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Mesoporous carbon capsules as electrode materials in electrochemical double layer capacitors†

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The performance of mesoporous carbon capsules as electrode materials in electrochemical double layer capacitors (EDLCs) was evaluated in the presence of a variety of electrolytes, including room temperature ionic liquids (ILs).

Electrochemical double layer capacitors (EDLCs) are high power density energy storage devices that operate through the separation of charge at the electrochemical interface between an electrode and a supporting electrolyte.[1,2] Numerous types of carbon materials, including activated carbons, carbon fabrics, nanotubes, and reduced graphene oxide, have been studied as electrode materials.[3–10] Although properties such as accessible surface area and pore structure are believed to play important roles in the ultimate performance of EDLCs, broadening the scope of carbons used in these devices may aid in developing a deeper understanding of their operation and facilitate subsequent optimization studies.

As described below, a unique high surface area carbon material was prepared and tested in EDLCs in the presence of aqueous as well as organic electrolytes. Since energy density is proportional to the square of the operating voltage,[1] organic electrolytes, including ionic liquids (ILs) (commonly defined as salts that melt below 100 °C),[11] were expected to exhibit improved performance over their aqueous analogues. Although EDLCs incorporating IL electrolytes typically exhibit lower specific capacitances than those containing aqueous electrolytes,[4] ILs have excellent thermal and chemical stability (particularly with respect to hydrolysis and oxidation), and wide operating temperatures, ranging from as low as −75 °C to over 350 °C.[12–14] Moreover, their low melting points afford bulk

materials with effective ion concentrations (typically on the order of 4–5 M) that are higher than electrolytes dissolved in organic solvents (typically *ca.* 1 M), such as acetonitrile (AN) or propylene carbonate (PC). Higher electrolyte concentrations may reduce gradients generated during charging or discharging and improve the duration of charge storage by limiting self-diffusive discharge.[15,16] Hence, the further study of ILs as electrolytes in EDLCs is warranted.

We recently reported a facile route to fabricating carbon capsules using organosilica nanospheres as a template with a structure consisting of a hollow macroporous core and a mesoporous shell.[17] Given their high specific surface area (1500 m² g⁻¹), high conductivity (330 S m⁻¹), and high carbon purity (*ca.* 90 wt%),§ we reasoned that these materials might exhibit good performance when used as electrode materials in EDLCs, as the aforementioned properties have been demonstrated to strongly influence device performance.[18,19]

Herein we report the use of the carbon capsules as electrode materials for EDLCs in aqueous and organic electrolytes. The specific capacitance values measured (up to 134 F g⁻¹ using *N*-methyl-*N*-octylpyrrolidinium trifluoromethanesulfonate as an electrolyte) are among the highest reported for carbon-based materials, particularly those incorporating ILs as the electrolyte.

The synthesis of the carbon capsules is illustrated in Fig. 1.[17] Solid core/mesoporous shell (SCMS) organosilica particles were oxidized with H_2O_2 (30 wt% in water) and sulfuric acid, followed by heat treatment at 800 °C for 1 h under N_2 flow. The carbonized products were further treated with hydrofluoric acid (40 wt% in water) to dissolve the silica framework, which afforded a porous carbon material.[17] To characterize the surface properties of the capsules, analysis was

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† Electronic supplementary information (ESI) available: Synthetic procedures, carbon capsule characterization, and EDLC characterization details. See DOI: 10.1039/c0cp02557g
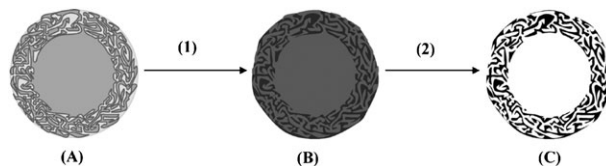‡ S. Murali and D. R. Dreyer contributed equally to this work.

