Molecular modeling of ionic liquids confined in nanoporous carbons

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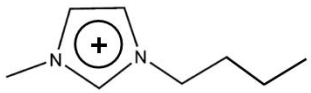
A fundamental understanding of the behavior of ionic liquids (ILs) inside nm-sized pores is crucial for the rational design of electrochemical double-layer capacitors (EDLCs) and dye-sensitized solar cells for energy storage. We have studied the structural and dynamical properties of the ILs [bmim$^+$][PF_6^-] and [dmim$^+$][Cl^-] confined inside a slit graphitic nanopore and a model CMK-3 material using molecular dynamics (MD) simulations. The structural properties of the confined ILs affect the electrical capacitance, and the dynamical properties of ILs inside nanopores influences the electrical resistance in an EDLC.



[bmim$^+$]: 1-butyl-3-methylimidazolium

[PF_6^-]

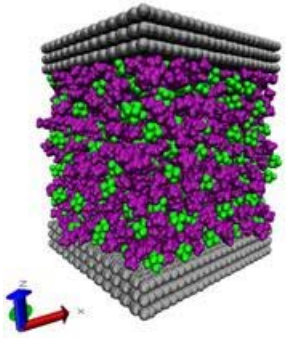
hexafluorophosphate

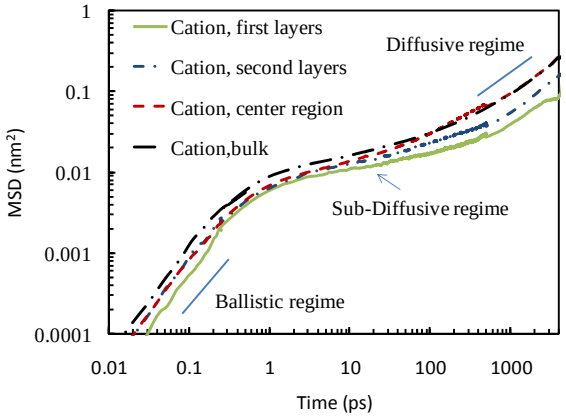
[dmim$^+$]: 1,3-dimethylimidazolium

[Cl^-]

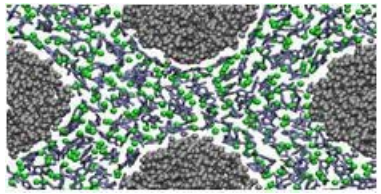
chloride

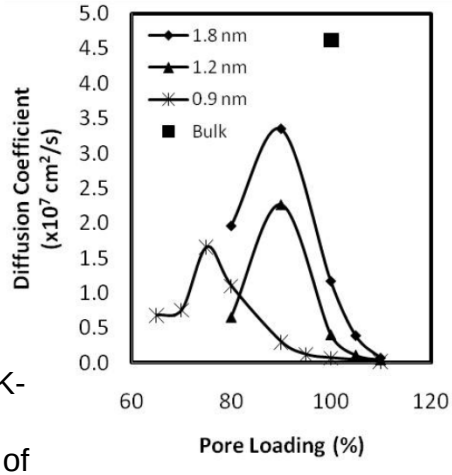
Structure of CMK-3





MD simulations of [bmim$^+$][PF_6^-] confined inside a slit-like graphitic nanopore of width 5.4 nm indicate that the dynamics of the confined ions (as measured by their mean squared displacements (MSDs) as a function of time) are highly heterogeneous and depend strongly on the distance of the ions with the pore walls. The ions in the center regions of the pore have dynamics that are very similar to those observed in a bulk IL at the same temperature. In contrast, the dynamics slow down appreciably as the ions get closer to the pore walls. These results suggest that *the dynamics of nanoconfined ILs are very complex and heterogeneous.*





We have also conducted MD simulations of the IL [dmim$^+$][Cl^-] confined inside nanoporous CMK-3 carbons. These are ordered mesoporous carbons consisting of hexagonally-packed nanorods with uniform diameters, and have been used in the past as electrodes in EDLCs. In CMK-3, the IL is adsorbed in the outer surfaces of the carbon nanorods. For any given pore size, the diffusivity of the confined cations (which is a measure of their mobility) reach maxima when the confined IL has a density below that of the bulk IL at the same temperature. In all cases, the dynamics of bulk IL are significantly faster than those of confined ILs. To the best of our knowledge, this is the very first simulation study of ILs confined in nanopores of geometry other than slit-like and cylindrical.