

## FIRST Center Research Perspective:

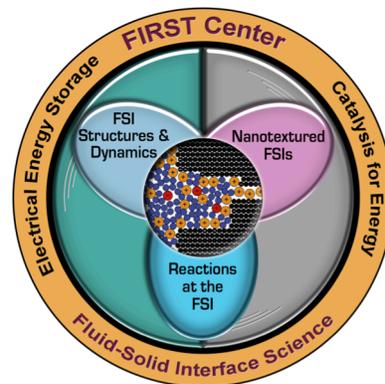
### *Integrated X-ray Reflectivity and Modeling Studies of Electrolyte Structures and Dynamics at Charged and Uncharged Planar Surfaces*

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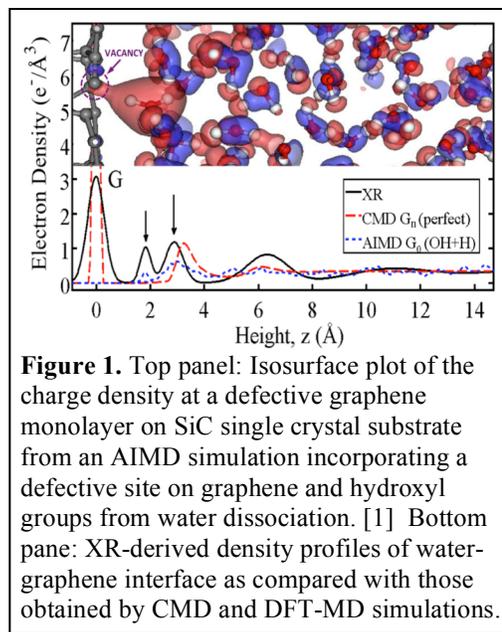
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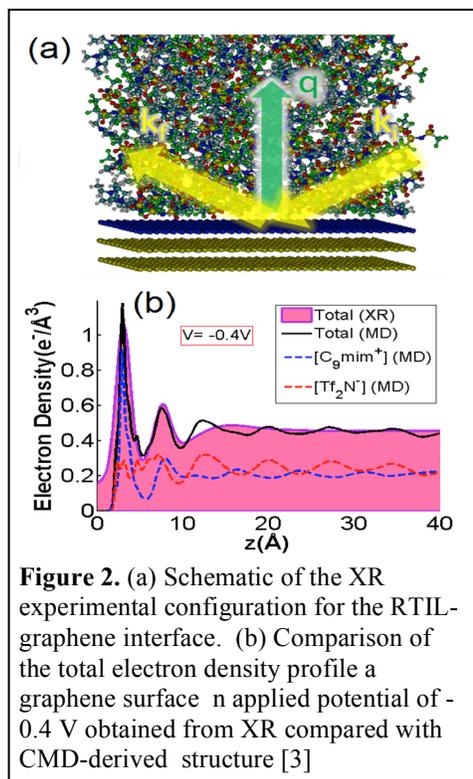
**Research Summary:** The study of planar fluid-solid interfaces provides a unique opportunity to test the models and theories that describe the fundamental interactions governing energy storage devices. We have used high resolution *in situ*, X-ray reflectivity (XR) combined with classical molecular dynamics (CMD) and *ab initio* molecular dynamics (AIMD) simulations to understand the nanoscale structure of water and room temperature ionic liquids (RTILs) at charged and uncharged epitaxial graphene (EG) surfaces grown on silicon carbide single crystal substrates. Through these studies, we observed experimentally that the epitaxial buffer layer of EG is more hydrophilic than the subsequent layers (**Figure 1**). These differences could be explained, with coordinated AIMD and CMD calculations, based on the interaction of water with graphene defect sites [1] and the interaction of the graphene buffer layer with the SiC substrate. Our studies on RTILs in contact with charged surfaces (**Figure 2**) revealed RTIL charge over-screening [2] consistent with the predictions of recent theories that incorporate ion correlation effects. Additional studies of RTILs at potential-controlled graphene surfaces showed that the RTIL structure exhibit distinct structures at negative and positive potentials, with oppositely-polarized anion-cation layering [3]. Real-time studies of the RTIL structure under potential control (**Figure 3**) reveal two surprising observations: switching between these distinct extreme potential structures happen unexpectedly slowly [3]; and, the interfacial RTIL structure exhibits hysteretic behavior during cyclic voltammetry [3]. Significantly, slower scan rates *increase* the magnitude of the observed hysteresis, suggesting that it originates from a potential barrier



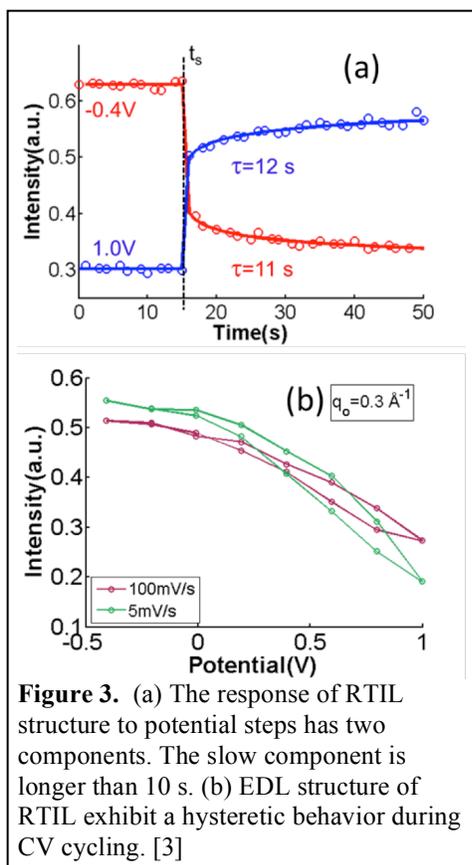
**Figure 1.** Top panel: Isosurface plot of the charge density at a defective graphene monolayer on SiC single crystal substrate from an AIMD simulation incorporating a defective site on graphene and hydroxyl groups from water dissociation. [1] Bottom panel: XR-derived density profiles of water-graphene interface as compared with those obtained by CMD and DFT-MD simulations.