Fig. 1 Illustration of the synthetic procedure used to prepare the carbon capsules studied herein. (A) Organosilica nanospheres; (B) silica/carbon composite (SiO_x–C); (C) mesoporous carbon capsule; (1) oxidation–sulfonation–carbonization of the organic moiety; (2) etching of silica (adapted from ref. 17).
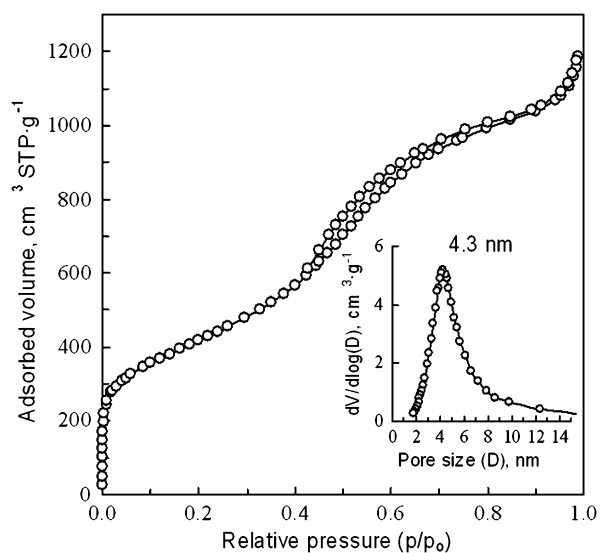
Fig. 2 Nitrogen sorption isotherm and pore size distribution of carbon capsules as determined using the BET and KJS methods.

performed using the Brunauer–Emmett–Teller (BET) method[20] via N_2 adsorption isotherms (Fig. 2) and the capsules exhibited a high specific surface area (1500 m^2 g^{-1}). A median pore size of 4.3 nm was calculated via the Kruk–Jaroniec–Sayari (KJS) method,[21] and the pore volume was measured to be 1.84 cc g^{-1}. A scanning electron microscope (SEM) image of the carbon capsules is shown in Fig. 3. The hollow core structure along with a core diameter of approximately 350 nm and a shell thickness of 50 nm was deduced from the transmission electron microscopy (TEM) images.[17] Powder X-ray diffraction (PXRD) analysis was also performed on the sample and the pattern obtained revealed a broad peak centered at $2\theta = 24°$ (Fig. 3), attributable to the amorphous nature of the carbon. From this, the d-spacing was measured to be 3.71 Å, which was consistent with π-stacking structures seen in other graphitic systems.[5,6] A bulk conductivity of 330 S m^{-1} was measured from powdered samples of these capsules using a two-point probe technique.[5] The material's high conductivity was found to effectively eliminate the need to add conductive fillers to the electrodes that were incorporated into the EDLCs described below.

Several of the electrolytes used in this study (e.g., KOH and tetraethylammonium tetrafluoroborate [TEA BF4] in AN) were selected because they are widely used in the characterization of
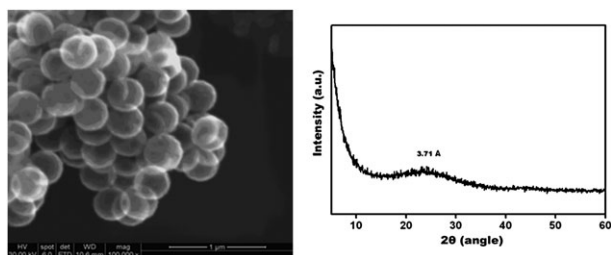

Fig. 3 (left) A scanning electron microscopy (SEM) image showing the spherical morphology of the carbon nanocapsules and (right) powder X-ray diffraction (PXRD) data showing a broad peak centered at $2\theta = 24°$.

