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ORIGINAL PAPER

Supercapacitive behaviors of worm-like mesoporous carbon in non-aqueous electrolyte

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Abstract This paper discusses the electrochemical behaviors of worm-like mesoporous carbon obtained in 1.0 mol L^{-1} $LiClO_4$/ethylene carbonate + dimethyl carbonate solution. The capacitance for nanoporous carbon system advances up to 147 F g^{-1} and a wide voltage window (2.5 V) for three electrode system was achieved. The specific energy and specific power reach as high as 127.6 Wh kg^{-1} and 5.0 kW kg^{-1}. These results show that worm-like mesoporous carbon can be used for high energy density and power density non-aqueous electrolyte supercapacitors.

Keywords Worm-like mesoporous · Non-aqueous electrolyte · Energy density · Power density

1 Introduction

Electrochemical capacitors (often called supercapacitors), which fill the gap between batteries and conventional capacitors, have attracted great attention due to high power density, excellent reversibility and long cycle life. Electrochemical capacitors can supply high power during several seconds and are very quickly rechargeable. High power and energy densities, reversibility, and very excellent cycling stability make electrochemical capacitors useful in energy storage devices for application such as electrical vehicles, portable electronic devices, uninterruptible power supply, and pulse laser techniques [1, 2].

Recently, many efforts have been devoted to the application of nanoporous carbon in electrochemical capacitors because of their favorable electronic conductivity, high chemical stability, and available specific surface area. Nanoporous carbon supercapacitors have been used as energy storage devices, such as hybrid vehicles, memory back-ups, rechargeable batteries, etc. [3–11]. The study on electrochemical properties of nanoporous carbon is a very important problem taking into account the development of electrochemical capacitors. Unfortunately, even if they have large surface area, the application in electrochemical capacitors is limited due to their micropores, which are less easily wetted by electrolytes, such that a large part of the surface exposed may not be utilized for charge storage. To overcome this drawback, uniform mesoporous size carbon has become popular as an alternative supercapacitor material.

Herein, we have investigated the electrochemical properties of worm-like mesoporous carbon (WMC) in a non-aqueous electrolyte of 1.0 mol L^{-1} $LiClO_4$ in ethylene carbonate/dimethyl carbonate (EC:DMC 1:1 by volume). For comparison, its electrochemical performance in an aqueous electrolyte of 6.0 mol L^{-1} KOH has been also presented. The unique mesoporous structure enables the WMC to present high capacitance in non-aqueous electrolyte, and it may also have great potential for practical applications due to its high energy density and power density.

2 Experimental section

2.1 Sample preparation

The worm-like mesoporous carbon was synthesized by using the MOF-5 framework ($Zn_4O(OOCC_6H_4COO)_3$) as template, one of the most representative MOFs which has a

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three-dimensional intersecting channel system (cavity diameter 18 Å), and glycerol as carbon precursor according to literature [12].

2.2 Characterization

The basic characteristics of the sample, such as X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM), had been reported in the previous Ref. [12]. The pore structure was characterized via nitrogen sorption using a Micromeritics Tristar 3000 system.

The working electrodes were prepared by mixing 80 wt% WMC, 15 wt% acetylene black (AB), and 5 wt% poly(tetrafluoroethylene) (PTFE). The mixture was dropped and pressed onto a foam nickel (10 × 20 mm) at 30 MPa for 5 min, and the mass of WMC was 6 mg. Cyclic voltammetry and galvanostatic charge/discharge measurements were conducted on a CHI 660B electrochemical workstation. The electrochemical performances of samples were evaluated in two electrolytes, involving 1.0 mol L^{-1} $LiClO_4$/EC + DMC and 6.0 mol L^{-1} KOH. All experiments were carried out at room temperature in a standard three-compartment cell. A platinum foil and a double salt bridge saturated calomel electrode (SCE) were used as the counter electrode and the reference electrodes for non-aqueous electrolyte, a nickel foil and an Hg–HgO were chosen as the counter electrode and the reference electrodes for aqueous electrolyte, respectively.

