

Online Supporting Information for:

**Solvent Effect on the Pore-Size Dependence of an Organic Electrolyte
Supercapacitor**

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General remarks about the classical DFT method:

DFT offers a powerful mathematical framework to describe the equilibrium properties of many-body systems in terms of the one-body density profiles. Classical DFT is an alternative to molecular dynamics or Monte Carlo simulation methods; it is computationally efficient and allows one to precisely tune the external parameters such as ion diameter and pore size over a large range of length scales. Because of its numerical efficiency, one may focus on the most important physical problems to be addressed without worrying too much about the molecular details. For a general introduction to the classical DFT, we refer the readers to two previous reviews [1-2].

Computational details:

The classical DFT calculations are based on the grand canonical ensemble (μVT), in which the chemical potentials of the salt and the solvent, volume and temperature are fixed. In this work, the chemical potentials are specified by a bulk solution of TEA-BF₄ in ACN at concentration 1.5 M. This concentration simply translates into a number density of 0.903 nm^{-3} for the cation or the anion; by using the experimental molecular volumes for TEA-BF₄ and ACN, we estimate the number density of the solvent molecules to be 8.49 nm^{-3} , about 10 times that of the cation or the anion. In other words, the organic electrolyte is numerically dominated by the solvent molecules. The particle concentrations inside the slit pore can be higher or lower than the bulk values depending on the specific system such as the pore size, surface potential, etc.

A coarse-grained model for the organic electrolyte was used in our DFT calculations. In this model, the cations and anions are represented by charged hard spheres of equal diameter ($\sigma_+ = \sigma_- = 0.5 \text{ nm}$) and valence ($Z_+ = -Z_- = 1$), each acetonitrile (ACN) solvent molecule is

represented by two touching spheres of the same size ($\sigma_{\delta+} = \sigma_{\delta-} = 0.3\text{nm}$) but opposite charges ($Z_{\delta+} = -Z_{\delta-} = 0.238$). The pair potential between charged hard spheres i and j is given by

$$u_{ij}(r) = \begin{cases} \infty, & r < (\sigma_i + \sigma_j)/2 \\ Z_i Z_j e^2 / \epsilon r, & r \geq (\sigma_i + \sigma_j)/2 \end{cases} \quad (1)$$

where r is the center-to-center distance, and e is the elementary charge. Dielectric constant $\epsilon = 1$ because we considered all components in the organic electrolyte explicitly. While the coarse-grained model is a drastic simplification for the organic electrolyte under investigation, we expect that it should be sufficient to address important questions concerning the pore-size dependence of the EDL capacitance.

The nanoporous electrode is modeled as a slit pore of two symmetric hard walls (see Figure 1 in the text). The wall potential on an ion or a solvent segment is given by

$$\beta\Psi_i(z) = \begin{cases} -2\pi l_B Z_i z' Q / e & \sigma_i/2 \leq z \leq d - \sigma_i/2 \\ \infty & \text{otherwise} \end{cases} \quad (2)$$

where $\beta = 1/k_B T$, k_B is Boltzmann constant, T is the absolute temperature (fixed at 298 K in this work), $l_B = \beta e^2 / \epsilon$ is the Bjerrum length, Q is the surface charge density of the wall, d is the surface-to-surface separation (or pore width), and z' is the distance from the nearest wall.

For given bulk densities of the ions and the solvent molecules, temperature (298 K), the pore size, and the surface potential, we solve for the one-dimensional density profiles of cations and anions, $\rho_\alpha(z)$, $\alpha = \pm$, as well as the solvent segments, $\rho_\gamma(z)$, $\gamma = \delta \pm$, across the slit pore by minimization of the grand potential[3]

$$\beta\Omega = \beta F \left[\rho_M(\mathbf{R}), \{\rho_\alpha(\mathbf{r})\} \right] + \int \left[\beta\Psi_M(\mathbf{R}) - \beta\mu_M \right] \rho_M(\mathbf{R}) d\mathbf{R} + \sum_{\alpha=+,-} \int \left[\beta\Psi_\alpha(\mathbf{r}) - \beta\mu_\alpha \right] \rho_\alpha(\mathbf{r}) d\mathbf{r} \quad (3)$$

