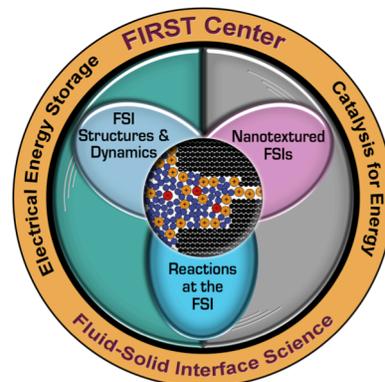


FIRST Center Research Perspective:

Structural and Dynamic Properties of Room Temperature Ionic Liquids Confined within Hierarchical Porous Materials

José Leobardo Bañuelos, Pasquale F. Fulvio, Gernot Rother, Sheng Dai, David J. Wesolowski
Oak Ridge National Laboratory (ORNL)

Guang Feng, Song Li, Peter Cummings
Vanderbilt University



Research Summary: The effects of nanotextured interfaces and confinement on room temperature ionic liquid (RTIL) structure and dynamics were determined by integrating small angle X-ray scattering (SAXS), small angle neutron scattering (SANS), neutron spin echo (NSE), and classical molecular dynamics (MD) simulations in the study of imidazolium- and pyrrolidinium-based ionic liquids confined within hierarchical mesoporous carbon and silica substrates. Confinement within mesoporous carbons results in significantly higher densities than bulk RTIL, whereas lower than bulk RTIL densities are found in mesoporous silicas. We find a pronounced slowing of the overall collective dynamics, including the presence of an effectively immobilized fraction of RTIL with dynamics several orders of magnitude slower than the bulk along the pore walls.

Technical Details: Small-angle scattering is a powerful tool that provides structural information on the subnanometer to several hundred nanometer length scales and was used here to measure how RTIL density changes within a mesoporous carbon network. Our team has developed new hierarchical porous carbon materials [1] that are of great interest for electric double layer capacitor (EDLC) applications. The structural properties of the RTIL 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[\text{C}_4\text{mim}^+][\text{Tf}_2\text{N}^-]$) confined in such materials were investigated by SAXS (at the Center for Nanophase Materials Sciences, ORNL) and SANS (at the Spallation Neutron Source, ORNL) and the experimental measurements were combined with MD simulations. Our integrated results of $[\text{C}_4\text{mim}^+][\text{Tf}_2\text{N}^-]$ confined in nanometer-scale carbon pores reveal densities that are > 3

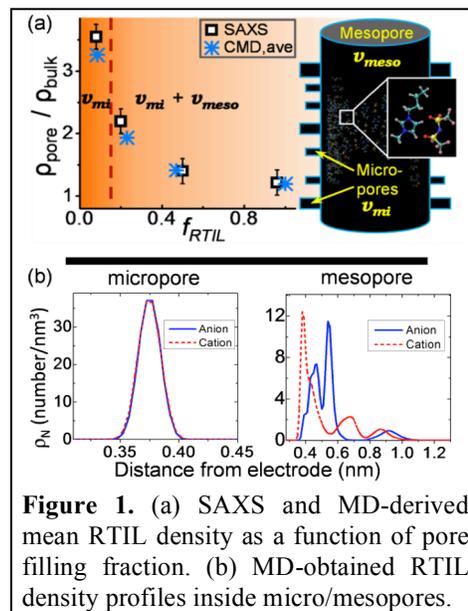


Figure 1. (a) SAXS and MD-derived mean RTIL density as a function of pore filling fraction. (b) MD-obtained RTIL density profiles inside micro/mesopores.

times higher (**Figure 1**) than that of the bulk liquid.[2] This densification results from the strong affinity of the RTIL cation with the carbon surface during the initial filling of slit-like, 0.75 nm micropores along the 7.8 nm cylindrical mesopore surfaces. Subsequent filling of the mesopore volume is accompanied by weak RTIL densification. The close proximity of the slit pore walls gives rise to a high RTIL-wall interaction potential that is strong enough to modify the RTIL ion coordination structure, resulting in less coordinated ions inside the micropores than in the bulk fluid and a low-excluded volume, high RTIL ion density configuration.

