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Outstanding room-temperature capacitance of biomass-derived microporous carbons in ionic liquid electrolyte

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ABSTRACT

A remarkable capacitance of 180 F·g^{-1} (at 5 mV·s^{-1}) in solvent-free room-temperature ionic liquid electrolyte, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, was achieved in symmetric supercapacitors using microporous carbons with a specific surface area of ca. 2000 m^2·g^{-1} calculated from gas sorption by the 2D-NLDFT method. The efficient capacitive charge storage was ascribed to textural properties: unlike most activated carbons, high specific surface area was made accessible to the bulky ions of the ionic liquid electrolyte thanks to micropores (1–2 nm) enabled by fine-tuning chemical activation. From the industrial perspective, a high volumetric capacitance of ca. 80 F·cm^{-3} was reached in neat ionic liquid due to the absence of mesopores. The use of microporous carbons from biomass waste represents an important advantage for large-scale production of high energy density supercapacitors.

1. Introduction

Electrical double layer capacitors (EDLCs) store charge by electrostatic interaction between electrolyte ions and electrode surface charges [1]. Room temperature ionic liquids (RTILs) [2] have been proposed as electrolytes for advanced and safe EDLCs for their wide stable electrochemical window, wide operational temperature range and non-volatility. However, RTILs exhibit high viscosity and low ionic conductivity at room temperature; hence, electrolyte ions have hindered access into the narrow micropores of commercial activated carbons (ACs). Thus, RTIL-based supercapacitors often show low capacitance and high resistance compared to those using conventional electrolytes, based on organic solvents (acetonitrile or propylene carbonate) [3,4,5,6]. In this regard, two different approaches have been pursued to circumvent the drawbacks of RTILs and make them efficient in supercapacitors: i) dissolving RTILs in small amounts of organic solvents to increase ionic conductivity [7], and ii) employing electrode materials with fully electrolyte-accessible (open) surface, such as exohedral carbons [8] or mesoporous carbons [9]. The first approach is achieved detrimentally to the maximum cell voltage. The second cannot provide high capacitance (due to the low specific surface area (SSA) of such materials), and also requires complex synthetic procedures and/or expensive synthetic precursors. Recent investigations demonstrated improvements in gravimetric capacitance by combining RTILs containing 1-ethyl-3-methylimidazolium (EMI$^+$) ion and micro/mesoporous carbons with high pore volume (~2 cm^3·g^{-1}) [10,11]. However, high mesopore volume is detrimental to the density of materials. Thus, volumetric capacitance, the most industry-demanded metric, can be adversely affected with such carbons.

In this work, a series of ACs derived from low-cost green precursors (olive pits) was synthesized [12] and tested as electrode materials in neat 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMI-TFSI) at room temperature. These carbons contain only micropores that can be easily fine-tuned through synthesis parameters. The results showed high gravimetric and volumetric capacitance using such mesopore-free materials and EMI-TFSI within 3 V, thus offering interesting opportunities for industrial development since ACs come from cheap and abundant natural precursors.

2. Experimental

ACs were prepared by chemical KOH activation of olive pits, as reported elsewhere [12,13]. Briefly, the precursor was carbonized in a tubular furnace under an Ar flow of 100 mL·min^{-1} by heating at

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5 °C·min^{-1} and dwelling for 2 h at 700 °C. The samples of carbon char were mixed with different amounts of KOH and heated up under the same conditions described in the first step. Last, the ACs were washed off with diluted HCl and water until neutral pH, and dried at 120 °C under vacuum overnight.