3 Results and discussion

Nitrogen sorption measurements to characterize the pore structure of the synthesized WMC are shown in Fig. 1. The porosity and surface area of an electrode material determine the extent of electrode–electrolyte interaction. The N_2 adsorption–desorption isotherm of WMC is defined as type IV, which is caused by the capillary condensation of mesopores in the materials. The BET surface area, the single point total pore volume, and adsorption average pore width are 818 m^2 g^{-1}, 1.43 cm^3 g^{-1}, and 7.01 nm, respectively (Table 1). The pore size distribution calculated from the adsorption branch by the BJH method is uniform and a peak is centered at ~9.32 nm (see Fig. 1b). It can be assumed that the presence of these mesopores will lead better electrolyte diffusion into the electrode while the micropores ensure a high surface area and facilitate a complete redox reaction and wettability, and thus rise to a higher capacitance. Escribano group also had proved that the pore size distribution of the carbon material strongly influences the electrochemical behavior [13]. Carbon materials with 3–13 nm pore diameter have the best voltammetry characteristics and the highest capacitance values. Therefore, as-synthesized WMC could be a good candidate as electrode material in supercapacitance application.

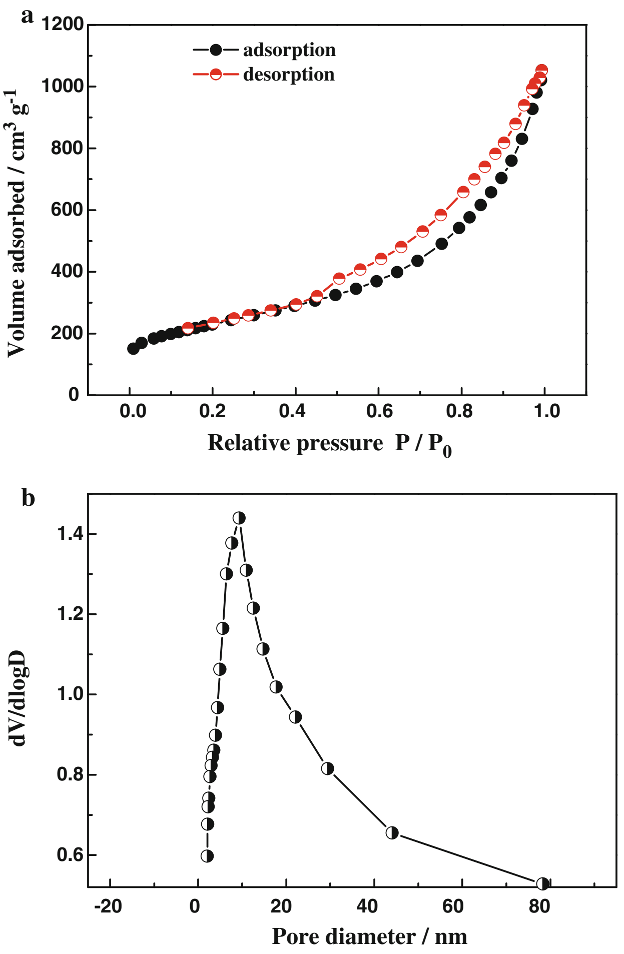

Fig. 1 N_2 adsorption–desorption isotherm (**a**) and the BJH pore size distribution curve (**b**) of WMC

Figure 2a shows the cyclic voltammetry curves of WMC in 1.0 mol L^{-1} $LiClO_4$/EC + DMC non-aqueous electrolyte at the sweep rates varying from 1 to 50 mV s^{-1}. It is well known that an ideal capacitance behavior of a carbon material electrode is expressed in the form of a rectangular shape on the voltammetry characteristics. However, in Fig. 2a the slopes of current variation versus potentials are obvious to indicate that forms IR drops in the carbon material electrodes, at the same time, the short penetration distance and the easy access to porous structures are very important in the electrochemical performance of WMC. Compared to the aqueous electrolyte, the penetration ability of EC + DMC electrolyte into the inner active surface of micropores is quite limited due to the large steric size of EC and DMC molecules. With the increase of sweep rate, the CVs become tilted. This reflects

Table 1 Pore structure parameters of WMC

Sample	S_{BET} ($m^2\ g^{-1}$)	V_{total} (N_2) ($cm^3\ g^{-1}$)	V_{micro} ($cm^3\ g^{-1}$)	V_{meso} ($cm^3\ g^{-1}$)	Ratio of mesopore (%)	$D_{average}$ (nm)
WMC	818	1.43	0.05	1.38	96.50	7.01