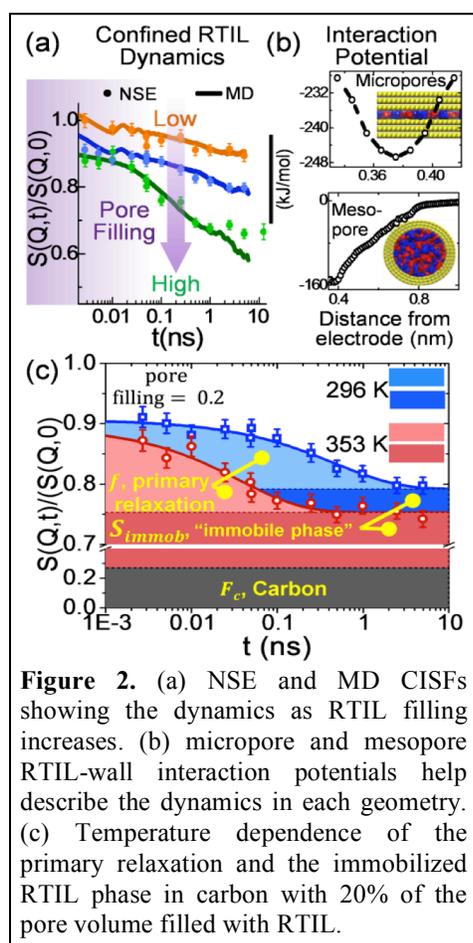


Figure 2. (a) NSE and MD CIFSs showing the dynamics as RTIL filling increases. (b) micropore and mesopore RTIL-wall interaction potentials help describe the dynamics in each geometry. (c) Temperature dependence of the primary relaxation and the immobilized RTIL phase in carbon with 20% of the pore volume filled with RTIL.

MD simulations predicted that the two different confining environments, namely the mesopore vs. micropore confinement, should each have a significant effect on the dynamic properties of this RTIL. In this direction, NSE allows measuring the coherent dynamics arising from spatially correlated groups in a system's structure and is a powerful tool for studying the dynamic properties of fluids under nanoconfinement. NSE may probe dynamics on time scales of a few picoseconds to several hundred nanoseconds and because the time-dependence is obtained directly in the normalized coherent intermediate scattering function (CISF), the CISF obtained from MD simulations may be computed for a direct comparison with experiment. NSE experiments and MD simulations [3] were used to investigate the dynamics of $[C_4mim^+][Tf_2N^-]$ confined in 5.8 nm-size mesoporous carbon, and in the same carbon material (**Figure 2a**) used in the aforementioned structural study. Both NSE and MD reveal a pronounced slowing of the overall collective dynamics, including the presence of an immobilized fraction of RTIL at the pore wall, whose characteristic decay time is estimated to be on the 100 ns time scale (**Figure 2c**). A fraction of the dynamics, corresponding to RTIL inside of 0.75 nm micropores located along the mesopore surfaces, are approximately two times faster than those of RTIL in direct contact with the walls of 5.8 nm and 7.8 nm cylindrical mesopores; this behavior is ascribed to differences in the ion-pore interaction potentials between the micropore and mesopore confinement geometries (**Figure 2b**). The strong micropore-RTIL interactions result in RTIL that is less coordinated within the micropores than its bulk counterpart. Increasing temperature from 296 K to 353 K reduces the immobilized RTIL fraction and results in nearly an order of magnitude increase in the RTIL dynamics (**Figure 2c**).

We systematically investigated the structural effects of confinement on the RTIL $[C_{10}MPy^+][Tf_2N^-]$ as a function of pore size and surface topology, composition (silica vs. carbon), and temperature using SANS and MD simulations. [4] We previously showed that intermediate range ordering (IRO) within the $[C_nMPy^+][Tf_2N^-]$ family of RTILs (where n is the alkyl chain length) scales with increased alkyl chain length; the length scale for the $[C_{10}MPy^+][Tf_2N^-]$ IRO is ~ 2.2 nm. [5] We find that the RTIL mean density is higher in carbon materials and lower in silica materials compared to the bulk density, and that the density approaches the bulk value as the size of confinement increases (**Figure 3**). The observed effects are likely due to the differences in the RTIL interaction strength

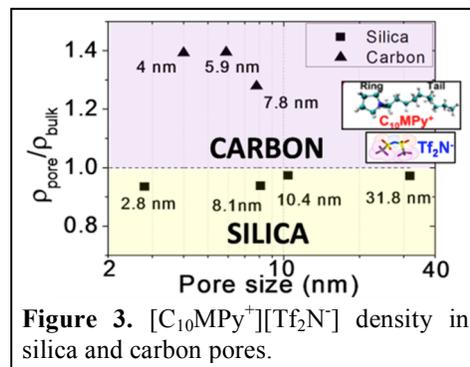


Figure 3. $[C_{10}MPy^+][Tf_2N^-]$ density in silica and carbon pores.