where $\mathbf{R} \equiv (\mathbf{r}_{\delta+}, \mathbf{r}_{\delta-})$ are two coordinates specifying the positions of two solvent segments, μ_α is the chemical potential of the ion α , μ_M is the chemical potential of the solvent, $\Psi_\alpha(\mathbf{r})$ stands for the external potential of cations and anions, and $\Psi_M(\mathbf{R})$ is the external potential for a solvent molecule, i.e. $\Psi_M(\mathbf{R}) = \varphi_{\delta+}(\mathbf{r}_{\delta+}) + \varphi_{\delta-}(\mathbf{r}_{\delta-})$, and F is the intrinsic Helmholtz energy.

The number densities of the positive and negative segments $\rho_{\delta+}(\mathbf{r})$ and $\rho_{\delta-}(\mathbf{r})$ are calculated from

$$\rho_{\delta+}(\mathbf{r}) = \int d\mathbf{R} \delta(\mathbf{r} - \mathbf{r}_1) \rho_M(\mathbf{R}), \quad (4)$$

$$\rho_{\delta-}(\mathbf{r}) = \int d\mathbf{R} \delta(\mathbf{r} - \mathbf{r}_2) \rho_M(\mathbf{R}). \quad (5)$$

The Helmholtz free energy F includes an ideal-gas contribution and an excess

$$\beta F = \int \left[\ln \rho_M(\mathbf{R}) - 1 \right] \rho_M(\mathbf{R}) d\mathbf{R} + \beta \int V_b(\mathbf{R}) \rho_M(\mathbf{R}) d\mathbf{R} + \sum_{\alpha=+,-} \int \left[\ln \rho_\alpha(\mathbf{r}) - 1 \right] \rho_\alpha(\mathbf{r}) d\mathbf{r} + \beta F^{ex}, \quad (6)$$

where V_b stands for the bonding potential of the solvent molecule

$$\exp \left[-\beta V_b(\mathbf{R}) \right] = \frac{\delta(|\mathbf{r}_{\delta+} - \mathbf{r}_{\delta-}| - \sigma_{\delta\pm})}{4\pi\sigma_{\delta\pm}^2}, \quad (7)$$

in which $\delta(r)$ is the Dirac function, $\sigma_{\delta+} = \sigma_{\delta-} = \sigma_{\delta\pm}$ is the monomer diameter. F^{ex} is the excess Helmholtz free energy arising from the thermodynamic non-ideality (viz. due to the excluded-volume effect and electrostatic interactions). In this work, we use the modified fundamental measure theory [4-5] to account for the hard-sphere repulsion, the first-order

thermodynamic perturbation theory to account for the chain connectivity [3, 6-7], and a quadratic functional expansion [3] to account for the electrostatic correlation. The detailed expression of each contribution and the numerical details can be retrieved from Ref. [8-9].

In evaluation of the Coulomb energy, we calculate the mean electrostatic potential (MEP) ψ from the density distributions of the ions by using the Poisson equation:

$$\nabla^2 \psi(\mathbf{r}) = -\frac{4\pi\rho_c(\mathbf{r})}{\epsilon}, \quad (8)$$

where $\rho_c(\mathbf{r})$ is the charge density distribution. Eq. (8) can be integrated with the boundary conditions $\psi(z=0) = \varphi_0$ and $\psi(z=d) = \varphi_d$. On the other hand, the surface charge density Q is obtained from the condition of charge neutrality.

The densities for both the ions and the solvent were initiated as a uniform distribution. After obtaining the equilibrium density profiles of ions and solvents as well as the surface density (Q) for the specified surface potential (φ_0), one proceeds to derive the integral capacitance, defined as $C = Q/(\varphi_0 - \psi_{PZC})$ where ψ_{PZC} is the potential at the point of zero charge. We chose φ_0 at 1.5 V; in our one-electrode setup (Figure 1 in the main text), this voltage is relative to the bulk solution; we also assume that there is a symmetric electrode at -1.5 V versus the bulk solution. ψ_{PZC} is zero in our case because of the symmetric cations and anions (that is, equal size) and solvent dipoles used in this work; following this symmetry, Q at 1.5 V is exactly the opposite of that at -1.5 V (that is, $-Q$). Hence the integral capacitance at the 1.5 V of the positive electrode is equal to that at the -1.5 V of the negative electrode; together they correspond to a voltage window of 3.0 V. This 3V voltage window is close to that is usually used to measure the capacitance of a supercapacitor with an organic electrolyte in a galvanostatic test [10] where voltage windows from 2.0 V to 2.7 V were used. Due to the symmetric carbon

