Short communication

Cooperation of micro- and meso-porous carbon electrode materials in electric double-layer capacitors

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ABSTRACT

The capacitive characteristics of micro- and meso-porous carbon materials have been compared in cyclic voltammetric studies and galvanostatic charge–discharge tests. Meso-porous carbon can keep certain high capacitance values at high scan rates, whereas micro-porous carbon possesses very high capacitance values at low scan rates but fades quickly as the scan rate rises up. For better performance of electric double-layer capacitors (EDLCs), the cooperative application of both kinds of carbon materials has been proposed in the following two ways: mixing both kinds of carbons in the same electrode or using the asymmetric configuration of carbon electrodes in the same EDLC. The cooperative effect on the electrochemical performance has also been addressed.

1. Introduction

Nowadays, electric double-layer capacitors (EDLCs) are drawing more and more attentions as an efficient energy storage device for electric power. The electric double-layer formed at the electrode/electrolyte interface stores electric charges and the capacitance is roughly proportional to the surface area of electrode. Because of their high surface areas, various porous carbon materials have been applied as the electrode materials for EDLCs. Numerous studies have shown that not only the specific surface area, but also the pore sizes of carbon material have a great influence on the capacitance of the electrode. Two categories of porous carbons are commonly used in EDLCs: micro- and meso-porous carbons. Both kinds have advantages and shortcomings. The micro-pores can sieve out most "superfluous" species (including solvation shell of the ions) and selectively accommodate the effective charge carriers (ions). Recently, Gogotsi and co-workers found that micro-pores smaller than 1 nm contribute an anomalous increase in the specific capacitance of porous carbon [1–3]. This discovery may pave the pathway for further applications of micro-porous carbons in EDLCs. However, the slow kinetics of ions transportation in micro-pores is

still a problem for the EDLCs discharged at high rates. With the increase in discharge rate, the specific capacitance of micro-porous carbon generally reduces sharply [4–6]. Meso-porous carbons also feature this behavior, but the drop-down tendency of capacitance becomes comparatively sluggish [4,7]. The abruptly reduced capacitance of micro-porous carbon as the discharge rate rises up not only reflects the slow diffusion of ions within micro-pores, but also concerns with the solvation/desolvation process of ions as they pass through the interface between porous carbon and electrolyte. This does not mean that meso-porous carbon will prevail in EDLCs markets. In fact, to guarantee the high gravimetric specific capacitance, the density of meso-porous carbon electrode material always gets very low [8]. Accordingly, the volumetric specific capacitance is sacrificed to some extent.

To avoid the above shortcomings of both micro- and meso-porous carbon electrode materials, and to make full use of their respective merits, an effective way is to adjust a porous carbon material with a suitable spectrum of pore sizes, ranging from micro- to meso-pores. To our best knowledge, few reports have been published on this point, probably due to a shortage of efficient and flexible techniques controlling the pore size distribution for a single carbon. As an alternative way to solve the above problem, physically mixing micro- and meso-porous carbons together at certain ratios is more practical and simple.

On the other hand, from the viewpoint of electrolyte instead of carbon electrode in the EDLCs, the problem of "asymmetry" of ions should be always faced. Here the term of "asymmetry" mainly

implies the difference between the sizes of anions and cations. An good example for the asymmetric electrolyte is Na_2SO_4 aqueous solution, which possesses the advantages like low cost, environmental benignity, etc. However, the rather big sizes of anions like HSO_4^-, and SO_4^{2-} ($SO_4^{2-} \cdot 12H_2O$, 0.53 nm) [9] may not only decrease the specific capacitance of micro-porous carbon positive electrode remarkably, but also can retard the fluent movement of the anions in the micro-pores and lead to the significant deterioration in the rate performance of positive electrode. In this case, meso-porous carbon abundant in wider pore opening is more suitable for the adsorption of bigger anions. By contrast, the ionic radius of hydrated Na^+ is much smaller (ca. 0.358 nm) [10] than the pore opening of most micro-porous carbons, so micro-porous carbons may be employed as negative electrodes to accommodate hydrated alkali cations. To meet the practical needs of asymmetric electrolyte salts, an asymmetric configuration of C/C′ is more favorable than the symmetric one of C/C in traditional EDLCs. C/C′ means that the positive and negative electrodes belong to different types of porous carbon, whereas C/C stands for the case that both the electrodes are identical in EDLCs.

