

Supporting Information to

# Ionic Liquids as Electrolytes for Electrochemical Double-Layer Capacitors: Structures that Optimize Specific Energy

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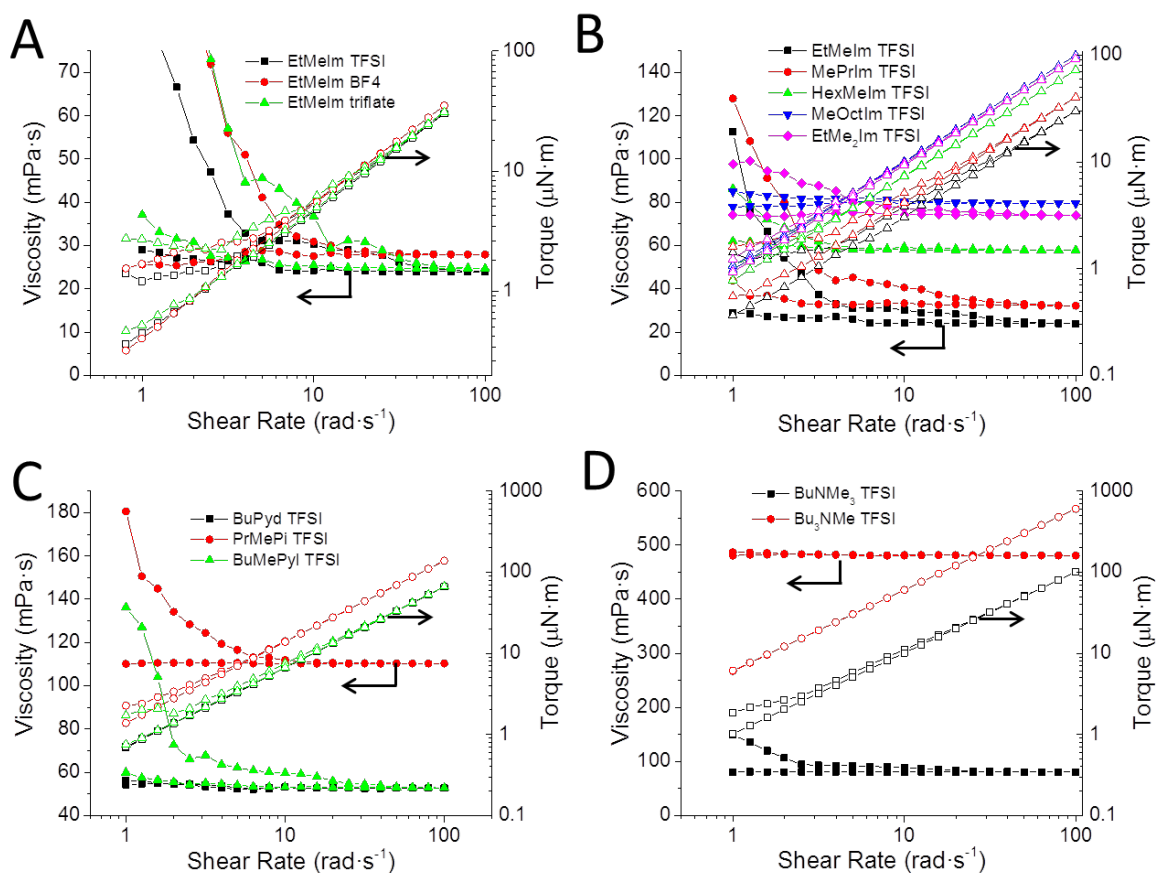
## Experimental

