

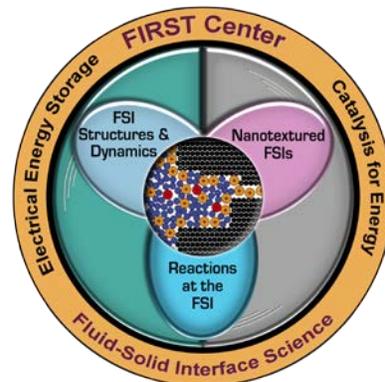
## FIRST Center Research Perspective:

### *Structure and Dynamics of Electrical Double Layer Using Integrated Scanning Probe Microscopy and Molecular Simulations*

Jennifer M. Black, Thomas Arruda, Pasquale F. Fulvio, Patrick C. Hillesheim, Sheng Dai, Sergei V. Kalinin, Nina Balke  
Oak Ridge National Laboratory (ORNL)

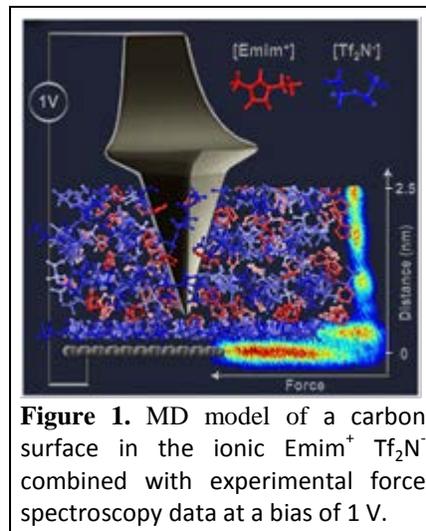
Guang Feng, Peter T. Cummings  
Vanderbilt University

Min Heon, Volker Presser, Jake K. McDonough, Yury Gogotsi  
Drexel University



**Research Summary:** We are using scanning probe microscopy (SPM) to study charge storage in electrochemical double layer capacitors (EDLCs). Force spectroscopy probes the electrical double layer (EDL) structure. Molecular dynamics (MD) simulations were used to predict ion density profiles at the carbon/ionic liquid interface and provide the spacing between the electrode surface and ion layers which could be verified experimentally (**Figure 1**). Reconfiguration of ions within the electrical double layer could be observed in response to an applied bias. Under applied potential the electrode charge is screened within  $\sim 1$  nm of the electrode surface and only ion layering within this distance is significantly affected by an applied potential.

Electrochemical Strain Microscopy (ESM), an SPM methodology developed at ORNL with FIRST Center support (see Research Perspective by Balke and Kalinin), was adapted to measure the expansion/contraction of EDLC electrodes *in-situ* caused by potential driven ion insertion/expulsion, providing a non-current based method of investigating ion insertion kinetics (**Figure 2**). The scanning probe technique was designed following macroscopic dilatometry studies of the expansion of carbon materials.[1, 2] An advantage of the scanning probe technique is the impressive  $z$  resolution ( $< 1$  nm) and lateral resolution ( $\sim 10$  nm), which is unmatched by other techniques. This technique was used to investigate microporous and mesoporous carbons, demonstrating the effect of pore size on the ion insertion kinetics, and allowing for the anion and cation insertion processes to be separated.[3, 4] For the first time molecular dynamics was used to predict the pressure exerted on pore walls filled with ionic liquid electrolytes under applied potential, offering insights into the molecular origin of strain observed experimentally in electrochemical capacitor electrodes.

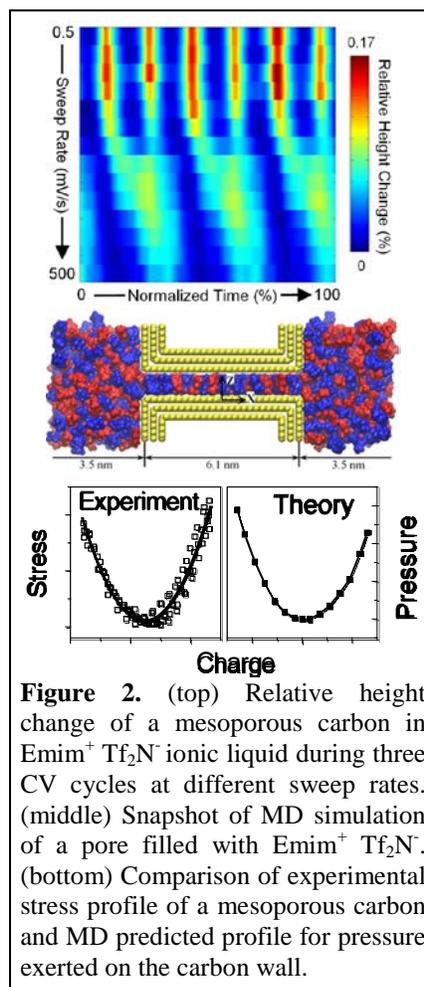


**Figure 1.** MD model of a carbon surface in the ionic Emim<sup>+</sup> Tf<sub>2</sub>N<sup>-</sup> combined with experimental force spectroscopy data at a bias of 1 V.

