Supercapacitor Capacitance Exhibits Oscillatory Behavior as a Function of Nanopore Size

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Recently, room-temperature ionic liquids (RTILs) have become promising candidates for electrolytes used in supercapacitors, because of their wide electrochemical windows, excellent thermal stability, non-volatility, relatively inert nature, and good ionic conductivity. Although, the electrical double layers (EDLs) at the interfaces of RTILs and planar electrodes have been studied extensively, the RTILs inside nanopores were poorly understood, especially, how the pore size affects the capacitance of nanopores filled with RTILs. Using molecular dynamics simulations, we studied supercapacitors composed of slit-shaped micropores ranging in size from 0.67 nm to 1.8 nm in a RTIL to investigate the dependence of capacitance (C) on the pore size (d). The capacitance versus pore size (i.e., the C-d curve) was found to exhibit two peaks located at 0.7 nm and 1.4 nm, respectively. Specifically, as the pore shrinks from 1.0 nm to 0.7 nm, the capacitance of the micropore increases anomalously, in good agreement with experimental observations. We report herein that the second peak within 1.0 – 1.8 nm is a new feature of the C-d curve. Furthermore, by analogy with the wave interference, we demonstrate that the interference of two electrical double layers near each slit wall can not only explain the entire C-d curve, including the anomalous character, but also predict the oscillatory behavior of C-d curve beyond 1.8 nm.