**Materials.** The ionic liquids butyltrimethylammonium ( $\text{Me}_3\text{BuN}$ ) bistrifluorosulfonylimide (TFSI), tributylmethylammonium ( $\text{Bu}_3\text{MeN}$ ) TFSI, 1-ethyl-3-methylimidazolium (EtMeIm or EMI) TFSI, 3-methyl-1-propylimidazolium (PrMeIm) TFSI, 1-hexyl-3-methylimidazolium (HexMeIm) TFSI, 3-methyl-1-octylimidazolium (OcMeIm) TFSI, 1-ethyl-2,3-dimethylimidazolium (EtMe<sub>2</sub>Im) TFSI, *N*-methyl-*N*-propylpiperidinium (PrMePi) TFSI, *N*-butyl-*N*-methylpyrrolidinium (BuMePyl) TFSI, *N*-butylpyridinium (BuPyd) TFSI, EMI triflate, and EMI  $\text{BF}_4$  all with a purity of 99% and a water content below 100 ppm were purchased from IoLiTec, phenol (>99%), formaldehyde (aqueous solution, 37 wt%), tetrahydrofuran, polytetrafluoroethylene (PTFE, 60 wt% in water), tetraethylorthosilicate (TEOS, 99%), L-lysine (98%), hydrochloric acid (37 wt%), potassium hydroxide, and sodium hydroxide were purchased from Sigma Aldrich, tetrahydrofuran (HPLC grade, >99.9%) and hydrofluoric acid (48–52 wt%) from Fisher Scientific. All chemicals were used without further purification. Water was deionized (DI) on site to a final resistivity of >18.0 M $\Omega$ -cm, using a Barnstead Sybron purification system.

**Conductivity Measurements.** Conductivity was measured using a custom-made conductivity cell, made of two temperature-controlled stainless steel plates and a Teflon spacer to hold the sample. The cell temperature was allowed to equilibrate at 25 °C for 15 min prior to measurements. Impedance measurements were carried out using a two-electrode cell with a Solartron 1255B frequency response analyzer and a SI 1287 electrochemical interface from Solartron (Farnborough, Hampshire, U.K.). The frequency range for these measurements was from 1 MHz to 1 Hz with a constant AC amplitude of 100 mV. Conductivities were calculated

from resistances obtained by fitting of impedance spectra with ZView software (Scribner Associates, Southern Pines, NC) in the 500 to 1 kHz range. The cell constant was measured using a 500  $\mu\text{S}/\text{cm}^2$  KCl conductivity standard. Each measurement was repeated five times.

**Viscosity Measurements.** Viscosity was measured on a TA Instruments AR G2 rheometer using parallel steel plates separated by 300  $\mu\text{m}$ . The shear rate was increased logarithmically from 1 to 100  $\text{rad/s}$ , then decreased at the same rate with 5 s equilibration and 5 s integration per point. The viscosity was determined by averaging data points during the decrease in shear rate; see Figure S1.



**Figure S1.** Viscosity and torque of ionic liquids sorted by (A) varied anions, (B) imidazolium-based cations, (C) nitrogen-containing cyclic cations, and (D) ammonium-based cations. The initial decrease in the measured viscosity with increasing shear rate is followed by level measurements as the shear rate was decreased again. This behavior is associated with shear ordering. The average of the data obtained during the shear rate decrease was used as the final reported number for viscosity.

