Microporous Carbon-Based Electrical Double Layer Capacitor Operating at High Temperature in Ionic Liquid Electrolyte

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Electrochemical capacitors (ECs), also known as supercapacitors, are electrochemical energy storage devices bridging the gap between conventional dielectric capacitors and batteries. Initially limited to high power applications requiring small-size cells such as power electronics or cordless electric tools, ECs are utilized today in a wide range of applications including transportation, where large-size cells are used for high power delivery/uptake. 1, 2 There is the need for developing supercapacitors operating at high-temperature for such applications as the replacement of the electrolytic capacitors under the car hood used for power electronics, where the operating temperature can be above 80 °C, 3 but conventional EC electrolytes using acetonitrile or propylene carbonate are limited to 60–70 °C. Room Temperature Ionic Liquids (RTIL) are solvent-free electrolytes which are known to be stable over a wide range of temperatures and show no degradation up to at least 100 °C. 4 RTIL have very low (often, negligible) vapor pressure even at 100 °C, and are not flammable, thus being much safer than conventional organic electrolytes. However, they suffer from a lower conductivity and high viscosity at room temperature that limits their use in EC in combination with conventional activated carbon electrodes. Low mobility of ionic liquids leads to high ESR and distorted cyclic voltammograms. 5 A number of ionic liquids have been tested as supercapacitor electrolytes above room temperature, 6, 7–10 but most of them produced capacitance values close to or below that of conventional supercapacitors with organic electrolytes (100 F/g). Our previous study using ethyl-methylimidazolium bis(trifluoromethanesulfonimide) (EMI-TFSI) 11 has shown that the pore size of carbon should match the ion size of the electrolyte, cyclic voltammograms exhibit an ideal capacitive behavior of the EDLC applications at high temperature, thus confirming the crucial role of micropores in enhancing the capacitance. The absence of any slope in the CV highlights the very good charge retention capability linked with a small leakage current (low self-discharge rate). The maximum capacitance was measured at about 130 F·g −1 for the TiC-CDC with pore size of 0.81 nm. This represents a 50% capacitance increase compared to a conventional activated carbon with broad pore size distribution in the same electrolyte at 60 °C, 10 thus confirming the key role of micropores in enhancing the capacitance. The maximum capacitance is reached when the 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. The

Experimental

The composite carbon electrodes were prepared by mixing 95% (w/w) of titanium carbide (TiC) derived carbon with 5% (w/w) polytetrafluoroethylene binder (PTFE, Du Pont). The structure evolution of TiC-CDC as a function of the synthesis temperature has been described in our previous publications 12, 13 and only some important characteristics are given below. 2 × 2 cm 2 CDC films (about 300 μm thick) were laminated onto treated Al foils 11 to prepare electrodes with a mass loading of ~15 mg·cm −2. 2-electrode cells were assembled using symmetric electrodes separated by 2 layers of 25 μm thick polymeric polytetrafluoroethylene (PTFE) membrane (W. L. Gore & Associates, Inc. USA). The cells were equilibrated at 100 °C for one hour prior to any characterization to stabilize the temperature. Electrochemical characterization (cyclic voltammetry and electrochemical impedance spectroscopy) was performed with a Biologic VMP2 Potentiostat (Biologic, France).

Results

TiC-CDC samples were prepared by chlorination of TiC powder for 3 h at temperatures from 400 to 1000 °C, and their pore structure was characterized using gas sorption (Ar and N 2 at 77 K and CO 2 at 300 K). 12 All Ar sorption isotherms were of Type I, corresponding to microporous materials. 13 Pore size (i.e., average pore width) increases with chlorination temperature from 0.68 nm up to 1.1 nm; an increase in ordering is also observed at high temperatures. 13 Ionic conductivity of PYR 14-TFSI electrolyte was about 15 mS·cm −1 at 100 °C. Anion and cation sizes are 0.7 and 1.1 nm in their longest dimension, respectively. 10

Figure 1 shows the cyclic voltammetry (CV) plots for the TiC-CDC samples with pore size of 0.68, 0.81 and 1.1 nm. All of the CVs were recorded at 5 mV·s −1 in PYR 14-TFSI electrolyte at 100 °C, between 0 and 2.5 V. All the CVs show a typical capacitive behavior as can be seen by the rectangular shape of the voltammograms, except for the small pore size sample (0.68 nm) where a minor distortion can be observed at low and high cell voltage. This is in strong contrast to many publications showing distortion of the CVs in ionic liquid electrolytes. 9, 15, 16 The minor distortion observed for the smallest pore size sample may be explained by a limited accessibility of these small pores to the large cations. 12, 17 The ideal capacitive behavior of the samples with pore size between 0.81 and 1.1 nm in PYR 14-TFSI electrolyte at 100 °C shows that these microporous carbons are suitable for EDLC applications at high temperature, thus confirming the crucial role played by the micropores in the charge storage mechanisms. 12, 18, 19

The absence of any slope in the CV highlights the very good charge retention capability linked with a small leakage current (low self-discharge rate). The maximum capacitance was measured at about 130 F·g −1 for the TiC-CDC with pore size of 0.81 nm. This represents a 50% capacitance increase compared to a conventional activated carbon with broad pore size distribution in the same electrolyte at 60 °C, 10 thus confirming the key role of micropores in enhancing the capacitance. The maximum capacitance is reached when the 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. The

