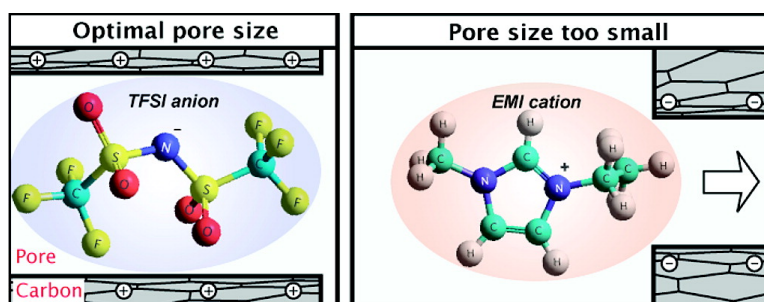


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## Relation between the Ion Size and Pore Size for an Electric Double-Layer Capacitor

Celine Largeot,<sup>†</sup> Cristelle Portet,<sup>‡</sup> John Chmiola,<sup>‡</sup> Pierre-Louis Taberna,<sup>†</sup> Yury Gogotsi,<sup>‡</sup> and Patrice Simon<sup>\*†</sup>

Université Paul Sabatier, CIRIMAT UNM CNRS 5085, 118 route de Narbonne, 31062 Toulouse Cedex 4, France, and Department of Materials Science and Engineering and A. J. Drexel Nanotechnology Institute, Drexel University, Philadelphia, Pennsylvania 19104

Received November 27, 2007; E-mail: simon@chimie.ups-tlse.fr

Electric double layer capacitors (EDLC), also known as supercapacitors or ultracapacitors, have received much attention recently because of their power delivery performance that perfectly fills the gap between dielectric capacitors and traditional batteries. With the growing development of renewable energy sources as well as hybrid electric vehicles (HEV), where peak power will be needed, these systems are thought to play an important role complementing or replacing batteries in the energy storage field.<sup>1</sup>

The most advanced devices, such as, carbon-based supercapacitors, store the energy through reversible ion adsorption on high specific surface area (SSA) carbons at the carbon/electrolyte interface. This surface storage explains the high power capability of these systems. Moreover, since there are no faradic reactions involved in the charge storage mechanism, EDLCs can sustain hundreds of thousands cycles without any noticeable performance change. However, as a consequence of the reversible electrostatic surface charging, these systems suffer from limited energy density. Today's EDLC research is largely focused on increasing their energy performance and temperature limit.<sup>2,3</sup>

We recently published results about the anomalous capacitance increase in carbon with pore size lower than 1 nm.<sup>4</sup> Using carbide-derived carbon (CDC) materials,<sup>5,6</sup> we demonstrated that, defying conventional wisdom about inaccessibility of small pores to solvated ions, these tailored subnanoporous materials exhibited very high capacitance in an acetonitrile-based organic electrolyte, with a volumetric energy twice as high as compared to standard activated carbons. These results were explained by a desolvation of the electrolyte ions entering subnanometer pores, leading to a sieving effect at pore sizes below the size of the solvated ions.

The aim of this paper is to determine the relationship between the ion size and the pore size when no solvent is present in the system and to answer the basic question: what is the best pore size to achieve the highest capacitance for EDLC? We used an ionic liquid (IL) as electrolyte to study the capacitive behavior of CDCs with controlled and tunable pore size just below and above the ion size. As solvent-free electrolytes, ILs offer the unique advantage of a well identified ion size since no solvation shell can form, which may help in understanding the so-called "sieving effect" that is of great importance for EDLCs<sup>7</sup> as well as for chemical and biomedical fields.