## **Preparation of Three-Dimensionally Ordered Mesoporous (3DOM) Carbon**

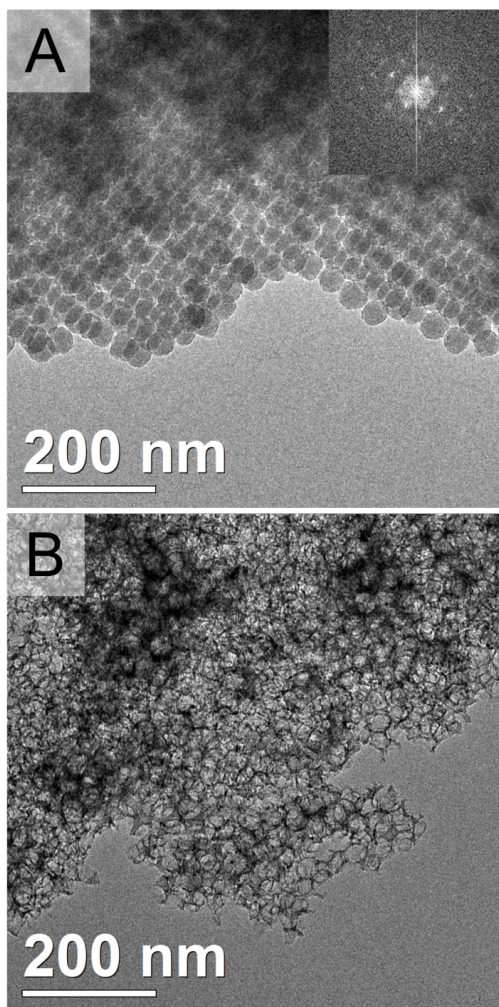
*Preparation of Silica Spheres.* Silica spheres were synthesized as previously described.<sup>1</sup> Briefly, a solution of L-lysine (70 mg) in water (70 g) was prepared in a 100 mL perfluoroalkoxy alkane round-bottom flask using a ¾ inch egg-shaped magnetic stir bar. While rapidly stirring, TEOS (5.4 g) was added dropwise and left to stir under ambient conditions for 1 h. This suspension was then heated in an oil bath at 90 °C while stirring at 500 rpm for 48 h under a condenser. TEOS (10.8 g) was again added dropwise in five equal portions, each 1 h apart, and the suspension was left for an additional 48 h. This was repeated once more for a total of 28 g of TEOS over the synthesis. The suspension was dried in a Petri dish at 70 °C overnight, then calcined at 550 °C for 6 h in air to remove residual organic components and form the colloidal crystal template. The final average silica sphere diameter was  $38.4 \pm 1.2$  nm, determined by measuring over 300 separate spheres.

*Preparation of Phenol-Formaldehyde Resol.* A phenol-formaldehyde (PF) resol was prepared according to an established method.<sup>2</sup> Briefly, phenol (61 g) was melted at 50 °C in a 500 mL glass round-bottom flask, followed by the addition of a 20 wt% aqueous NaOH solution (13.6 g). An aqueous formaldehyde solution (37 wt%, 200 mL) was added dropwise while stirring. The solution was heated to 70 °C and left for 1 h while stirring at 300 rpm with a Teflon-coated magnetic stir bar to increase the extent of polymerization. The product was neutralized to pH ~7 using an aqueous HCl solution (0.6 M, ~30 mL). Water was removed through rotary evaporation at 40 °C, and the polymer was re-dispersed in THF to achieve a concentration of 50 wt%. After the NaCl precipitate was allowed to settle overnight, the solution was isolated by decanting. The resulting stock solution was stored in a refrigerator until use.

*Preparation of 3DOM Carbon.* The 3DOM carbon was prepared following a literature procedure.<sup>3</sup> Briefly, the PF resol solution was vacuum infiltrated into the silica template (1:1 w:w) for 1 h at 40 °C, followed by cross-linking the resol at 120 °C for 24 h in a covered glass dish. The PF/silica composite was pyrolyzed under flowing nitrogen at 900 °C (1 °C/min ramp rate to 600 °C, then 5 °C/min to 900 °C). The silica template was removed through hydrothermal treatment in 6 M KOH for 48 h at 180 °C. The carbon product was isolated through vacuum filtration and washed repeatedly, then allowed to soak in DI water for 30 minutes, followed by additional washing until the pH of the effluent was ~7.

### 3DOm Carbon Characterization

Transmission electron microscopy (TEM) images were obtained on an FEI Technai T12 microscope operated at 120 kV with a LaB<sub>6</sub> filament. Samples were prepared by suspending them in ethanol and bath sonicating for 15 min. Cu grids coated in Formvar were dipped into the resulting suspension and dried. The TEM images of the templating spheres and the 3DOm C product are shown in Figure S2.