Based on the above expectations, we propose the application of multi-type porous carbon materials in EDLCs. To simply model the cooperative effects of multi-type porous carbons on the performance of electrodes or EDLCs, two kinds of commercial porous carbon samples, namely, EC-600JD and Maxsorb have been picked up as the representatives for both meso- and micro-porous carbons, respectively. In this study, the electrochemical tests have been performed on both micro/meso-porous carbon composite electrodes and the total micro/meso-porous carbon "hybrid" EDLCs in the Na_2SO_4 aqueous solution.

2. Experimental

The porous carbon electrode materials employed in this study were EC-600JD and Maxsorb, with the B.E.T. specific surface area values of 1368 and 1333 $m^2 g^{-1}$, respectively. From the pore size distribution results, it can be observed that EC-600JD belongs to meso-porous carbon, while Maxsorb is a typical micro-porous carbon material.

Electrodes were fabricated by mixing the active electrode material (porous carbon) and TAB (teflonized acetylene black) at the weight ratio of 2–1. The composite was pressed on a stainless mesh (1 cm^2 area), with typically 6 mg active material applied to each electrode.

Cyclic voltammetric (CV) studies were performed by CHI660C potentiostat/galvanostat to assess the electrochemical performance of porous carbon-based composite electrodes. Galvanostatic charge–discharge cycles were also measured by a Land cell tester. The cutoff voltages were set at 0 and 1.2 V. The electrochemical cells used here were two-electrode or three-electrode beaker cells filled with the electrolyte of 1 M Na_2SO_4 aqueous solution. In a two-electrode cell, both the positive and negative electrodes were porous carbon-based composite electrodes. A three-electrode cell comprised a porous carbon-based composite working electrode, a platinum flag counter electrode, and the Ag/AgCl reference electrode.

3. Results and discussion

Cyclic voltammetry has become one of the most popular methods to evaluate the capacitive characteristics of electrode materials in previous studies on electrochemical capacitors. Fig. 1 compares two series of cycle voltammograms (CVs) for EC-600JD and Maxsorb electrodes, respectively, recorded at different scan rates in the three-electrode cells. Generally speaking, the CV curves demon-
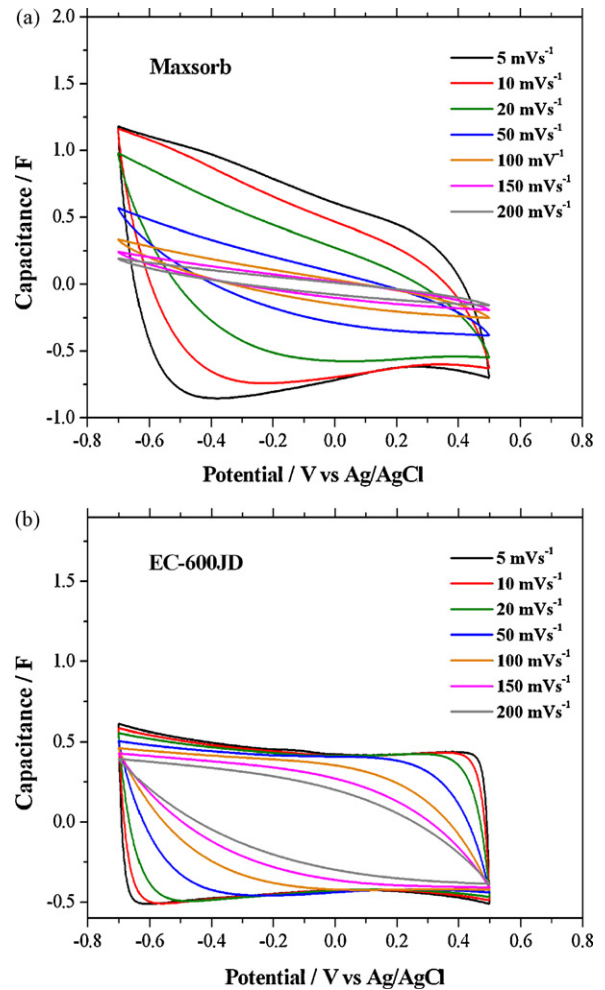