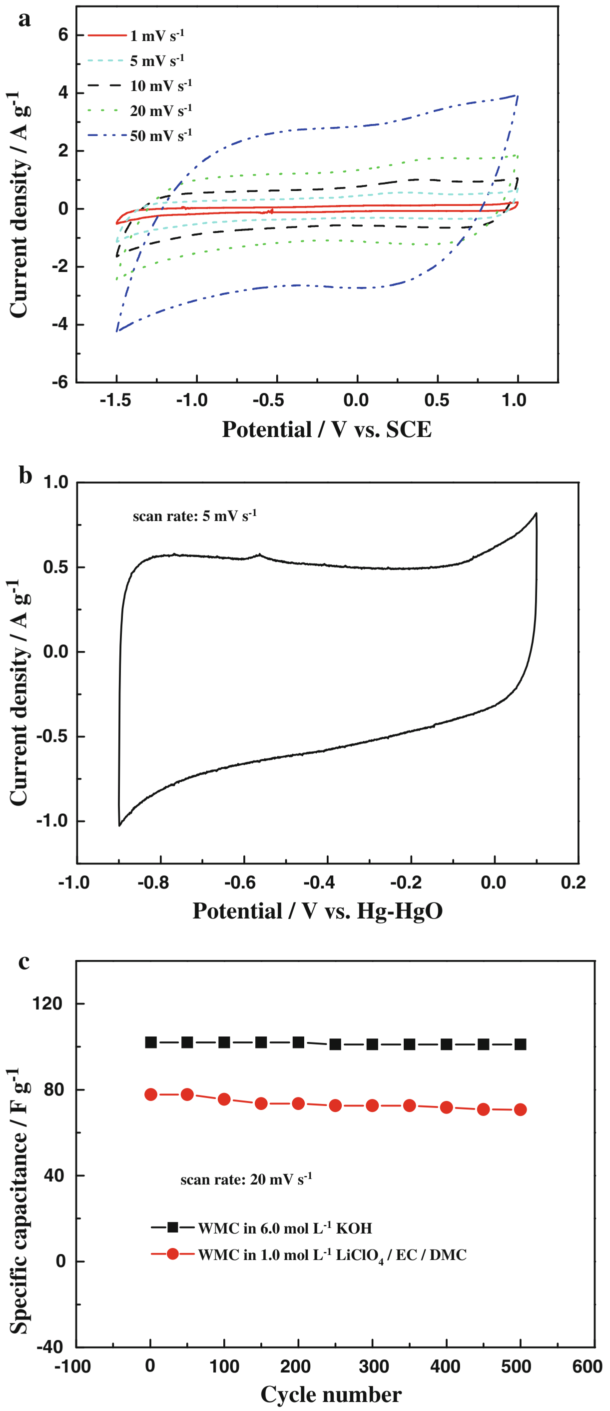

Fig. 2 Cyclic voltammograms of WMC in 1.0 mol L^{-1} $LiClO_4$/EC + DMC electrolyte (**a**) and 6.0 mol L^{-1} KOH electrolyte at a sweep rate of 5 mV s^{-1} (**b**), and cycle life of WMC in $LiClO_4$/EC + DMC and KOH electrolytes (**c**)

that the IR drop for electrolyte motion in carbon pores affects the double-layer formation mechanism at high sweep rates, in which the charge stored is recognized to be distributed. The increase in the cathodic current and anodic current with the sweep rate intensifies the potential difference between the top and bottom of the pores, and results in the delayed current response as shown in the tilted voltammograms. It is well-known that in the aqueous electrolytes, the OH^- anions are adsorbed in the bare state and thus their size is much smaller than that of EC and DMC. The ions could diffuse into the inner surface of mesoporous channels and even the microporous channels and the CV curve maintains a relatively good rectangular shape, indicating its excellent capacitance behaviors (see Fig. 2b). Cycling stability of WMC was evaluated by repeated cyclic voltammetry at a rate of 20 mV s^{-1} in 1.0 mol L^{-1} $LiClO_4$/EC + DMC and 6.0 mol L^{-1} KOH, as shown in Fig. 2c. The cycling stability of WMC in 6.0 mol L^{-1} KOH has better than in 1.0 mol L^{-1} $LiClO_4$/EC + DMC. There is a decrease of 9% in the initial capacitance in $LiClO_4$/EC + DMC and a ~0.2% decrease in KOH after 500 cycles. This is because the large steric size of EC and DMC molecules may block some small pores during cycling measurement.