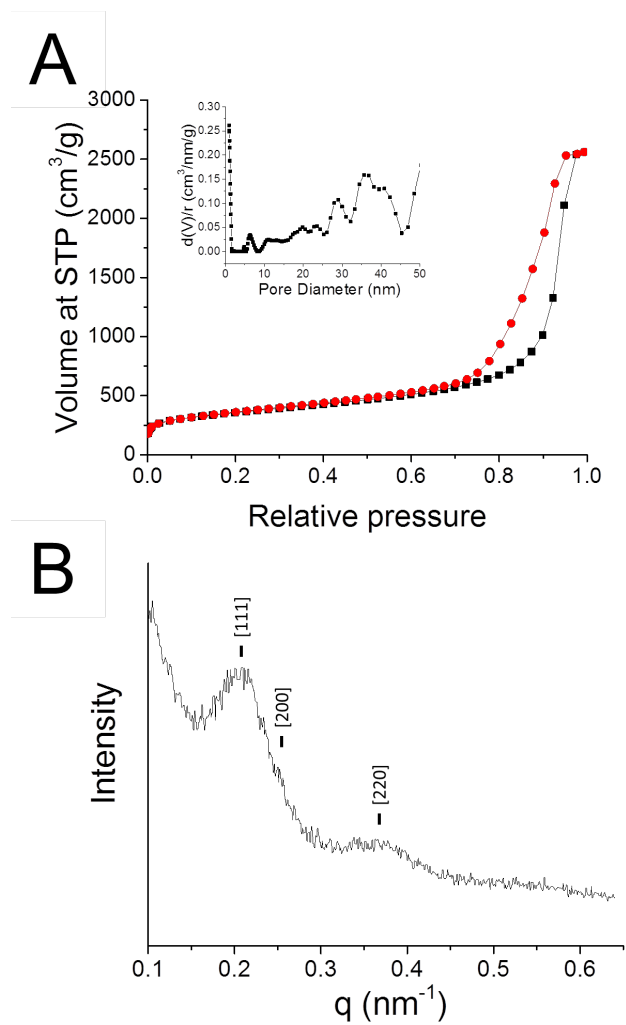


**Figure S2.** TEM images of (A) the silica colloidal crystal used as a template (FFT inset) and (B) the resulting 3DOm carbon used as an electrode material showing the open, interconnected pore structure.

Nitrogen sorption was performed using a Quantachrome Autosorb iQ instrument. 3DOm carbon samples were outgassed for 12 h at 200 °C prior to analysis. The total surface area and other pore characteristics were calculated using the quenched-solid-density-functional-theory (QSDFT) adsorption model optimized by Quantachrome for mesoporous carbon materials with spherical pores. The 3DOm carbon material gives a type IV isotherm with a type H1 hysteresis (Figure S3A), typical for 3DOm and other mesoporous structures, indicating a well-formed bulk pore structure. A total surface area of 1074 m<sup>2</sup>/g was measured. The pore size distribution plot showed two primary peaks (Figure S3A, inset), one at 37 nm and one at 29 nm. These values correspond to the observed sizes of the pores and the windows seen in the TEM images.

Small-angle X-ray scattering (SAXS) was used to determine the extent of pore ordering. The measurements were carried out on a Rigaku RU-200BVH 2D SAXS instrument operating with a pathlength of 183 cm using a 12 kW, rotating Cu anode and a Siemens Hi-Star multiwire area detector. In the SAXS pattern (Figure S3B), two clear peaks can be observed, at  $q = 0.21$  and  $0.36 \text{ nm}^{-1}$ , along with a shoulder at  $q = 0.25$ , which index well to the expected face-centered cubic array of pores. Further, the  $d_{111}$  value is 30.5 nm, which would match an ideal pore array with diameters of 37.4 nm, consistent with the observed peak in the gas sorption pore size distribution.