Fig. 1. Cyclic voltammograms of Maxsorb (a) and EC-600JD (b) electrodes at different scan rates in the electrolyte of 1 M Na_2SO_4 aqueous solution.

strate nearly rectangular shape at low scan rates, especially for the sample of EC-600JD. With the increase in the scan rate, the area surrounded by CV curve shrinks, implying the decrease in the capacitance value delivered by the porous carbon electrodes. An irregularly asymmetric feature in the CV curve of Maxsorb should be noted even at the slowest scan rate of 5 mV s^{-1}. The region in the positive potential range from 0 to 0.5 V is significantly smaller than that in the negative potential range from −0.2 to −0.5 V vs. Ag/AgCl. This fact can be ascribed to the sensitive and selective adsorption ability of micro-pores in Maxsorb towards the ionic sizes. The positive portion corresponds to the adsorption/de-sorption of anions with bigger sizes while the negative portion relates to the adsorption/de-sorption of cations with smaller sizes.

From the CV curves, the specific capacitances (SC) values of electrode materials can be estimated by the following formula: $SC = Q(2m \Delta V)^{-1}$. Here Q stands for the charge obtained by the integrated area of the CV curves; m represents the mass of electrode material (6 mg); and ΔV means the potential range. Fig. 2 compares the relationship between the SC values and scan rate in the positive (0 to 0.5 V), negative (−0.2 to −0.7 V) and total (0.5 to −0.7 V) potential ranges, respectively. For both EC-600JD and Maxsorb electrodes, the SC values corresponding to various potential ranges rank in the following order: $SC_- > SC_{total} > SC_+$. The differences between SC_- and SC_+ appear more prominent in the case of Maxsorb than that of EC-600JD. Another fact worthy of notice is the drop-down of SC values along with the increase in scan rate. The declining speeds in the curves of Maxsorb are much sharper than those of EC-600JD.
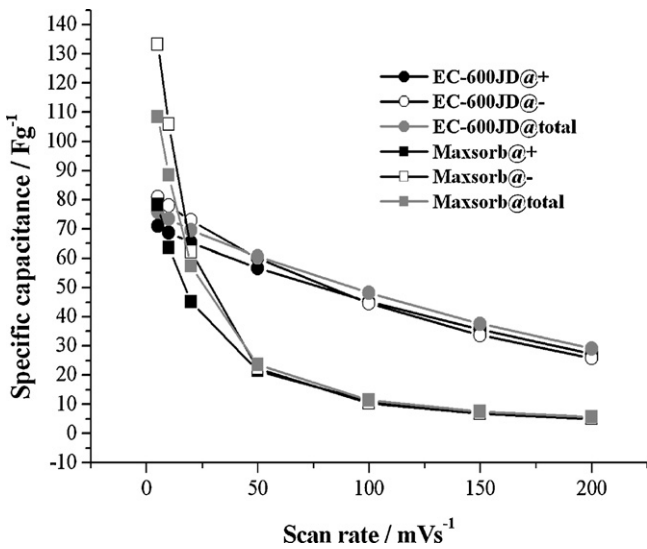
Fig. 2. Relationships between the specific capacitance values and scan rate in different potential ranges for the electrodes of Maxsorb (a) and EC-600JD (b). *Note*: The inset symbols "+", "−" and "total" stand for the potential ranges from 0 to 0.5 V, −0.2 to −0.7 V, and 0.5 to −0.7 V vs. Ag/AgCl, respectively.

This trend reflects that ions movement in micro-pores (Maxsorb) is much more sluggish than in the meso-pores (EC-600JD).