TiC-CDCs have recently demonstrated great potential for controlling pore size.<sup>4,6,8,9</sup> TiC-CDC samples were presently prepared by chlorination for 3 h at temperatures from 400 to 1000 °C, and their pore structure was characterized using gas sorption (Ar and N<sub>2</sub> at 77 K and CO<sub>2</sub> at 300 K). All Ar sorption isotherms were of Type 1 (see Supporting Information for details), corresponding to microporous materials. Pore size (i.e., average pore width) increases with chlorination temperature, in the range of 0.65–1.1

**Table 1.** CDC Porosity Measurements Using Ar Gas Sorption Technique

chlorination temperature (°C)	BET SSA (m <sup>2</sup> /g)	pore volume (cc/g)	average pore width (nm)	maximum pore width <sup>a</sup> (nm)
400	1113	0.51	0.65	1.12
500	1140	0.50	0.68	1.18
550	1202	0.51	0.72	1.29
600	1269	0.60	0.74	1.23
700	1401	0.66	0.76	1.41
800	1595	0.79	0.81	1.54
1000	1625	0.81	1.10	2.80

<sup>a</sup> 85% of pore volume is below this size.

nm (Table 1). An increase in ordering is also observed at high temperatures.<sup>4</sup>

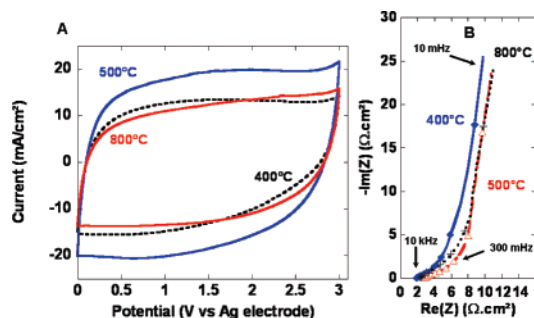
Electrochemical characterizations of CDC electrodes were conducted at 60 °C in ethyl-methylimidazolium-bis(trifluoromethane-sulfonyl)imide ionic liquid (EMI-TFSI). Ion sizes were calculated as 0.79 and 0.76 nm in the longest dimension for TFSI and EMI ions, respectively. The EMI-TFSI ion sizes are within the range of the CDC pore size. Moreover, the anion and cation sizes are very close. This allows us to assume that approximately the same pore size is required for carbon anode and cathode. Cyclic voltammetry (20 mV/s) as well as galvanostatic experiments (from 5 up to 100 mA/cm<sup>2</sup>) were conducted between 0 and 3 V in 2-electrode cells (see Supporting Information for details). No faradic effects and very reproducible behavior have been observed (Figure 1). The electrochemical impedance spectroscopy (EIS) plot is typical for an EDLC behavior.<sup>4,12</sup>

Figure 2 shows the change of the CDC specific capacitance (F/g) versus the chlorination temperature, calculated from the galvanostatic experiment at 5 mA/cm<sup>2</sup>. This plot is in excellent agreement with results obtained for an organic electrolyte solution:<sup>4</sup> the capacitance decreases for samples prepared in the 500–1000 °C range when the pore size increases from 0.74 up to 1.1 nm, thus confirming the key contribution of the subnanometer micropores in the charge storage in EDLCs electrode. Also important to mention is that the capacitance values of these CDCs are more than 160 F/g and 85 F/cm<sup>3</sup>, while standard activated carbons with large and broader pore size distributions are known to present capacitance values lower than 100 F/g and 50 F/cm<sup>3</sup> in ionic liquids under the same or similar testing conditions.<sup>10–15</sup> We confirmed these values by conducting measurements on a commercial activated carbon from Kuraray and receiving 91 F/g and 45 F/cm<sup>3</sup> under the same conditions. This clearly highlights the need for fine-tuning the pore size of porous materials in the subnanometer range for EDLC application.

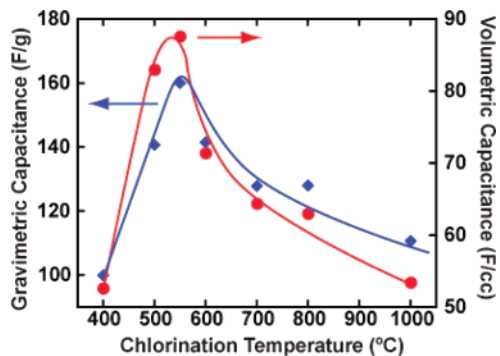
The huge decrease of both gravimetric and volumetric capacitances for samples prepared at 400 °C points out the limitation we are facing. This should be explained by the carbon pore size that

<sup>†</sup> Université Paul Sabatier.