**Technical Details:** Ionic liquids form an alternating structure of anion/cation layers at the solid/liquid interface. As an AFM tip approaches the surface it detects forces as it moves through

the dense ion layers. We have investigated the bias-dependent structure of the electrical double layer formed at a highly oriented pyrolytic graphite/ionic liquid ( $\text{Emim}^+ \text{Tf}_2\text{N}^-$ ) interface using force spectroscopy.[5] Subnanometer ion layer spacings were observed experimentally and compared to ion density calculations using MD simulations and an excellent agreement between the two methods was observed (**Figure 1**). At the potential of zero charge (PZC), MD calculations predict that the first ion layer adjacent to the surface consists of cations and anions both parallel and perpendicular to the electrode surface, and both of these molecular orientations could be detected with force spectroscopy. At  $\pm 1$  V the addition of Coulombic forces results in a preferred ion orientation parallel to the electrode surface. The calculated ion–electrode distances match the distances extracted from the force distance curves. Beyond  $\sim 1.0$  nm, the charge on the electrode is almost completely screened, which implies that the charged electrode primarily affects the ions within 1.0 nm. Beyond the first ion layer, the ions show a layered structure without a preferred orientation and a characteristic anion–anion and cation–cation spacing of around 0.7 nm similar to the bulk properties of the ionic liquid. Through the integration of experiment and theory a comprehensive picture of the EDL structure at various applied potentials was achieved improving our understanding of charge storage in EDLC's on a molecular level.

During charge/discharge of porous carbon electrodes ions move in and out of the pores resulting in miniscule volume changes. We developed an SPM method to monitor the volume changes *in-situ* under electrochemical control, providing a non-current based method of investigating the kinetics of the insertion/deinsertion of ions into porous carbons.[3, 4] The volume changes of carbons having different surface areas and pore size distributions were examined to investigate the effect of pore size on electrode strain and ion kinetics in  $\text{Emim}^+ \text{Tf}_2\text{N}^-$  ionic liquid electrolyte.[4] The cation and anion insertion processes could be separated and the kinetics of each examined. It was revealed that both anion and cation kinetics were hindered in the carbon with the smallest pore size, and the anion kinetics were slower than that of the cation for each carbon tested. MD simulations were performed to compare with and provide molecular insights into the electrode expansion observed experimentally under applied potential (**Figure 2**). This was the first MD work investigating the pressure exerted on porous electrodes under applied potential in an ionic liquid electrolyte. The shape of the calculated pressure profile matches closely with the strain profiles observed experimentally. With this fundamental understanding of the mechanisms of charging and strain generating process, it will be possible to design materials and electrodes with optimized structures in order to minimize electrode expansion while maintaining the highest possible energy and power densities.



**Figure 2.** (top) Relative height change of a mesoporous carbon in  $\text{Emim}^+ \text{Tf}_2\text{N}^-$  ionic liquid during three CV cycles at different sweep rates. (middle) Snapshot of MD simulation of a pore filled with  $\text{Emim}^+ \text{Tf}_2\text{N}^-$ . (bottom) Comparison of experimental stress profile of a mesoporous carbon and MD predicted profile for pressure exerted on the carbon wall.

**Significant Impacts on Science and Technology:** Electrochemical double layer capacitors (EDLC's) are a vital component of today's energy storage systems and are capable of very high power density. A recent approach to improving the energy density of these devices is to use ionic liquid electrolytes, however there lacks a fundamental understanding of the charge storage mechanism in these electrolytes, including the structure of the electrical double layer and how it evolves with potential, as well as the ion kinetics during charge/discharge. Predictive understanding of the charge storage in ionic liquid/carbon systems may lead to improved materials/devices with optimized performance. Our scanning probe microscopy studies help shed light on the charge storage of EDLC electrodes in ionic liquid electrolytes. Combining force spectroscopy results with insights from molecular dynamics (MD) simulations provides a comprehensive picture of the electrical double layer (EDL) structure for uncharged and charged carbon in an ionic liquid electrolyte. In the future the use of a 3-electrode cell will allow for investigation of the dynamics of the EDL structure under potential control. A new scanning probe microscopy technique was developed to measure electrode expansion/contraction caused by potential-driven ion insertion/expulsion with very high spatial resolution. Monitoring the electrode volume using this technique allows the kinetics of the ion insertion process to be investigated using a non-current based technique. For the first time, all-atom molecular dynamics simulations were used to relate the pressure exerted on pore walls to the expansion/contraction of porous carbon electrodes during non-redox charge/discharge cycling. MD calculations offer insights into the molecular origins of strain observed experimentally in electrochemical capacitor electrodes.

***Publications and Manuscripts:***

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