From the above observations, two ways can be expected to combine the applications of both the micro-and meso-porous carbon electrodes in EDLCs. The first way is to make a single composite electrode containing both the micro- and meso-porous carbon materials. Fig. 3 shows the relationships between SC values and the scan rates for the composite electrodes with different mixing ratios of Maxsorb and EC-600JD. As expected, with the increase in the EC-600JD content, the fall-down speed of SC values becomes slower along with the rise in scan rate. On the other hand, with the increase in Maxsorb content, the SC values of composite electrodes get bigger apparently at slow scan rates. In the practical applications, the choice of the mixing ratio of micro- and meso-porous carbon materials depends on the situations. Anyhow, the composite electrode is very flexible to cater to the needs of both energy density (high capacitance at low scan rates) and power density (high capacitance at high scan rates).
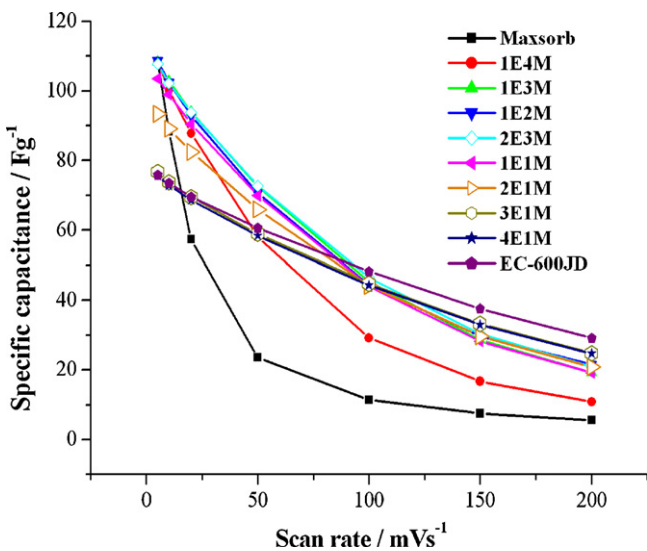

Fig. 3. Relationships between the specific capacitance values and scan rate for the composite electrodes with different mixing ratios of Maxsorb (M) and EC-600JD (E).
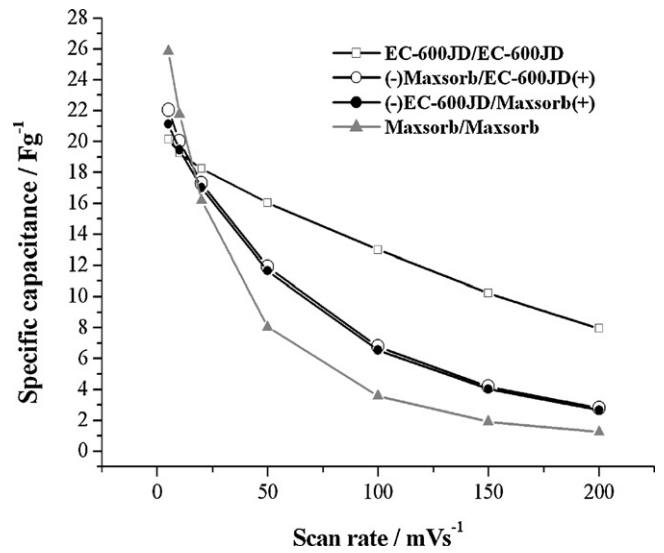

Fig. 4. Relationships between the specific capacitance values and scan rate for the EDLCs with different cell configurations.