between the two distinct layered structures observed at the positive and negative static potentials.

**Technical Details:** These studies require the close coordination within the FIRST team. The XR experiments are conducted at the Advanced Photon Source at ANL. CMD and AIMD studies are done by the Vanderbilt and the ORNL groups. The RTILs used in experiments are synthesized by the ORNL group and the EG substrates are supplied by the Drexel group. XR is the preeminent experimental tool to obtain sub-nanometer resolution structural information about solid/liquid interfaces. The specular reflectivity signal is measured as a function of the momentum transfer ( $Q$ ) in specular geometry (**Figure 2a**). The laterally averaged EG and EDL structures (i.e., as a function of height) are obtained from the experimental XR data. Our studies have explored three types of carbon electrolyte interfaces: the EG/water interface [1], static RTIL structures on uncharged [2] and charged EG [3], and the dynamic RTIL structure on EG during cyclic voltammetry and potential step measurements [3]. Our recent work has demonstrated novel and inter-related observations: 1) the static RTIL



**Figure 2.** (a) Schematic of the XR experimental configuration for the RTIL-graphene interface. (b) Comparison of the total electron density profile at a graphene surface at an applied potential of -0.4 V obtained from XR compared with CMD-derived structure [3]



**Figure 3.** (a) The response of RTIL structure to potential steps has two components. The slow component is longer than 10 s. (b) EDL structure of RTIL exhibit a hysteretic behavior during CV cycling. [3]

structure at high and low potentials are distinct and due to cation/anion separated layers distributed above the ion surface, based on both X-ray reflectivity data and molecular dynamics simulations; 2) the potential dependent RTIL structure exhibits hysteresis during cyclic voltammetry (CV) scans (at scan rates of 5-100 mV/sec); and 3) the RTIL interfacial structure shows both fast ( $\ll 1$  sec) and slow ( $\sim 11$  sec) relaxation times after rapid voltage steps (e.g., from -1 V to +0.4 V). Measurements of X-ray reflectivity data as a function of time,  $R(Q,t)$ , during CV scans reveals that the RTIL structure and its hysteresis can be conceptualized as due to the coexistence of two distinct structures corresponding to the high (+) and low (-) voltage structures, in which the hysteresis is due to the fractional occupations of the extreme potential structures (n<sup>+</sup> vs. n<sup>-</sup>) [4]. This picture of an apparently bistability in the RTIL structure has been confirmed through molecular dynamics (MD) simulations. The source of the unexpectedly long relaxation times remains mysterious (although it has been seen previously by other spectroscopic probes) and a topic of current investigation.

**Significant Impacts on Science and Technology:** Our integrated modeling, simulation, and experimental

investigations of the molecular-scale structure of the electrolyte-graphene interface has provided unique insights and validates our understanding of the fundamental interactions of carbon-electrolyte interfaces. This is a broad cross-cutting area of study in FIRST. More generally, the interaction of RTIL electrolytes with nano-structured graphitic electrodes is foundational to their development as a promising solution to high power density forms of energy storage (i.e., as supercapacitors). The unexpected slow and hysteretic response that we observed illustrates that there are significant gaps in our understanding in these systems. Nevertheless, the excellent agreement that we have achieved between experiments and modelling illustrates a powerful approach for connecting the macroscopic electrochemical properties to the nanoscale structure at the RTIL electrolyte/electrode interfaces.

### ***Publications and Manuscripts:***

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2. Zhou, H.; Rouha, M.; Feng, G.; Lee, S. S.; Docherty, H.; Fenter, P.; Cummings, P. T.; Fulvio, P. F.; Dai, S.; McDonough, J.; Gogotsi, Y. Nanoscale perturbations of room temperature ionic liquid structure at charged and uncharged interfaces. *ACS Nano*, 6, 9818. **(2012)**.
3. Uysal, A.; Zhou H.; Feng G.; Lee, S. S.; Li, S.; Fenter, P.; Cummings, P. T.; Fulvio, P. F.; Dai, S.; McDonough, J.; Gogotsi, Y. Structural Origins of Potential Dependent Hysteresis at the Electrified Graphene/Ionic Liquid Interface. *J. Phys. Chem. C*, 118, 569. **(2014)**.
4. Uysal, A.; Zhou H.; Feng G.; Lee, S. S.; Li, S.; Fenter, P.; Cummings, P. T.; Fulvio, P. F.; Dai, S.; McDonough, J.; Gogotsi, Y. Potential and temperature dependent changes in room temperature ionic liquid structure at epitaxial graphene interface, *in preperation*.