Direct Dynamical Simulation of Filling of Carbon Nanotube Forest Electrochemical Double-layer Capacitors

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Abstract The transport parameters can be substantially different in nanoporous materials, such as these, e.g., viscosities might differ substantially with nanoscale confinement from their value for macroscopic (bulk) systems. A recent work[1] has shown that more general interactions must be included in the numerical simulation data to resolve these questions conclusively. In our previous study[2], we exhaustively studied propylene carbonate as a solvent for EDLCs, reported experimental and molecular simulation results on PC interfaces. This validation paves the way to direct simulation of dynamical filling and performance of CNT-based EDLCs. Here, we present all-atom molecular dynamics simulations of electrochemical double-layer capacitors based on CNT forests with propylene carbonate tetraethylammonium-tetrafluoroborate (PC:TEA-BF4) solutions. Preliminary results are showed in FIG. 1. We explicit characterizations of the charging and discharging process, including electrolyte composition in the pores, the rates that charging responses equilibrate and pore size dependence. Also, we consider the kinetic characteristics associated with the confinement and the anisotropic environment.

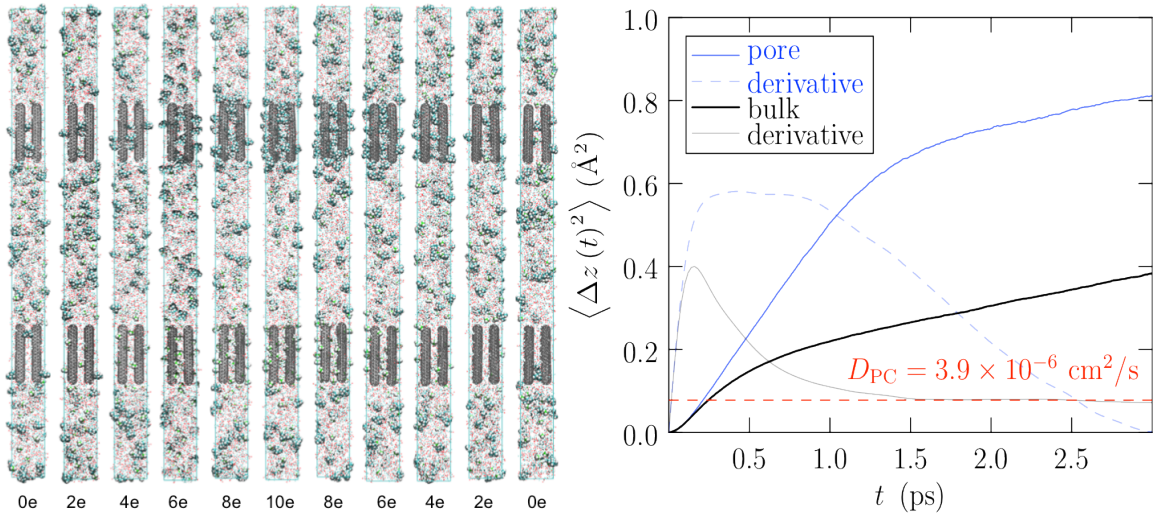


Figure 1: (left) Snapshots of configurations extracted from large scale molecular dynamics simulation of ionic charge filling of a CNT forest in response to changes in the charge of the

nanotube electrodes. The solution is tetra-ethylammonium tetra-fluoroborate in propylene carbonate (TEA-BF_4/PC). The middle sections show the filling of nanometer scale pores with bulky TEA^+ cations when the nanotube electrodes are charged strongly negatively. (right) Mean-square z-displacement and corresponding derivative of a propylene carbonate (PC) molecule in the interstitial spaces of the CNT forest, compared to a PC molecule in the bulk solution reservoir. (T,p) = (300K,1atm) and the electrolyte concentration is about 1M. In this case, the CNTs are discharged (neutral) so that differences reflect just the confinement. The pores have a nominal diameter of 1nm.

[1] P. Zhu, *et al., J. Chem. Phys.* **137,** (17) (2012): "Pairing of 1-hexyl-3-methylimidazolium and tetrafluoroborate ions in n-pentanol."
[2] X. You, *et al., J. Chem. Phys.* **138**, 114708 (2013): "Interfaces of propylene carbonate."