient CO_2 reduction catalysts. We demonstrate that the inclusion of explicit water molecules at a first-principles level of accuracy is necessary to predict experimentally observed trends in Au/Cu NP surface composition; in particular, we find that Au-coated core-shell NPs are thermodynamically favored in vacuum, independent of Au/Cu chemical potential and NP size, while NPs with mixed Au-Cu surfaces are preferred in aqueous solution. Furthermore, we show that both CO and O_2 adsorption energies differ significantly for NPs with the equilibrium surface composition found in water and those with the equilibrium surface composition found in vacuum, suggesting large changes in CO_2 reduction activity. Our results emphasize the importance of understanding and being able to predict the effects of catalytic environment on catalyst structure and activity. In addition, they demonstrate that first-principles-based NN potentials provide a promising approach for accurately investigating the relationships between solvent, surface composition and morphology, surface electronic structure, and catalytic activity in systems composed of thousands of atoms [2].

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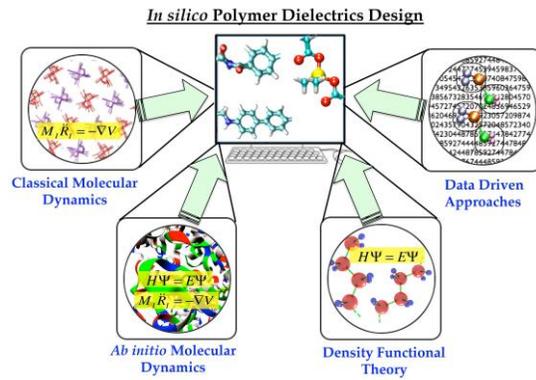[2] N. Artrith, and A. M. Kolpak, submitted (2014).

A Multiscale Design Strategy for Advance Polymer Dielectrics

Ghanshyam Pilania[1], Chenchen Wang[2], R. Ramprasad[2]

[1]Materials Science and Technology Division, Los Alamos National Laboratory, NM 87545 USA

[2]Department of Materials Science and Engineering, University of Connecticut, CT 06269 USA

High energy density capacitors are required for several pulsed power and energy storage applications, including food preservation, nuclear test simulations, electric propulsion of ships and hybrid electric vehicles. The maximum electrostatic energy that can be stored in a capacitor dielectric is proportional to its dielectric constant and the square of its breakdown field. The current standard material for capacitive energy storage is polypropylene which has a large breakdown field but low dielectric constant. We are involved in a search for new classes of polymers superior to polypropylene using first principles computations combined with coarse grain molecular dynamics, effective medium theory and machine learning methods [1]. Essential to this search are schemes to efficiently compute the dielectric constant of polymers and the intrinsic dielectric breakdown field, as well as methods to determine the stable structures of new classes of polymers and strategies to efficiently navigate through the polymer chemical space offered by the periodic table. These methodologies have been combined with statistical learning paradigms in order to make property predictions rapidly, and promising classes of polymeric systems for energy storage applications have been identified. Some of the polymer polymers predicted using our computational methodology have recently been synthesized and have been shown to have improved dielectric properties over conventional polymer dielectrics [2].

Figure 1: Various components that were used in our computational design strategy for advance polymer dielectrics.

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Unveiling role of salt in Li-ion transfer through boundary between SEI and liquid electrolyte in Li-ion battery: a multi-thousand-atom DFT study

Shuji Ogata,[1] Nobuko Ohba[2], Takahisa Kouno[3]

[1]Graduate School of Engineering, Nagoya Institute of Technology, Japan
[2]Toyota Central Research & Development Laboratories, Inc., Japan
[3]Institute for Solid State Physics, The University of Tokyo, Japan

The solid-electrolytes interphase (SEI), formed on the graphite anode at the first charging, plays essential roles in currently used Li-ion batteries (LIBs). The SEI transfers Li-ions but blocks electron current, and works to prevent further decomposition of the electrolyte. The desolvation and solvation processes of the Li-ion at the interface between the SEI and liquid electrolyte are crucial to determine the throughput rate or power of the LIB. Large-scale, first-principles molecular dynamics (FPMD) simulation of the desolvation/solvation processes is therefore highly desired. The electronic density-functional theory (DFT) is suited well for the FPMD simulation of such dynamics due to its balance between physical accuracy and computation speed. The real-space grid based implementation of the DFT (RGDFT) that uses the finite difference method for derivatives of variables, has attractive features of parallelizability and applicability to various boundary conditions in addition to universality in target materials. Taking the divide-and-conquer strategy we have recently proposed the linear-scaling, divide-and-conquer-type real-space grid DFT code (DC-RGDFT) [1] to further speedup the FPMD simulation.