The second way is to apply both micro- and meso-porous carbon electrodes as separate electrodes within the same EDLCs. The CV measurements have also been performed on the EDLCs including the following two-electrode sets: symmetrical cells of Maxsorb/Maxsorb and EC-600JD/EC-600JD, and asymmetric cells of (−)Maxsorb/EC-600JD(+) and (−)EC-600JD/Maxsorb(+). The weights of positive and negative electrodes in each EDLC are equal. CV curves characteristic of capacitive behaviors at different scan rates can be got. The SC values of EDLCs have been calculated according to the following formula: $SC = Q(2M\Delta V)^{-1}$. Here Q stands for the charge obtained by the integrated area of the CV curves; M represents the total mass of both electrode materials in each EDLC (12 mg); and ΔV means the working voltage range (1.2 V). Fig. 4 compares the relationships between SC values and the scan rates for the EDLCs with different cell configurations. As expected, the curves corresponding to asymmetric cells locate in the region between the curves of two symmetric cells. As compared to the symmetrical cell composed of both micro-porous carbon electrodes (Maxsorb/Maxsorb), the asymmetric cells demonstrate elevated specific capacitance values at high scan rates after the replacement of one micro-porous carbon by the meso-porous carbon electrode. Espe-
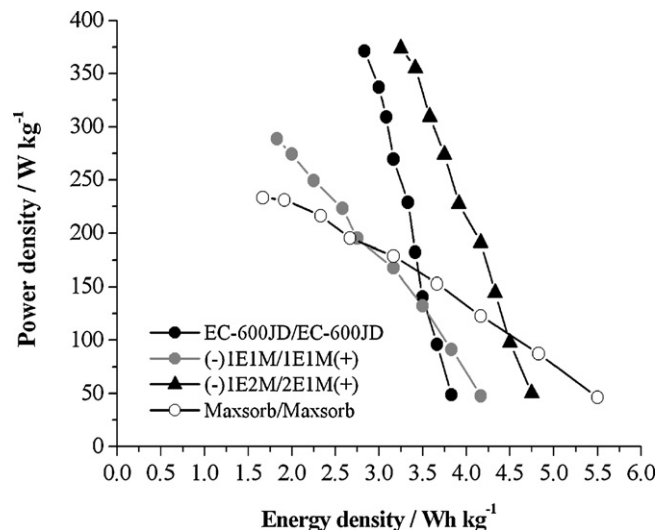

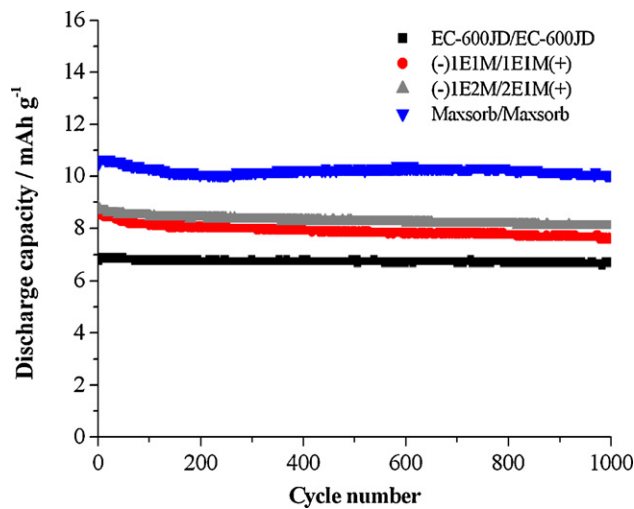**Fig. 5.** Ragone plot of different capacitors.

Fig. 6. Cycle performance of different capacitors at the constant current density of 166.67 A/g. The discharge capacity values were calculated by taking account the total mass of both electrode active materials in each capacitor.

cially, the asymmetric cell of (−)Maxsorb/EC-600JD(+) possesses a little higher SC values than those of (−)EC-600JD/Maxsorb(+) at low scan rates. This implies that meso-porous carbon-based electrodes are more suitable for the adsorption of bigger ions in EDLCs. Of course, two composite electrodes containing different mixing ratios of micro-/meso-porous carbon materials can also be utilized in the same EDLC. This situation becomes more complex and the improvement in energy and power densities can be clearly observed in the Ragone plot (Fig. 5). The energy and power densities were evaluated from the galvanostatic discharge curves by taking account the total mass of both electrode active materials. The symmetric capacitor of (−)1E1M/1E1M(+) merely shows a simple compromise between the symmetric capacitors of

EC-600JD/EC-600JD and Maxsorb/Maxsorb. By contrast, the asymmetric capacitor of (−)1E2M/2E1M(+) delivers much bigger energy and power densities, although the capacitors of (−)1E1M/1E1M(+) and (−)1E2M/2E1M(+) contain the same contents of EC-600JD and Maxsorb. The cycle performance of the above capacitors is shown in Fig. 6. All these four capacitors have stable cycle life.

4. Conclusion

The cooperation of micro-and meso-porous carbon electrode materials in EDLCs contributes significantly to the improvements in the performance of EDLCs. Two ways of coordination has been proposed: mixing micro-/meso-porous carbon materials in the same electrode and using separate micro- and meso-porous carbon electrodes in the same EDLC. Both ways provide flexible measures to meet the practical needs of EDLCs in the terms of both the energy and power densities.

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