

## Dependence of electric double layer capacitance on ionic liquid structure and electrode nanostructure and polarity.

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Electrical double layer capacitors (EDLCs), or supercapacitors, continue to gain an increasing attention as promising electrical energy storage devices that can be complementary to batteries, particularly when high power density and fast power delivery/uptake and long cycling life are required. The EDLCs store energy via the accumulation of ions in a nanometer-thick layer at electrochemically-stable high specific surface area active electrodes. A notable improvement in EDLC performance has been achieved due to recent advances in understanding charge storage mechanisms, development of advanced nanostructured electrodes and electrochemically stable electrolytes such as room temperature ionic liquids (RTILs). Despite extensive experimental work on these systems, the specifics of what happens inside and on the surfaces of most promising nanostructured electrodes are still not well understood. In this presentation, we will show how molecular dynamics simulations using state-of-the-art methodologies offer crucial insight into understanding the molecular level phenomena that influence supercapacitor performance and provide guidance for the design of novel materials.

Specifically, we systematically investigate the performance of various RTILs in nanoconfined geometries and on various nanoparticle surfaces. Our simulations show that the capacitance on positive and negative electrodes can be very asymmetric, as for example shown in Fig. 1 for [EMIM][TFSI] RTIL in subnanometer wide slit graphene nanopores.<sup>1</sup>

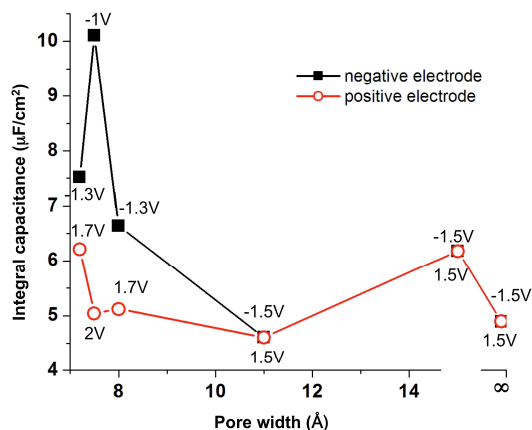


Figure 1. The dependence of the integral capacitance (IC) as a function pore width for the negative and positive electrodes at the applied potential difference between electrodes  $\Delta U=3V$ . Also shown are the corresponding values for the positive and negative electrodes (relative to bulk electrolyte).

Such asymmetry has not been observed on flat electrodes or nanopores wide enough to fit several layers of ions along the nanopore cross section. Moreover, systematic analysis of several RTILs showed that some RTILs, such as e.g. [Pyr13][FSI], do not show this asymmetry even in the very narrow nanopores, indicating that this phenomenon is a complex interplay of anion/cation asymmetry in shape, size, details of charge distribution, and specifics of ion-surface interactions. Recent experimental measurements of these RTILs on CDC and nanotube forest electrodes have confirmed the presence of

strong capacitance asymmetry as a function of electrode polarity and RTIL composition.<sup>2</sup>

We also discuss which nanoscale structural characteristics of electrodes (nanopore size, surface roughness and curvature) are beneficial for the capacitance enhancement as well as examine the mechanisms of ion mobility in the nanoconfined geometries during charging/discharging processes. Using the obtained molecular level insight we discuss how to optimize the design and selection of electrolyte/electrode combinations to achieve increased capacitance in ELDC.

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### References

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