N_2 adsorption was conducted using an ASAP2460 instrument (Micromeritics). The samples were outgassed under vacuum at 250 °C for 24 h before analysis. N_2 isotherms were measured at 77 K for relative pressures (P/P_0) between 10^{-7} and 0.995. The SSA and pore size distribution (PSD) were calculated using the SAIEUS software with 2D-NLDFT [14]. The differential pore volume (dV/dlgL) was calculated as:

$$\left.dV\middle/d\lg L\right. = \left.dV\middle/dL\right. L \ln 10 \tag{1}$$

Average pore size was calculated as the weighted average from PSD, according to Eqs. (2) or (3):

$$L_0 = \left.\int_{V_{min}}^{V_{tot}} LdV \middle/ (V_{tot} - V_{min})\right. \tag{2}$$

$$L_i = \left.\int_{V_{is}}^{V_{tot}} LdV \middle/ (V_{tot} - V_{is})\right. \tag{3}$$

where L_0 and L_i correspond to the average pore size and the average ion-inaccessible pore size, L the pore size, V_{is} the ion-inaccessible pore volume, and V_{tot} the total pore volume from the cumulative DFT distribution [12].

The electrodes were made by mixing 95 wt% of ACs with 5 wt% of polytetrafluoroethylene (PTFE) binder from a 60 wt% aqueous dispersion. The mixture was stirred in ethanol to form a dough further rolled to a thickness of ~170 μm and dried under vacuum at 120 °C overnight. Disk electrodes of 11 mm diameter were cut out with the electrode mass between 7 and 8 mg·cm^{-2}. Two-electrode symmetric supercapacitors were assembled in Swagelok® cells using two identical activated carbon electrodes, a borosilicate glass fiber separator (Whatman GF/B) and EMI-TFSI, 99.9% (Solvionic) as electrolyte. Cell assembly was conducted in a glove box under Ar atmosphere with < 1 ppm of water and oxygen.

Electrochemical measurements were done at room temperature, 20 °C, using a multichannel potentiostat/galvanostat VMP3 (Biologic): cyclic voltammetry (CV) at a scan rate of 5 mV·s^{-1}, galvanostatic cycling (GC) at 0.1–30 A·g^{-1}·of active material per electrode and electrochemical impedance spectroscopy (EIS) from 1 MHz to 10 mHz.

Gravimetric and volumetric electrode capacitance (C) was calculated using Eqs. (4) and (5), respectively:

$$C = \left.2\cdot\int Idt \middle/ (U\cdot m)\right. \tag{4}$$

$$C = \left.2\cdot\int Idt \middle/ (U\cdot\pi\cdot r^2\cdot h)\right. \tag{5}$$

where I is the current, t the discharge time, U the voltage, m the active material mass per electrode, r the radius and h the electrode thickness.

Series resistance was evaluated from the intercept of the real axis at high frequency of the Nyquist plot, and in-pore ionic resistance from the intercept of quasi-vertical line at low frequency with the real axis after excluding the series resistance [15].

3. Results and discussion

Textural properties are shown in Fig. 1 and Table 1. Since the maximum capacitance of carbide-derived porous carbons was found at pore size of ~0.72 nm using neat EMI-TFSI [16], pores narrower than 0.70 nm are considered poorly accessible to electrolyte ions due to the ion-sieving effect. Ion-accessible pore volume and surface area calculated using this cut-off (> 0.70 nm), d_{50} and d_{90} are listed in Table 1. d_{50} and d_{90} are the pore widths corresponding to 50 and 90% of the total pore volume and their use was recently suggested for assessing PSD [17]. All the ACs have pores in the micropore range (< 2 nm) and, as reported elsewhere [18], PSD is widened with the higher KOH/carbon ratio. Thus, AC2 exhibits the smallest L_0 and d_{50} among the studied ACs. Although AC3–AC6 have similar SSA, an increasing L_0 is observed from AC3 to AC6. Moreover, the difference between d_{90} and d_{50} increases correspondingly, meaning higher pore size dispersity with more KOH.