with the pore walls of the silica and carbon mesopores as has been observed for a different RTIL. [6] The ps- to ns- collective dynamics of $[C_{10}MPy^+][Tf_2N^-]$ in the bulk state and confined in 2.8 nm and 8.1 nm silica pores were investigated using NSE [7] at several length scales and temperatures. MD simulations could help determine whether the slower dynamics observed under confinement are due to the slow RTIL dynamics over the entire pore space, or if there are identifiable RTIL-pore-wall vs. RTIL-pore-center dynamics.

Significant Impacts on Science and Technology: Through our integrated SAXS, SANS, NSE, and MD simulation efforts we extracted quantitative information on the structure and dynamics of RTIL electrolytes confined inside structurally complex porous materials. Our observations highlight the importance of including the effects of a porous substrate's internal surface morphology, especially roughness and microporosity, on the resulting electrolyte structural properties and performance in electrical energy storage applications. This work provides experimental verification to recent work aimed at understanding ion/pore size/geometric effects in carbon supercapacitor systems, and at describing the complex features of RTILs near surfaces, including the extent to which RTIL dissociation may occur. The current observations shed light on how high the electrical double layer capacitance could be achieved in hierarchical microporous-mesoporous carbons for use in energy storage devices. These findings may help explain why desirable properties in supercapacitors are obtained when pore size is chosen carefully with respect to a given electrolyte.

Publications and Manuscripts:

1. Zhai, Y.; Dou, Y.; Zhao, D.; Fulvio, P. F.; Mayes, R. T.; Dai, S. Carbon Materials for Chemical Capacitive Energy Storage. *Adv. Mater.* **2011**, *23* (42), 4828-4850.
2. Bañuelos, J. L.; Feng, G.; Fulvio, P. F.; Li, S.; Rother, G.; Dai, S.; Cummings, P. T.; Wesolowski, D. J. Densification of Ionic Liquid Molecules within a Hierarchical Nanoporous Carbon Structure Revealed by Small-Angle Scattering and Molecular Dynamics Simulation. *Chem. Mater.* **2013**, **10.1021/cm4035159**.
3. Banuelos, J. L.; Feng, G.; Fulvio, P. F.; Li, S.; Rother, G.; Arend, N.; Faraone, A.; Dai, S.; Cummings, P. T.; Wesolowski, D. J. Coherent Dynamics of a Room Temperature Ionic Liquid Confined within Hierarchical Porous Carbon: A Neutron Spin Echo and Atomistic Simulation Study. *Carbon* **2014**, **In Review**.
4. Banuelos, J. L.; Li, S.; Feng, G.; Fulvio, P. F.; Do, C.; Rother, G.; Cummings, P. T.; Dai, S.; Wesolowski, D. J. Pore size, Composition, and Temperature Effects on the Structure of a Confined Long-Chain Pyrrolidinium-Based Ionic Liquid. **2014**, **in preparation**.
5. Li, S.; Bañuelos, J. L.; Guo, J.; Anovitz, L. M.; Rother, G.; Shaw, R. W.; Hillesheim, P. C.; Dai, S.; Baker, G. A.; Cummings, P. T. Alkyl Chain Length and Temperature Effects on Structural Properties of Pyrrolidinium-based Ionic Liquids: a Combined Atomistic Simulation and Small Angle X-ray Scattering Study. *J. Phys. Chem. Lett.* **2011**, *3* (1), 125-130.
6. Li, S.; Han, K. S.; Feng, G.; Hagaman, E. W.; Vlcek, L.; Cummings, P. T. Dynamic and Structural Properties of Room-Temperature Ionic Liquids near Silica and Carbon Surfaces. *Langmuir* **2013**, *29* (31), 9744-9749.
7. Banuelos, J. L.; Li, S.; Feng, G.; Fulvio, P. F.; Faraone, A.; Rother, G.; Cummings, P. T.; Dai, S.; Wesolowski, D. J. Nanoconfinement-Induced Perturbations of the Molecular-Scale Collective Dynamics of a Pyrrolidinium-Based Ionic Liquid. **2014**, **in preparation**.