In this research, we apply the DC-RGDFT to investigate the microscopic mechanisms of the Li-ion transfer through the boundary between the SEI and liquid electrolyte in the LIB by the FPMD simulation [2]. A relatively large simulation system (about 2400 atoms) for the boundary is modeled using di-lithium ethylene di-carbonate (Li_2EDC), ethylene carbonate (EC), and $LiPF_6$ for the SEI, solvent, and salt, respectively. After inserting Li-ions in the Li_2EDC region, we perform the FPMD simulation for several ps using the DC-RGDFT. In the cases without salt, we find enhanced stability of the Li-ion at the EDC-EC boundary where both EDC and EC molecules bind to the Li-ion, which acts to impede the Li-ion transfer through the boundary. In regard to impedance for the Li-ions, the EDC-EC boundary, which is in reality only about 4 Å in depth, can be regarded as effectively 12-20 Å in depth of bulk EDC. In the case with 1.0 M $LiPF_6$ salt included in liquid EC, we find that the Li-ion transfer rate through the EDC-EC boundary becomes about twice as high as that in the case without salt. Separate DFT calculations about the reaction energy profiles of small model systems clarify that the energy required to detach a Li-ion from the boundary decreases to 0.9 eV from 1.7 eV if PF_6^- exists. The lowering in the detaching energy of the Li-ion results from weakening of the interaction between the Li-ion and EDC due to strong binding of PF_6^- to the Li-ion at the boundary. The temperature dependence of the Li-ion transfer rate is analyzed also.

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Unlocking the potential of cation-disordered oxides for lithium batteries

Alexander Urban, Jinhyuk Lee, Xin Li, and Gerbrand Ceder

Department of Materials Science and Engineering,
Massachusetts Institute of technology, Cambridge, MA 02139, USA

Ordered lithium metal oxides, especially layered oxides such as lithium cobalt oxide, are the most important class of cathode materials for lithium-ion batteries in consumer electronics. The well-orderedness of these oxides, e.g., the segregation of lithium and metal cations into distinct layers, is commonly regarded as essential for sufficient lithium mobility, and cation mixing has been observed to result in deteriorating lithium extraction and re-intercalation capacity. During the past decades much scientific effort has therefore been geared towards the engineering of novel perfectly ordered cathode materials.
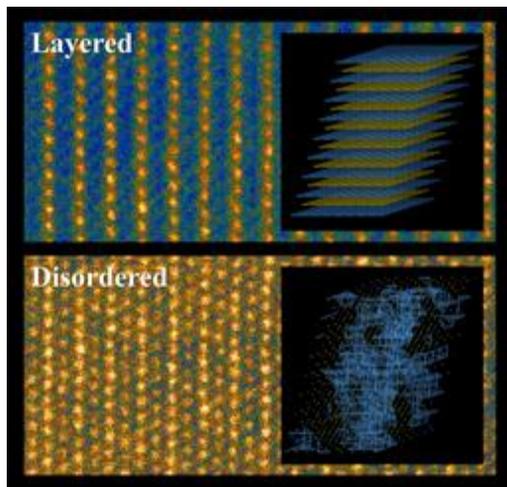
Figure 1: STEM image of layered (top) and cation-disordered (bottom) LMCO. The insets show the 3-d structure of the layered oxide (top) and the percolating network of lithium diffusion channels in the disordered oxide (bottom).

In contrast to these established believes we recently found that cation-disordered lithium-excess molybdenum chromium oxide (LMCO) provides a very high reversible electrochemical capacity. Using a combination of first-principles electronic structure calculations and large-scale Monte-Carlo simulations of lithium percolation we are not only able to explain the good performance of LMCO, we can also point out under which conditions cation-disordered lithium-excess materials are likely to exhibit high capacity. This fundamental understanding of lithium diffusion and percolation in lithium metal oxides will open up an entirely new compound space for the search for better lithium-ion battery materials.

[1] J. Lee, A. Urban, X. Li, D. Su, G. Hautier, and G. Ceder, Unlocking the potential of cation-disordered oxides for rechargeable lithium batteries, Science 343 (2014) 519-522.

Ab-initio-based Cluster Expansion Study of the Phase Transformation and Voltage Fade of the Layered Li$_x$MnO$_3$

Eunseok Lee and Kristin A. Persson

Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

Li$_2$MnO$_3$ is believed to be a key material to determine the properties of the 'Li-excess' composite materials, which are attracting attention as promising cathode materials for Li-ion batteries. The material is intriguing as it shows electrochemical activity even though the oxidation state of Mn is already Mn4+. Although several previous studies point to oxygen release, conversion reactions and peroxide formation as possible oxidation mechanisms, none of them has been clarified. In addition, the material experiences the phase transformation from the layer structure to the spinel-like structure during the cycles of lithiation/delithiation. Despite the significant effects of phase transformation on the structural stability and electrochemical performance, the mechanism of the phase transformation has yet been revealed.

In this talk, we present our computational work on the electrochemical activity and structural stability of stoichiometric Li$_x$MnO$_3$ ($0 \leq x \leq 2$). The ternary cluster expansion method is used to describe the thermodynamic stability of Li$_x$MnO$_3$ and the elastic band method is used to calculate the activation energy barrier of electrochemical kinetics in Li$_x$MnO$_3$. We observe that the Li$_2$MnO$_3$ structure is electrochemically active on delithiation and that charge neutrality during the delithiation is maintained by the oxidization of a fraction of the oxygen ions. Furthermore, we also observe that Mn-migration to the Li layer is thermodynamically and kinetically favorable at lower Li content, indicating a tendency towards the spinel structure transformation. Based on our observations, we propose a path of phase transformation from the layered structure to spinel-like structure and explain the mechanism of voltage fade. Oxygen stability is also discussed.