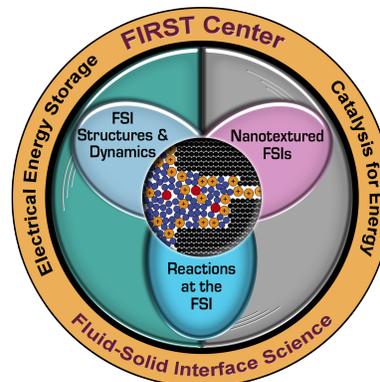


## FIRST Center Research Perspective:

### *Molecular Insights into Carbon Supercapacitors Based on Room-Temperature Ionic Liquids*

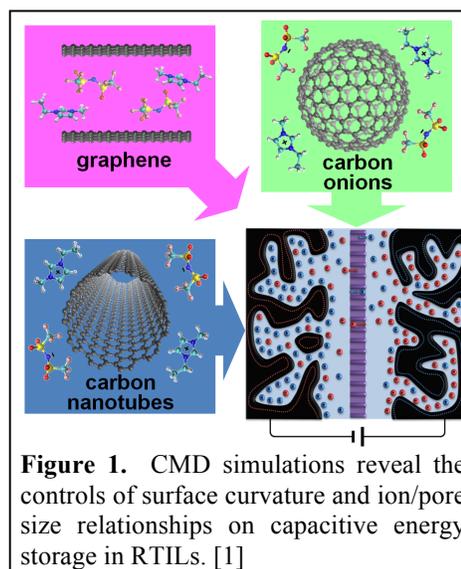
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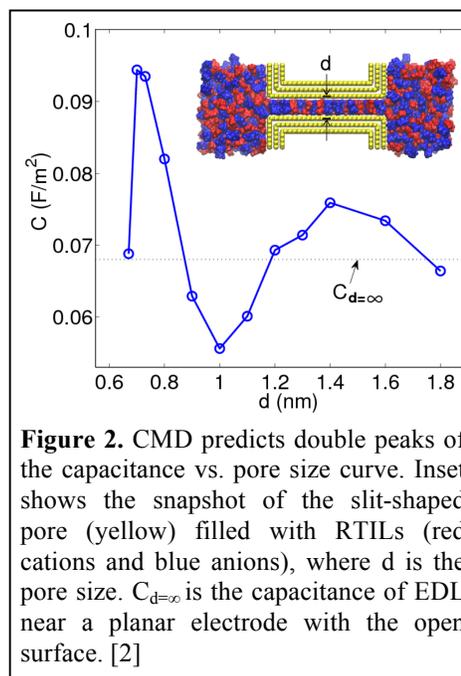
**Research Summary:** The performance of supercapacitors is determined by the electrical double layers (EDLs) formed at electrolyte/electrode interfaces. To understand the energy storage mechanism underlying supercapacitors, classical molecular dynamics (CMD) simulations (**Figure 1**) were used to study the capacitive behavior of supercapacitors consisting of room-temperature ionic liquid (RTIL) electrolytes and different types of carbon electrodes.[1]

The capacitance of supercapacitors with porous electrodes was found to correlate closely with the specific nature of RTILs (*e.g.*, structure of ion, cation/anion size asymmetry), the generic features of pores (*e.g.*, ion-pore interactions, short-ranged electrostatic interactions), and the applied potential. Supercapacitors composed of RTILs on the outer, positively curved surface of onion-like carbons (OLCs) or carbon nanotubes (CNTs) exhibited significant effects on capacitance and the distinctive feature that differential capacitance varies only weakly with voltage. Furthermore, the investigations of temperature influence revealed a positive temperature dependence of capacitance for supercapacitors with OLC-based electrodes and a weak dependence of capacitance on temperature for CNT-based supercapacitors, in line with experimental observations.