EDLC devices and therefore serve as benchmarks.[1,2] In comparison, ILs have not been optimized as electrolytes in EDLCs (with attention to structure–property relationships) as they tend to give limited overall specific capacitance (typically less than 100 F g^{-1}).[4] While the key factors that contribute to the performance of ILs in EDLCs are not fully understood, variables such as ionic conductivity, viscosity, and electrochemical stability are believed to be important.[22,23] The ILs selected for study herein exhibit excellent electrochemical and thermal stability, as well as high ion conductivity. Moreover, some of the ILs studied have found widespread use in a range of electrochemical applications.[24] While two of the ILs were solids at room temperature, these salts were dissolved in AN (20 vol%) to allow for ion conduction within the EDLC. Finally, with the exception of 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM PF_6), which was purchased from a commercial source, the ILs selected

Table 1 Electrolyte structure and specific capacitance (expressed in F g^{-1}) of EDLCs fabricated from carbon capsules incorporating various electrolytes (indicated)

Entry	Electrolyte	Galvanostatic charge–discharge[a]		Cyclic voltammetry[b]	
		2000 mA g^{-1}	1000 mA g^{-1}	100 mV s^{-1}	40 mV s^{-1}
1	KOH (5 M aq.)	134	136	103	90
2	$NEt_4^+BF_4^-$ (1 M in AN)	97	111	109	103
3	[structure]	93	107	111	98
4	[structure]	94	96	91	93
5[c]	[structure]	120	128	112	115
6	[structure]	112	114	105	107
7[c]	[structure]	122	134	86	99
8	[structure]	92	95	70	72
9	[structure]	120	122	100	122

[a] Constant current galvanostatic charge–discharge measurements were performed using a potentiostat at 1000 and 2000 mA g^{-1} on two-electrode EDLC cells with aqueous or organic compounds as the electrolyte, as described in the table. [b] Cyclic voltammetry was performed using a potentiostat at 40 and 100 mV s^{-1} on two-electrode EDLC cells with aqueous or organic materials as the electrolyte, as described in the table. [c] Solid IL (at room temperature) was dissolved in 20 wt% AN to allow for ion conduction.

(Table 1) were synthesized by alkylation of their tertiary amine precursors, followed by anion metathesis.†

The electrode materials, test methods, and two-electrode cell used to characterize the performance of the aforementioned materials were prepared or performed, respectively, according to previously reported methods.[4,25] Carbon electrodes (bound with approximately 5 wt% PTFE) were prepared and rolled to a thickness of approximately 75 μm. The nominal weight of each electrode was 6 mg. These electrodes were then soaked in the electrolyte (6 M KOH [aq.], 1 M TEA BF_4 in AN, or an IL) and tested in a two-electrode cell assembly (Fig. S3†) using cyclic voltammetry (CV) at scan rates of 40 and 100 mV s^{-1}, as well as galvanostatic charge–discharge (also known as constant-current charge–discharge [CC]) at current densities of 1000 and 2000 mA g^{-1}.

As summarized in Table 1, excellent compatibility of the carbon capsules with a wide range of electrolytes was observed, as demonstrated by their consistently high specific capacitance values. For example, several of the ILs (e.g., BMIM PF$_6$, **4**, and **8**) showed good performance with an average capacitance of 97 F g^{-1}, while ILs **5**, **6**, **7**, and **9** exhibited values that were up to 38% higher (i.e., a specific capacitance of 134 F g^{-1} was measured when **6** was used as the electrolyte). Fig. 4 shows a representative example of the cyclic voltammetry and galvanostatic charge–discharge curves for carbon capsule electrodes soaked in IL **6**. When the voltage scan rate was increased from 40 mV s^{-1} to 100 mV s^{-1}, the variation in specific capacitance was less than 2% (107 F g^{-1} versus 105 F g^{-1}). This result suggested to us that charge propagation was retained at high scan rates, and may be a result of the high conductivity of the carbon capsules as well as the high ionic conductivity/low viscosity intrinsic to the IL.[12] Ultimately, we measured specific capacitances of 114 F g^{-1} and 112 F g^{-1} from galvanostatic discharge curves at constant currents of

1000 and 2000 mA g^{-1}, respectively. The internal cell resistance (Z axis from the Nyquist plot, shown in Fig. 4) was 7.79 Ω at a frequency of 675 Hz.