electrodes used in the supercapacitor assembly, the voltage window at 2.7 V can be understood as that the positive electrode is at 1.35 V and the negative at -1.35 V. If we use a smaller voltage window such as 2.3 V, that would correspond to a 1.15 V surface potential in our one-electrode setup. We found that the capacitance versus the pore size remains pretty much the same (see Figure S1 below).

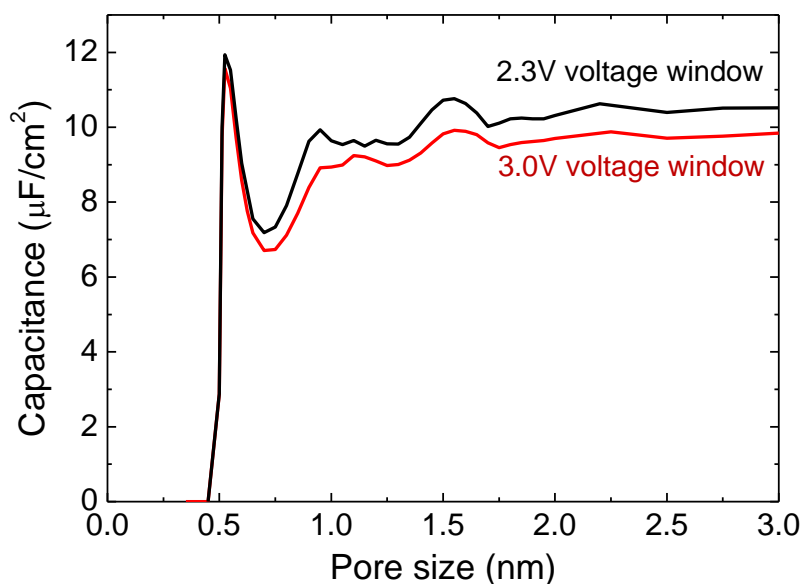


Figure S1. Integral capacitance versus pore size at two different voltage windows: 2.3 V and 3.0 V, which correspond to a surface potential of 1.13 V and 1.50 V, respectively, in our one-electrode simulation setup (Figure 1 in the main text).

Density profiles inside the 0.525nm and 0.75nm slit pores:

Figures S2 and S3 below show density profiles of ions and solvents inside the 0.525nm and 0.75 nm slit pores, respectively, and are discussed in the main text.

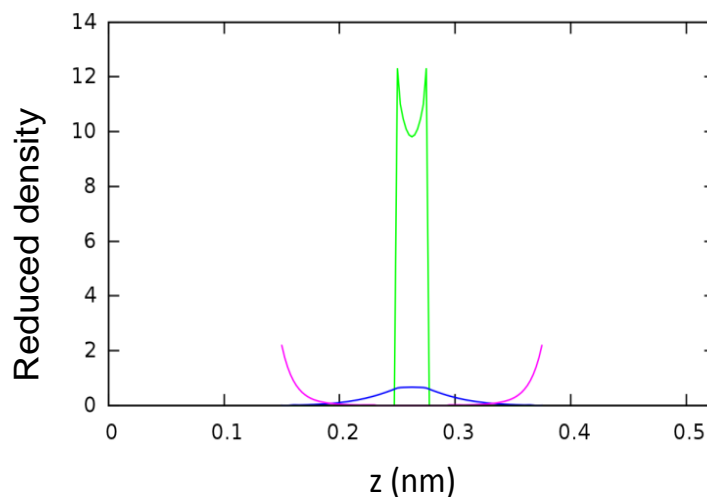


Figure S2. Reduced density profiles of the anion (green), and the negative segment (pink) and the positive segment (blue) of the dipolar solvent across the 0.525-nm slit pore at 1.5 V surface potential.