**Technical Details:** CMD simulations constitute a unique tool to provide detailed molecular insights into the capacitive behavior of RTIL-based supercapacitors with different types of carbon electrodes.[1-6] To enhance the energy density of supercapacitors, porous carbons are developed as promising electrodes mainly due to their highly increased surface area. CMD simulations of porous supercapacitors with slit-shaped micropores in the RTIL [emim][Tf<sub>2</sub>N] were performed to characterize the relation between capacitance (*C*) and pore size (*d*). [1, 2] As shown in **Figure 2**, the *C*-*d* curve exhibits two peaks at 0.7 and 1.4 nm, respectively. Specifically, the



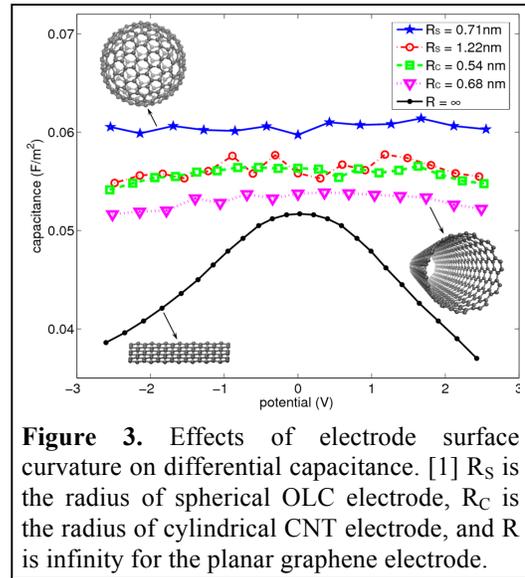
**Figure 1.** CMD simulations reveal the controls of surface curvature and ion/pore size relationships on capacitive energy storage in RTILs. [1]



**Figure 2.** CMD predicts double peaks of the capacitance vs. pore size curve. Inset shows the snapshot of the slit-shaped pore (yellow) filled with RTILs (red cations and blue anions), where  $d$  is the pore size.  $C_{d=\infty}$  is the capacitance of EDL near a planar electrode with the open surface. [2]

anomalous capacitance increase below 1.0 nm observed in our CMD simulations agrees well with experimental findings; for pore size above 1.0 nm, a second peak occurs, which is a new feature, revealed for the first time by CMD simulation. A concept of EDL interference was introduced to explain origins of the simulation-predicted two-peak C-d curve and a model based on such concept was proposed to predict an oscillatory behavior of C-d curve over a wide range of pore size for different ILs, based on the structure and capacitance of the EDL at the planar electrode with open surface.[1, 2]

To increase the device power density, supercapacitors with surface-curved electrodes have been developed, since the positively curved surface can be readily accessible for electrolyte ions.[1, 3-6]. CNTs with cylindrical curvature and OLCs with spherical curvature have such positively curved surfaces to facilitate ion access. CMD simulations of CNTs or OLCs surrounded by the RTIL [emim][Tf<sub>2</sub>N] were performed to investigate the influences of surface curvature and applied potential on the capacitance of supercapacitors with these surface-curved carbon electrodes. As shown in **Figure 3**, there is a bell-shaped capacitance-potential (C-V) curve observed for the EDL at a planar graphene electrode, which



**Figure 3.** Effects of electrode surface curvature on differential capacitance. [1]  $R_s$  is the radius of spherical OLC electrode,  $R_c$  is the radius of cylindrical CNT electrode, and  $R$  is infinity for the planar graphene electrode.

agrees with many previous studies. However, for the supercapacitors based on nanoscale CNTs or OLCs, the differential capacitance depends weakly on the electrode potential, which is qualitatively different from the behavior for planar electrodes.[1] Specifically, this feature becomes more pronounced with increasing the curvature (or reducing the radius) of the CNT or OLC [3, 6]; the capacitances for CNT- and OLC-based electrodes are higher than that near planar graphene [3-6]; the capacitance of cylindrical or spherical electrode increases with surface curvature [3, 6]; the capacitance for EDLs at spherical surface is higher and increases faster than that of cylindrical surface [1]. These interesting observations can be explained by the increased ion accumulative ability with the surface curvature and the stronger ion accumulative ability of spherical surface than cylindrical one. Moreover, the investigation of the temperature effects on the performance of IL-based supercapacitors with surface-curved electrodes revealed that the capacitance of CNT-based supercapacitors is nearly independent of temperature, due to little variation in the EDL structure, and the capacitance of OLC-based supercapacitors increases with temperature, due to the decrease of EDL thickness with increasing temperature.