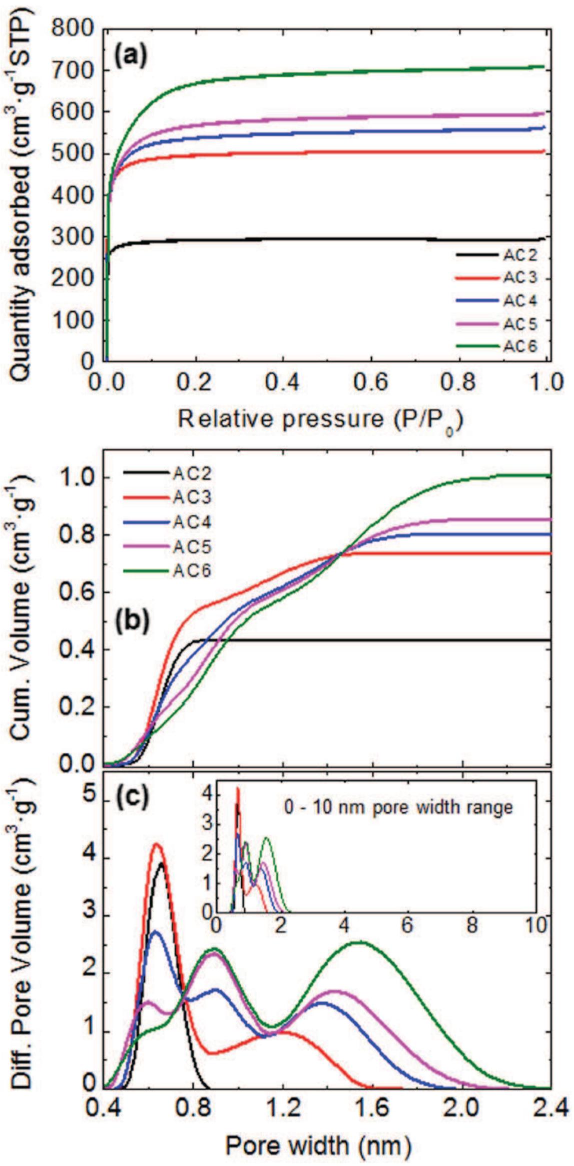

Fig. 1. (a) N_2 adsorption/desorption isotherms (b) cumulative (c) differential pore volume (dV/dlgL) vs pore size calculated by the 2D-NLDFT model.

Fig. 2a and b show the CVs of symmetric cells for AC2-AC6 at 5 mV·s^{-1} in EMI-TFSI. Most of the samples exhibit rectangular CVs typical of supercapacitors. Most importantly, high specific capacitance of 179 F·g^{-1}, 163 F·g^{-1} and 171 F·g^{-1} was measured for AC4, AC5 and AC6, respectively. To our knowledge, such high capacitance values have never been reported for purely microporous carbons in neat RTILs. By contrast, AC2 shows very low gravimetric capacitance since d_{90} is below 0.75 nm, thus poorly accessible to cations and anions, in agreement with the accessible SSA of only 292 m^2·g^{-1} (Table 1). Compared with AC2, AC3 shows decent gravimetric capacitance with huge distortion at high polarisation, meaning that, even with higher SSA, not all the pores are easily accessible to the electrolyte. The increase in d_{50} beyond 0.70 nm and the associated L_i, such as that

Table 1
Textural properties of the ACs.

Sample Name	KOH-carbon Ratio	DFT-SSA ($m^2 \cdot g^{-1}$)	Volume ($cm^3 \cdot g^{-1}$)	L_0 (nm)	d_{50} (nm)	d_{90} (nm)	DFT-SSA (> 0.70 nm) ($m^2 \cdot g^{-1}$)	Volume (> 0.70 nm) ($cm^3 \cdot g^{-1}$)	L_i (> 0.70 nm) (nm)
AC2	2	1362	0.439	0.66	0.65	0.75	292	0.107	0.74
AC3	3	2048	0.738	0.78	0.68	1.19	713	0.328	0.97
AC4	4	1965	0.807	0.98	0.83	1.45	1031	0.523	1.14
AC5	5	1986	0.858	1.01	0.91	1.55	1223	0.642	1.15
AC6	6	2084	1.010	1.18	1.04	1.73	1486	0.844	1.30