**Figure S3.** (A) Nitrogen sorption isotherm of the 3DOm carbon showing the characteristic type IV isotherms with type H1 hysteresis for mesoporous carbon and in the inset the QSDFT-modeled pore size distribution. (B) SAXS pattern for the 3DOm carbon.

## Electrochemical Stability at $J_{\text{cut-off}}$ of 0.1 and 5.0 mA/cm<sup>2</sup>

Electrochemical stability limits of ILs at the less common  $J_{\text{cut-off}}$  values of 0.1 and 5 mA/cm<sup>2</sup> are provided in Table S1. The  $J_{\text{cut-off}}$  value of 0.1 mA/cm<sup>2</sup> yielded unreasonably small potential windows for ILs and was not large enough to allow distinction of the redox peaks from the background current. This is evident from high standard deviations and poor data reproducibility at this  $J_{\text{cut-off}}$  value.

**Table S1. Electrochemical Stability of Room Temperature ILs (V vs. Ag<sup>+</sup>/Ag)**

	cathodic stability		anodic stability		potential window	
	0.1 mA/cm <sup>2</sup>	5.0 mA/cm <sup>2</sup>	0.1 mA/cm <sup>2</sup>	5.0 mA/cm <sup>2</sup>	0.1 mA/cm <sup>2</sup>	5.0 mA/cm <sup>2</sup>
EtMeIm BF <sub>4</sub>	-1.663 ± 0.180	-2.599 ± 0.023	0.425 ± 0.011	2.100 ± 0.015	2.088 ± 0.180	4.699 ± 0.028
EtMeIm OTf	-1.547 ± 0.021	-2.665 ± 0.013	0.213 ± 0.551	1.903 ± 0.199	1.760 ± 0.551	4.568 ± 0.199
EtMeIm TFSI	-1.422 ± 0.190	-2.599 ± 0.015	1.225 ± 0.040	2.251 ± 0.017	2.647 ± 0.194	4.850 ± 0.023
MePrIm TFSI	-1.973 ± 0.148	-2.631 ± 0.005	1.393 ± 0.037	2.359 ± 0.010	3.366 ± 0.153	4.990 ± 0.011
HexMeIm TFSI	-2.068 ± 0.562	-2.917 ± 0.012	1.489 ± 0.192	2.649 ± 0.016	3.557 ± 0.594	5.566 ± 0.020
MeOctIm TFSI	-1.749 ± 0.270	-3.179 ± 0.029	1.493 ± 0.048	3.009 ± 0.037	3.242 ± 0.274	6.188 ± 0.047
EtMe <sub>2</sub> Im TFSI	-2.513 ± 0.102	-2.975 ± 0.030	1.569 ± 0.070	2.291 ± 0.021	4.082 ± 0.124	5.266 ± 0.037
Bu <sub>3</sub> NMe TFSI	-1.863 ± 0.048	-3.939 ± 0.126	1.589 ± 0.071	> 4.0*	3.452 ± 0.086	> 7.9*
BuNMe <sub>3</sub> TFSI	-2.335 ± 0.029	-3.783 ± 0.033	1.505 ± 0.096	3.241 ± 0.049	3.840 ± 0.100	7.024 ± 0.059
BuMePyl TFSI	-2.303 ± 0.612	-3.657 ± 0.026	1.527 ± 0.052	3.321 ± 0.122	3.830 ± 0.614	6.978 ± 0.125
PrMePi TFSI	-2.841 ± 0.609	-3.871 ± 0.026	1.571 ± 0.096	3.951 ± 0.128	4.412 ± 0.619	7.822 ± 0.131
BuPyd TFSI	-1.197 ± 0.156	-1.657 ± 0.044	1.499 ± 0.105	3.148 ± 0.060	2.696 ± 0.188	4.805 ± 0.074

\* Current density not reached within the scanned potential window (0 to 4 V).

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