Electrodes soaked in the aqueous electrolyte exhibited a specific capacitance of 136 F g^{-1} as measured by the galvanostatic discharge at a current density of 1000 mA g^{-1}, while those soaked in the organic electrolyte showed a slightly lower specific capacitance of 111 F g^{-1} at the same current density. The EDLCs displayed a negligible decrease in capacitance under successive cycles of applied potential, and may show improvement over other mesoporous carbon spheres and activated carbon in this regard.[23,27,28]

Finally, to provide points of comparison, two high surface area carbon materials were tested under otherwise identical conditions. Microwave exfoliated graphene oxide (MEGO) and chemically-reduced graphene oxide (CReGO), prepared as described previously,[5,30] were measured to have specific capacitances of 41 and 25 F g^{-1}, respectively, when IL **6** was utilized as the electrolyte.† Collectively, these results suggested to us that the chemical and physical structure inherent to the nanocapsules employed enhanced the EDLC performance compared to analogous devices containing MEGO or CReGO. Further studies as well as the optimization of the carbon materials and ILs described herein are underway.

In conclusion, we have demonstrated that mesoporous, high surface area carbon capsules perform well as electrode materials when incorporated into EDLCs. The carbon capsule's unique surface structure combined with its high electrical conductivity rendered the material compatible with numerous electrolytes. As a result, EDLCs exhibiting specific capacitances as high as 134 F g^{-1} were prepared using an IL, which is among the highest reported for such types of electrolytes. Historically, electrodes soaked in ILs have shown inferior specific capacitances compared to electrodes soaked in aqueous electrolytes.[4,26] However, we found that electrodes composed of the present carbon material prepared with aqueous electrolytes behaved very similarly to those prepared with ILs. Collectively, these results may establish a new avenue toward generating high performance EDLCs that perform well with electrochemically stable organic electrolytes, rather than relatively less stable aqueous electrolytes.

Notes and references

§ The composition was determined by elemental combustion analysis to be predominantly carbon (89.33 wt%), oxygen (6.13 wt%), and sulfur (2.56 wt%).

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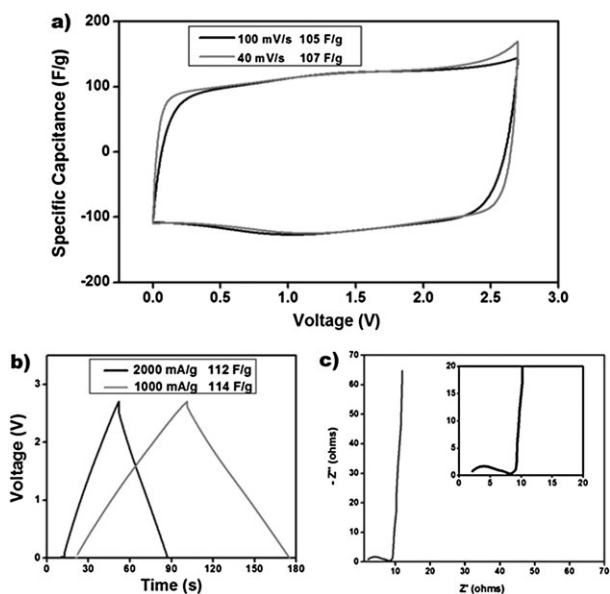4 M. D. Stoller, S. Park, Y. Zhu, J. An and R. S. Ruoff, *Nano Lett.*, 2008, **8**, 3498.

Fig. 4 EDLC performance of the carbon capsules in IL **6**; (a) cyclic voltammetry curves at scan rates of 40 and 100 mV s^{-1}; (b) galvanostatic charge–discharge curve at current densities of 1000 and 2000 mA g^{-1} and (c) Nyquist plot (0.02 Hz < ν < 1 MHz) used to characterize the internal cell resistance.

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