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maximum capacitance was obtained for a carbon pore size of about 0.81 nm in the PYR$_{14}$-TFSI electrolyte, which is shifted to a larger pore size electrolyte as compared to EMI-TFSI (0.7 nm). This can be explained by the difference in the cation size (0.79 nm for EMI$^+$ vs 1.1 nm for PYR$_{14}^+$). The long pyrrolidinium ion can probably be confined in the pores with the average diameter smaller than 1 nm, but different pore sizes may be required to achieve the best possible performance for the cathode and anode of the device using this electrolyte. The gravimetric capacitance decrease for carbons with the largest pore size (1.1 nm) is explained by an increase in the unoccupied pore volume due to a less efficient use of space inside the pores of carbon, because the pores being larger than the ion size are still too small to accommodate more than one ion. The maximum capacitance was theoretically predicted for pore size being close to the ion size.

Figure 2 shows the Electrochemical Impedance Spectroscopy (EIS) plots for the 0.68, 0.81 and 1.1 nm pore size samples at the rest potential (OCV). All the plots are typical for a capacitive behavior and confirm that there is no faradic reaction involved in the charge storage. The high-frequency series resistance of the cells ($R_{HF}$) is in the range of 1 to 2 Ohm.cm$^2$. This low resistance value is associated with the improved conductivity of the ionic liquid at 100°C, since the ionic resistance of bulk electrolyte makes the main contribution to $R_{HF}$.

When the frequency is decreased, the influence of the carbon porosity and thickness on the migration rate of the ions from the electrolyte inside the electrode can be seen. The quasi-vertical line at low frequency is due to the capacitive behavior. This is consistent with the distortion observed on the CV in Figure 1.

Figure 3a shows the change of the ionic resistance of the electrode versus the carbon pore size. The ionic resistance of the electrode is obtained using equation 1

$$R_{ionic} = R_L - R_{HF}$$

where $R_{HF}$ is the extrapolation of the low frequency linear behavior to the real axis and $R_{HF}$ - the resistance at high frequency. The ionic resistance of the electrode that corresponds to the electrolyte inside the porous carbon network decreases when the pore size is increased from 0.68 to 0.81 nm, then levels off (Figure 3a). This behavior confirms that pore sizes less than 0.81 nm lead to a limitation in the electrolyte accessibility into small pores, due to steric effects, probably for the cations (the largest of the two ions).

Figure 3. Evolution of ionic resistance versus the chlorination temperature of TiC-CDC cells recorded in the PYR$_{14}$-TFSI electrolyte at 100°C (a) and evolution of the real part of the capacitance versus frequency (b).
The real part of the capacitance was calculated from the EIS data according to equation 2:

$C' (\omega) = -Z'' (\omega) / [w |Z(\omega)|^2 ] \quad [2]$

where $|Z(\omega)|^2$ is the modulus of the impedance $Z(\omega)$, $Z'' (\omega)$ - the imaginary part of the impedance, and $\omega$ - the frequency. $C'(\omega)$ is the real part of the capacitance $C(\omega)$; the low frequency value of $C'(\omega)$ is the capacitance obtained during dc measurements.\textsuperscript{22}

Figure 3b shows the change of $C'(\omega)$ versus the frequency. For frequencies $> 1\, \text{Hz}$, the measured capacitance is very small since only the outer surface of carbon particles are active. When the frequency is decreased, the contribution of the pores can be seen.\textsuperscript{23} The sample with the 0.68 nm pore size, which is significantly smaller than the cation size, has the lowest capacitance. At constant frequency, the capacitance increases with the pore size, except for the 1.1 nm sample, which is in good agreement with previous observations.\textsuperscript{12} Whatever the frequency used, the maximum capacitance is observed for the 0.81 nm sample, thus confirming the importance of matching the pore size and the ion size.\textsuperscript{12}

This study shows that the PYR14-TFSI electrolyte can be used for high temperatures supercapacitors working at 100 °C. The pore size of the electrode should correspond to the ion size of the electrolyte to maximize the capacitance. The capacitance is low when the pore size is too small to allow ions entering the pores. When the pore size is bigger than the ion size, the capacitance also decreases. The maximum capacitance measured is about 50% higher compared to activated carbon,\textsuperscript{10} inducing ~50% increase in energy density. The carbon/ion interactions are stronger in subnanometer pores, which can also explain the increase of capacitance observed comparing to conventional activated carbon. The development of high energy density, high-temperature supercapacitors can be achieved by using adapted carbon/RTIL electrolyte couples.

Acknowledgment

Y.G.'s effort at Drexel University was supported by the NSF-ESPRC International Collaboration in Chemistry grant CHE-0924570. C.L. PhD grant at Université Paul Sabatier was funded by the French Delegation Générale pour l’Armement. Collaboration between the participating universities was supported by a Partnership University Fund (PUF) grant. The authors thank Dr. J. Chmiola and Dr. C. Portet (at Drexel University at the time of that study) for experimental help and Prof. A. Kornyshev (Imperial College, London) for helpful discussions.

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