As illustrated in Fig. 3a, the charge/discharge behaviors of WMC in non-aqueous electrolyte are investigated and the curves are asymmetrical triangles, exhibiting the non-linearity in part. The similar phenomenon was found when we had investigated the electrochemical characterizations of carbon nanospheres as electrode materials in supercapacitor. Carbon materials prepared under low temperature contain some functional groups, such as –OH and –COOH, which provide the pseudocapacitance via redox reaction in charge/discharge [5]. Conway's group gave three factors to explain this as follows: (1) that of the direct ESR; (2) and of redistribution of charge within the pores of the carbon material structure during charging or discharging; (3) any pseudocapacitance contribution due to redox-active surface functional groups [14]. The charge/discharge curves in Fig. 3b are linear and symmetrical, and the IR drop is not obvious, which shows good capacitance, highly reversible charge/discharge efficiency. However, in contrast to aqueous system, the non-aqueous capacitors have a wide potential window and obtain the higher energy density and power density. The specific capacitance of the WMC is calculated as follows:

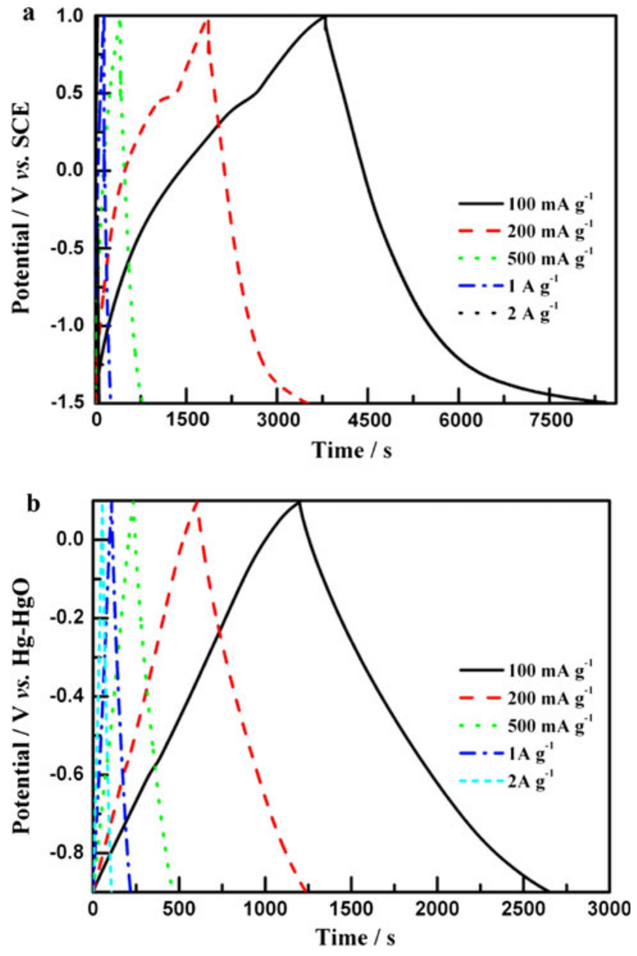

Fig. 3 Galvanostatic charge/discharge curves in 1.0 mol L^{-1} $LiClO_4$/EC + DMC electrolyte (**a**) and 6.0 mol L^{-1} KOH electrolyte (**b**)

$$C = \frac{it}{\Delta V m} \tag{1}$$

where i is the current of charge/discharge, t is the duration time of discharge, ΔV is the potential window (2.5 V), and m is the mass of active materials in the supercapacitor. The specific energy density (E) and power density (P) are calculated as follows:

$$E = \frac{1}{2} C (\Delta V)^2 \tag{2}$$

$$P = \frac{i \Delta V}{m} \tag{3}$$

where C is the specific capacitance, m, ΔV, and i have the same meanings mentioned above [15]. Based on Eq. 2, two methods can be considered to enhance the energy density of a supercapacitor. One is to increase the specific capacitance of the electrode material and the other enlarges the operating voltage. Since the energy density of a supercapacitor is proportional to the square of the operating voltage and the latter is a more effective way to improve the energy density. Based on Eq. 3, increasing the operating voltage is also a strategy to improve the power density. The nanoporous carbon-based supercapacitors in aqueous electrolytes could suffer from the low specific energy and specific power because of their restricted potential window of approximately 1.0 V. On the other hand, the use of non-aqueous electrolytes would provide a wide stable potential window, which can contribute to improve energy density and power density. Table 2 lists specific capacitance, specific energy, and specific power derived from WMC electrode in non-aqueous and aqueous electrolytes. The WMC electrode gives a similar maximum specific capacitance of ~147 F g^{-1} in 6.0 mol L^{-1} KOH aqueous solution and 1.0 mol L^{-1} $LiClO_4$/EC + DMC non-aqueous solution. While, Hulicova et al. [16] also reported on carbon material in aqueous and non-aqueous supercapacitors, which were prepared by pyrolysis the mixture of melamine, formaldehyde, and fluorine mica at 1000 °C, performing better in KOH compared to $TEABF_4$/PC and the obtained capacitance was only 84.61 F g^{-1} versus 30.48 F g^{-1}. In this study, the performance of as-synthesized WMC is superior to them in aqueous and non-aqueous electroytes. It is noted that the comparatively specific energy and specific power of WMC electrode for non-aqueous and aqueous electrolytes are listed in Table 2. For a specific power of 0.1 kW kg^{-1}, the specific energy of capacitor using the 6.0 mol L^{-1} KOH electrolyte is calculated to be 20.3 Wh kg^{-1}. When the specific power is increased to

Table 2 The effect of current density of charge/discharge on specific capacitance, specific power, and specific energy in 1.0 mol L^{-1} $LiClO_4$/EC + DMC and 6.0 mol L^{-1} KOH electrolyte

Current density (A g^{-1})		0.1	0.2	0.5	1	2
Specific capacitance (F g^{-1})	$LiClO_4$/EC + DMC	147	136	68	45	20
	KOH	146	128	110	104	100
Specific power (kW kg^{-1})	$LiClO_4$/EC + DMC	0.25	0.5	1.25	2.5	5.0
	KOH	0.1	0.2	0.5	1.0	2.0
Specific energy (Wh kg^{-1})	$LiClO_4$/EC + DMC	127.6	118.1	59.0	39.1	17.4
	KOH	20.3	17.8	15.3	14.4	13.9

2.0 kW kg^{-1}, a decrease in the specific energy to 13.9 Wh kg^{-1} is observed. In contrast to KOH electrolyte, in the 1.0 mol L^{-1} $LiClO_4$/EC + DMC electrolyte, the specific energy of the capacitor is significantly improved up to 127.6 Wh kg^{-1} with a specific power of 0.25 kW kg^{-1}. With the increase of specific power (5.0 kW kg^{-1}), the specific energy is also maintained at 17.4 Wh kg^{-1}. Although the specific capacitances of WMC electrodes are very near in both electrolytes, due to the broad potential window of 2.5 V, the specific energy in the non-aqueous electrolyte is six times more than that in KOH. The significant improvement in the specific energy in the 1.0 mol L^{-1} $LiClO_4$/EC + DMC electrolyte indicates that the mesoporous carbon and the use of the non-aqueous electrolyte could be an effective way to improve the specific energy of supercapacitors. Therefore, the development of nanoporous carbon-based electrodes is quite important in enhancing the energy and power density for supercapacitors in non-aqueous system.

4 Conclusions

In summary, we have evaluated the electrochemical behavior of WMC with high mesoporous ratio. Especially, the energy density and power density have been investigated in $LiClO_4$/EC + DMC electrolyte. A wide voltage window of 2.5 V is obtained in $LiClO_4$/EC + DMC and the specific capacitance and the specific energy is up to 147 F g^{-1} and 127.6 Wh kg^{-1} at current density of 100 mA g^{-1}, respectively.

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