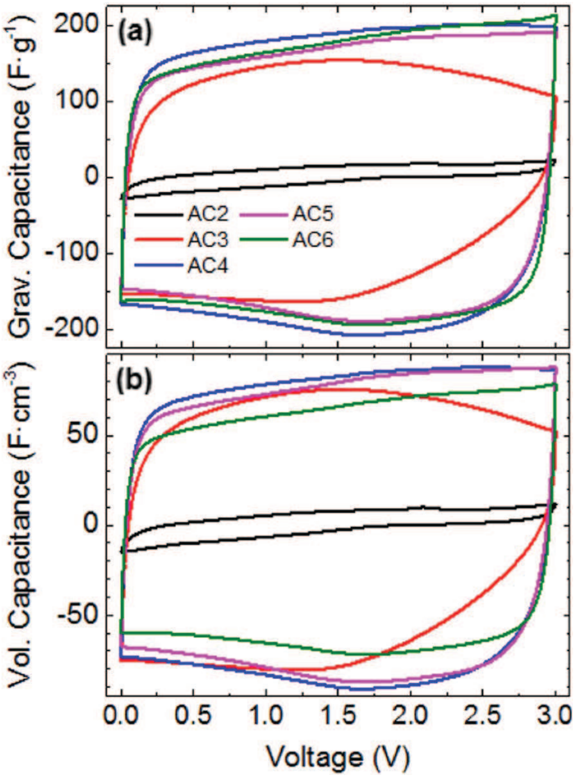

Fig. 2. Cyclic voltammograms of ACs from olive pits at a scan rate of 5 mV·s^{-1} in neat EMI-TFSI at room temperature [20 °C] (a) gravimetric and (b) volumetric capacitance.

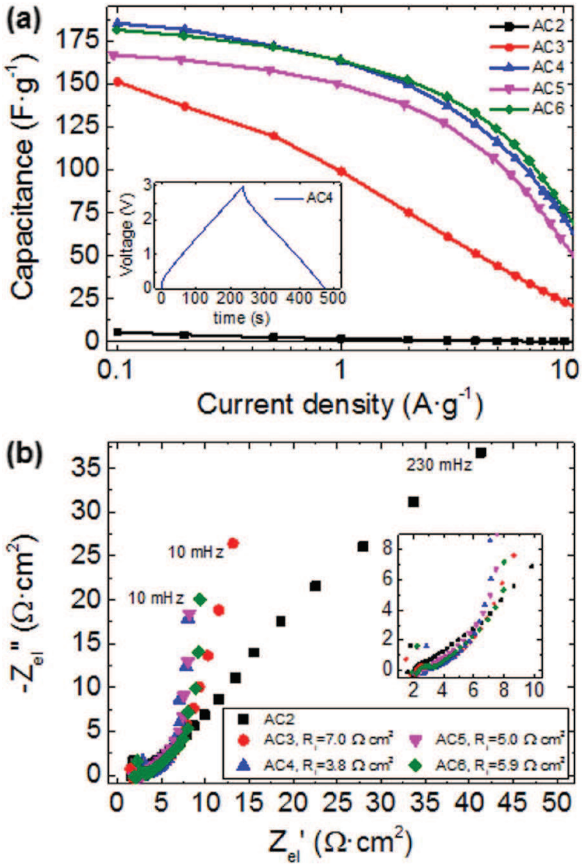

Fig. 3. (a) Capacitance of ACs in neat EMI-TFSI as a function of current density (inset - galvanostatic charge-discharge profile at 1 A·g^{-1}); (b) Nyquist plot Ohm·cm^2 per electrode (inset - high frequency range).

achieved for AC4, enable a nice typical capacitive signature within 3 V. Thus, AC4 has a PSD wide enough to provide good access for EMI$^+$ and TFSI$^-$ ions to a large part of microporous surface, also achieving high gravimetric capacitance. Further increasing L_i shows no improvement in capacitance (from AC4 to AC6). The higher capacitance of AC4 vs AC5 can arise due to stronger ion confinement due to narrower PSD as suggested theoretically [19] and experimentally measured [16,17,22].