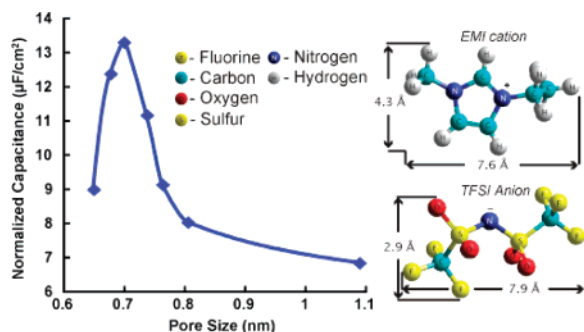
<sup>‡</sup> Drexel University.



**Figure 1.** Cyclic voltammetry at 20 mV/s (A) and EIS plots (B) between 10 kHz and 10 mHz for the 400, 500, and 800 °C samples, in EMI-TFSI electrolyte at 60 °C.



**Figure 2.** Specific gravimetric (F/g) and volumetric (F/cm<sup>3</sup>) capacitances change versus the chlorination temperature for CDC electrodes tested in neat EMI-TFSI electrolyte at 60 °C. A standard activated carbon designed for organic electrolyte-based supercapacitors reached 90 F/g and 45 F/cm<sup>3</sup> under the same experimental conditions.



**Figure 3.** Normalized capacitance change vs the pore size of the CDC samples prepared at different temperatures; normalized capacitance is obtained by dividing the specific capacitance by the SSA. HyperChem models of the structure of EMI and TFSI ions show a size correlation.

might be too small for ion accessibility. As the average pore size goes below 0.68 nm, there is an increased portion of pores that cannot be accessed by the electrolyte ions.

A better understanding of the relation between pore and ion size can be obtained from a plot of the normalized capacitance ( $\mu\text{F}/\text{cm}^2$ ) versus the CDC pore size (Figure 3).

Results presented in Figure 3 clearly point out the pore size effect. When the pore size is decreased from 1.1 down to 0.7 nm, normalized capacitance increases; a maximum is reached at  $\sim 0.7$  nm and then a large specific capacitance decrease is observed below 0.7 nm. This definitely rules out the way charge storage is traditionally described in EDLC materials, with ions adsorbed on both pore walls: CDC pore size is in the same range as the ion size and there is no space available for more than one ion per pore.

The accuracy of the porosity measurements (see Supporting Information) leads to the conclusion that the maximum capacitance obtained for a pore size of 0.7 nm is in good agreement with the ion size. At this point, pore size is perfectly adapted to the ion size and ion adsorption is achieved in the most efficient way, by minimizing the free space available. When pore size is increased, the average distance between pore wall and the center of the ion ( $d$ ) increases and then the capacitance for pores larger than around 0.7 nm decreases according to

$$C = \epsilon A/d \quad (1)$$

where  $A$  is the surface area,  $d$  is the separation between carbon and ions, and  $\epsilon$  is the local dielectric constant of the electrolyte. If the pores become even 50% larger than the optimum pore size (1.1 vs 0.68 nm), there is still room for just one ion per pore, which should be oriented along the longest dimension of the pore, naturally leading to a lower volumetric capacitance. When the pore size is decreased below 0.68 nm, there is less and less space available for double layer charging since ions cannot get into the smallest pores; as a consequence the capacitance is decreased.

Thus, this work has shown that the pore size leading to the maximum double-layer capacitance is very close to the ion size. Both larger and smaller pores lead to a significant drop in capacitance. This work suggests a general approach to selecting a porous electrode/electrolyte couple, which has been now proved for both solvated salts and solvent-free liquid electrolytes.

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**Supporting Information Available:** Detailed experimental procedures, gas sorption measurements, electrochemical characterization including voltammetry, galvanostatic cycles and EIS measurements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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