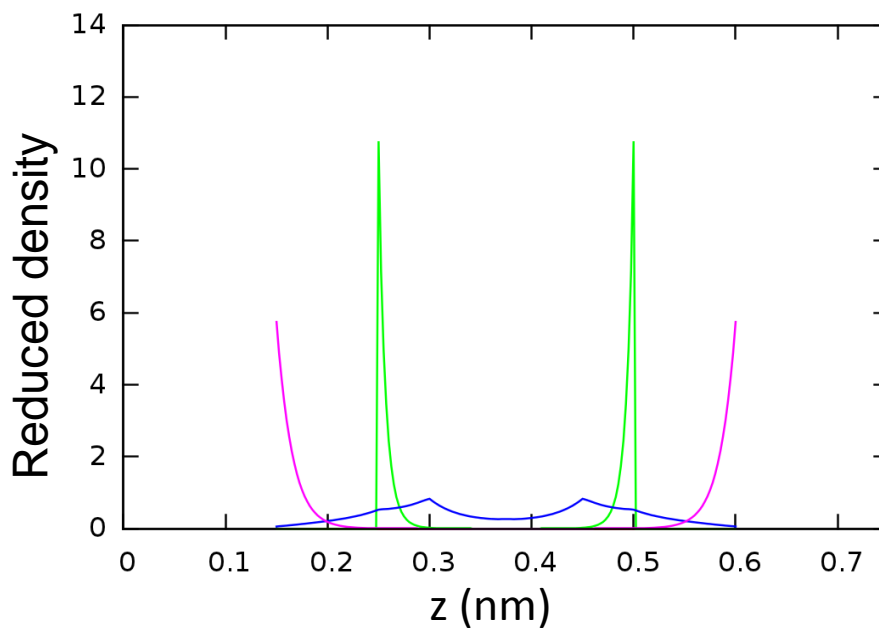


Figure S3. Reduced density profiles of the anion (green), and the negative segment (pink) and the positive segment (blue) of the dipolar solvent across the 0.75-nm slit pore at 1.5 V surface potential.

References:

1. Wu, J.Z., *Density functional theory for chemical engineering: From capillarity to soft materials*. Aiche Journal, 2006. **52**(3): p. 1169-1193.
2. Wu, J.Z. and Z.D. Li, *Density-functional theory for complex fluids*. Annual Review of Physical Chemistry, 2007. **58**: p. 85-112.
3. Li, Z.D. and J.Z. Wu, *Density functional theory for planar electric double layers: Closing the gap between simple and polyelectrolytes*. Journal of Physical Chemistry B, 2006. **110**(14): p. 7473-7484.
4. Yu, Y.X. and J.Z. Wu, *Structures of hard-sphere fluids from a modified fundamental-measure theory*. Journal of Chemical Physics, 2002. **117**(22): p. 10156-10164.
5. Roth, R., et al., *Fundamental measure theory for hard-sphere mixtures revisited: the White Bear version*. Journal of Physics-Condensed Matter, 2002. **14**(46): p. 12063-12078.
6. Jiang, J.W., et al., *Thermodynamic properties and phase equilibria of charged hard sphere chain model for polyelectrolyte solutions*. Molecular Physics, 2001. **99**(13): p. 1121-1128.
7. Jiang, J., et al., *A molecular-thermodynamic model for polyelectrolyte solutions*. The Journal of Chemical Physics, 1998. **108**(2): p. 780-784.
8. Yu, Y.X., J.Z. Wu, and G.H. Gao, *Density-functional theory of spherical electric double layers and zeta potentials of colloidal particles in restricted-primitive-model electrolyte solutions*. Journal of Chemical Physics, 2004. **120**(15): p. 7223-7233.
9. Li, Z.D. and J.Z. Wu, *Density functional theory for polyelectrolytes near oppositely charged surfaces*. Physical Review Letters, 2006. **96**(4): p. 048302.
10. Chmiola, J., et al., *Anomalous increase in carbon capacitance at pore sizes less than 1 nanometer*. Science, 2006. **313**(5794): p. 1760-1763.