More interestingly, Fig. 2b shows that a high volumetric capacitance of 80, 75 and 63 F·cm^{-3} was achieved for AC4, AC5 and AC6, respectively. Such high values in RTILs are unusual for biomass-derived microporous carbons with irregular porosity and are comparable or even higher than in solvent-based electrolytes [20]. Since the volumetric capacitance is a key parameter from industrial prospective regarding device miniaturization, these results are highly promising for the energy density of devices. Obviously, high volumetric capacitance was achieved thanks to the moderate pore volume in strictly microporous carbons, which distinguishes them from carbons with ultrahigh-pore volume (~2 cm^3·g^{-1}) that also provide high gravimetric capacitance, but have significant mesoporosity, which is detrimental to volumetric performance [9]. A recent study [21] also reports high gravimetric capacitance in neat IL electrolyte for a carbon with ~20% higher pore volume than that of AC4, detrimentally to the volumetric capacitance (not calculated).

Rate capability is an important metric in supercapacitor performance, which depends on the complex interplay between textural and electrical properties of porous carbons and in-pore ion transport [22,23]. Fig. 3 shows that capacitance retention is poor for AC2 and AC3, due to the poorly accessible porous structure. It increases for AC4–AC6 showing similar capacitance retention of ~65% at 5 A·g^{-1} and ~40% at 10 A·g^{-1}. The similar capacitance retention for AC4 to AC6 evidences that AC4 provides a well-suited PSD to ensure not only high capacitance, but also sufficiently fast ion transport in micropores. No harsher activation conditions are required other than a KOH-carbon ratio of 4 at 700 °C. The observed capacitance loss can be linked to the limited ionic conductivity (8.4 mS·cm^{-1}) and high viscosity (28.0 mPa·s) of EMI-TFSI [6]. For the conventional EDLC salt, $TEABF_4$, conductivity reaches up to 60 mS·cm^{-1} in acetonitrile [24] and 20 mS·cm^{-1} in propylene carbonate [25].

Nyquist plots (Fig. 3b) show typical capacitive impedance response with a quasi-vertical line at the low frequency (except for AC2), and a ~ 45° slope line in the medium frequency due to the porous electrode RC distribution [26,27]. Fig. 3b demonstrates a rather low series resistance, varying between 2.0 and 2.8 Ω·cm^2 for AC4-AC6 electrodes, whereas the in-pore ionic resistance fluctuates within 3.8–7.0 Ω·cm^2.

The last confirms that the porosity of AC4 is well adapted to provide efficient ion transport with EMI-TFSI, and further pore enlargement is not needed for high power demand.

Both low series and in-pore resistance are comparable with the literature data for another ionic liquid with the same cation ($EMI^+ BF_4^-$) [9]. In that case, carbons with a significant mesopore volume favoured more rapid in-pore ion transport, detrimentally to volumetric capacitance. By contrast, our results are obtained with the ACs of a d_{90} below 2 nm, thereby suggesting that mesoporosity is not always required to ensure fast propagation of RTIL ions inside pores. Overall, impedance data also evidence efficient high-rate operation with RTILs and the studied microporous carbons.

4. Conclusions

In summary, microporous carbons from olive pits deliver a high capacitance of 180 $F \cdot g^{-1}$ and a low resistance of 4 $\Omega \cdot cm^2$ at room temperature in neat EMI-TFSI ionic liquid. This work reveals efficient capacitive response with RTILs and strictly microporous carbons, which also enables a high volumetric capacitance of 80 $F \cdot cm^{-3}$. Furthermore, carbons were prepared from biomass waste via a regular chemical activation procedure, which excludes complicated high-cost synthetic routes and synthetic precursors, and is therefore easily scalable.

Although the electrochemical behaviour showed good agreement with the ion-accessible area, it is still difficult to know the best carbon microstructure (PSD, relationship between ion-accessible SSA and volume …) due to the lack of techniques to probe carbon geometric topology, and in-situ ion transport. Apart from the accessibility of pores to ions, other parameters, including surface chemistry and defects [28], need to be thoroughly investigated to provide detailed insight into the outstanding performance of microporous carbons in RTILs.

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