**Significant Impacts on Science and Technology:** Molecular insights into RTIL-based carbon supercapacitors, revealed by CMD simulations, could facilitate the design and development of a new generation of energy storage devices.[1] For the porous electrodes, the double-peaked capacitance versus pore size curve not only shows a good agreement with experimental observations for the peak at 0.7 nm and predicts a new feature of the second peak at 1.4 nm, but also provides a possible explanation for the absence of capacitance increase in microporous electrodes in some experiment; for polydisperse pore size distributions, the peaks and troughs of the predicted capacitance interfere, resulting in an average capacitance that is apparently independent of average micropore size. Based on the introduced concept of EDL interference, a

mathematic model was proposed to predict how the capacitance changes with pore size for supercapacitors with different ILs, with given structure and capacitance of the EDL at a planar electrode with the open surface. For the surface-curved supercapacitors, the weak potential dependence of the capacitance of EDLs near nano-sized CNT or OLC electrodes invites further experimental explorations to take advantage of this phenomenon, and could benefit the future design and improvement of supercapacitors with stable performance, by fabricating electrodes with cylindrical and/or spherical nanoscale-curved surfaces.

***Publications and Manuscripts:***

1. Feng, G.; Li, S.; Presser, V.; Cummings, P. T. Molecular Insights into Carbon Supercapacitors Based on Room-Temperature Ionic Liquids, *J. Phys. Chem. Lett.*, **2013**, 4 (19), 3367–3376. [[10.1021/jz4014163](https://doi.org/10.1021/jz4014163)]
2. Feng, G.; Cummings, P. T. Supercapacitor Capacitance Exhibits Oscillatory Behavior as a Function of Nanopore Size, *J. Phys. Chem. Lett.*, **2011**, 2 (22), 2859-2864. [[10.1021/jz201312e](https://doi.org/10.1021/jz201312e)]
3. Feng, G.; Jiang, D. E.; Cummings, P. T. Curvature Effect on the Capacitance of Electric Double Layers at Ionic Liquid/Onion-Like Carbon Interfaces, *J. Chem. Theory Comput.*, **2012**, 8 (3), 1058-1063. [[10.1021/ct200914j](https://doi.org/10.1021/ct200914j)]
4. Li, S.; Feng, G.; Fulvio, P. F.; Hillesheim, P. C.; Liao, C.; Dai, S.; Cummings, P. T. Molecular Dynamics Simulation Study of the Capacitive Performance of a Binary Mixture of Ionic Liquids near an Onion-Like Carbon Electrode, *J. Phys. Chem. Lett.*, **2012**, 3 (17), 2465-2469. [[10.1021/jz3009387](https://doi.org/10.1021/jz3009387)]
5. Feng, G.; Qiao, R.; Huang, J.; Dai, S.; Sumpter, B. G.; Meunier, V. The Importance of Ion Size and Electrode Curvature on Electrical Double Layers in Ionic Liquids. *Phys. Chem. Chem. Phys.*, **2011**, 13 (3), 1152-1161. [[10.1039/C0CP02077J](https://doi.org/10.1039/C0CP02077J)]
6. Feng, G.; Li, S.; Atchison, J. S.; Presser, V.; Cummings, P. T. Molecular Insights into Carbon Nanotube Supercapacitors: Capacitance Independent of Voltage and Temperature, *J. Phys. Chem. C*, **2013**, 117 (18), 9178-9186. [[10.1021/jp403547k](https://doi.org/10.1021/jp403547k)]