Ions, electrolytes, nano-pores, ultracapacitors, and energy storage

Modeling the selective partitioning of cations into negatively charged nanopores in water, L. Yang, S. Garde
J. Chem. Phys. **126**, 084706 (2007)

Anomalous Increase in Carbon Capacitance at Pore Sizes Less Than 1 Nanometer, J. Chmiola, G. Yushin, Y. Gogotsi, C. Portet, P. Simon, P. L. Taberna,
Science, **313**, 1760 (2006)

Osmotic water transport through carbon nanotube membranes, A.Kalra, S.Gardet, G.Hummer
Proc. Nat. Acad. Sci., **100**, 10179 (2003)

Recommended with a Commentary by Albert Migliori, LANL.

Of the many "emergent" properties of carbon nanotubes that are utterly baffling when contemplated in the context of already-baffling bulk carbon, hydrodynamics is certainly high on the list. Hydrodynamics appears to be of central importance to the "electrical double-layer capacitor" (EDLC) or supercapacitor. An EDLC consists of identical electrodes and a conducting ionic liquid in between. The physics is configured such that as a voltage is applied, charges in the liquid of one sign line up along an electrode, with charges of the other sign moving from the interior of the electrode to near its surface. The electric fields in this charged double-layer (CDL) can reach 3V/nm, or an energy density of $3x10^9$ J/m^3 in a polarizable liquid. Such extreme electric fields and the associated electrostrictive pressures (3GPa) induce measurable quantum confinement in the electrodes, change the electronic and other properties of the electrodes and electrolyte drastically, and produce the highest energy density of any capacitor for energy storage. But unlike the usual capacitor, actual motion of charged ions stores the energy, and this is where hydrodynamics comes in.

For any capacitive energy storage device to be useful, it must have large surface area per unit volume. An obvious choice for the electrodes, then, are carbon nanotubes, and they have been modeled and measured in such applications. Early weakly-tested models, such as those of Kalra et al. predict flow rates through CNTs of order 6 molecules/ns and, applying those same models only to organic nanopore proteins, good agreement was found. The models, though, predicted some wonderful effects that beg for experiment. One such is frictionless flow. A few years later, Chmiola et al. measured the "specific capacitance" in an heretofore unexplored very small pore size (0.6nm). Pores larger than twice the size of the electrolyte ion plus its solvation shell were thought to be required for both minimizing the time needed to discharge the supercapacitor and maximizing its specific capacitance. Chmiola measured huge increases in specific capacitance and discharge/charge rates (dependent on hydrodynamics) for pores as small as the bare ion radius, a complete surprise, and suggesting that at least some of Kalra's computations were correct. Later, Yang et al. produced simulations that, though they did not contain some of the physics accurately at the mouth of a CNT, did show anomalous

increases in the ability to stuff ions into CNTs as the driving force increased, but, more importantly, predicted reductions in the time to move ions into CNTs, making contact with Chimiola's measurements, again suggesting that Kalra was on to something. But, even wilder, was Yang's prediction that water molecules partition into the CNT and form a single-file hydrogen-bonded wire, in which each water molecule donates and accepts one hydrogen bond to and from its neighbors on the left and right. Properties of such "wires" have been explored by others.

The frictionless flow, and hydrogen-bonded wires, suggest inertial effects are present in what would seem, at first blush, the most damped of all possible hydrodynamics systems. Are there undamped resonance modes? Superflow? These theoretical studies beg for more measurements to sort them out, and the relevance to energy storage is a strong motivation to construct such measurements.