Short communication

Cresol–formaldehyde based carbon aerogel as electrode material for electrochemical capacitor

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Abstract

Carbon aerogels have been prepared through a polycondensation of cresol (Cm) with formaldehyde (F) and an ambient pressure drying followed by carbonization at 900 °C. Modification of the porous structures of the carbon aerogel can be achieved by CO_2 activation at various temperatures (800, 850, 900 °C) for 1–3 h. This process could be considered as an alternative economic route to the classic RF gels synthesis. The obtained carbon aerogels have been attempted as electrode materials in electric double-layer capacitors. The relevant electrochemical behaviors were characterized by constant current charge–discharge experiments, cyclic voltammetry and electrochemical impedance spectroscopy in an electrolyte of 30% KOH aqueous solution. The results indicate that a mass specific capacitance of up to $78 \, \mathrm{F \, g^{-1}}$ for the non-activated aerogel can be obtained at current density $1 \, \mathrm{mA \, cm^{-2}}$. CO_2 activation can effectively improve the specific capacitance of the carbon aerogel. After CO_2 activation performed at 900 °C for 2 h, the specific capacitance increases to $146 \, \mathrm{F \, g^{-1}}$ at the same current. Only a slight decrease in capacitance, from 146 to $131 \, \mathrm{F \, g^{-1}}$, was observed when the current density increases from 1 to $20 \, \mathrm{mA \, cm^{-2}}$, indicating a stable electrochemical property of carbon aerogel electrodes in 30% KOH aqueous electrolyte with various currents.
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Keywords: Carbon aerogel; Electrochemical capacitor; Specific capacitance; Aqueous electrolyte

1. Introduction

Supercapacitors, as energy storage devices, have a high energy density, great power density and long cycle life [1], and are of great interest in use of hybrid electrical vehicles, digital telecommunication systems, computers and pulsed laser system, etc. Since the energy density and cycle life of conventional rechargeable batteries were found to decrease with increasing power density, and conventional capacitors were too low capacity to deliver enough energy, supercapacitors become the promising device in this field [2]. Supercapacitors fall into two categories: electric double-layer capacitors (EDLCs) and redox pseudocapacitors. The performance of EDLCs is based on the accumulation of charges in the electrical double-layer without the faradaic reactions. Since charges are separated within a very short distance, the capacitance of EDLCs is usually very high compared with that of conventional capacitors. The capacitance of the EDLCs is proportional to the electrode/electrolyte interface. The micropores of electrode play an essential role for ions adsorption although a significant fraction of the micropores may not be electrochemically accessible, and the mesopores are necessary for their quick transportation to the bulk of the material [3–5].

Porous carbons, due to their large specific surface area, high pore accessibility, excellent thermal and chemical stability as well as relative low cost, are extremely attractive as electrode materials for EDLCs. Activated carbon, carbon blacks or carbon nanotubes as electrodes have been widely investigated [6–10]. Carbon aerogels, first patented by Pekala in 1990, have a monolithic three-dimensional porous network consisting of carbon nanoparticles, which exhibit a high surface area, controllable pore size distribution, and good electrical conductivity [11]. Using carbon aerogels as electrode materials is promising and interesting. Relevant research regarding to this subject has been conducted by Pekala's and Fricke's group [12–15]. The electrochemical behaviors of carbon aerogel

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electrodes obtained from resorcinol–formaldehyde (RF) system are competitive with commercially available carbon materials. However, a key factor in the limitation for an industrial production is the price of resorcinol. In the present study, cresol was used as an alternative material to prepare carbon aerogel by sol–gel method via ambient pressure drying. The obtained carbon aerogels exhibit high specific surface area. The electrochemical behavior of the sample as electrode materials in EDLCs was characterized by constant current charge/discharge, cyclic voltammetry (CV), and electrochemical impedance spectroscopy.

2. Experimental

2.1. Preparation of carbon aerogel

Chemically pure cresol (Cm), with a composition of 27.8% phenol, 14.7% o-cresol, 45.5% m,p-cresol and 12.0% others, was used. Formaldehyde (F) is 37–40% aqueous solution with an analytical purity of sodium hydroxide and ethanol. All chemicals were used as received without further purification. CmF aerogel were synthesized through polycondensation of Cm with F catalyzed by sodium hydroxide (Cat). Because the solubility of cresol in water is only about 2 wt.% at 25 °C, certain amount of ethanol (E) was added as a co-solvent to increase the solubility of cresol in water and lead a homogeneous system. The CmF aqueous solution with a molar ratio of Cm:F:E:water:Cat being 6:12:10:60:0.1 was kept at 90 °C for 7 days to obtain the CmF aquagel. After being dried at 50 °C at ambient pressure directly, the obtained monolithic CmF organic aerogels, about 10 g, were carbonized in a tubular furnace with quartz tube of 25 mm i.d. under flowing nitrogen of 80 ml min^{-1} using the ramp cycle as: 25–250 °C in 60 min, held at 250 °C for 30 min, 250–600 °C in 300 min and held at 600 °C for 30 min, 600–900 °C in 60 min and kept at 900 °C for 30 min, then the furnace was allowed to cool down to room temperature under the nitrogen flow. The obtained CmF carbon aerogel sample was denoted as CmF. For the CO_2 activation experiment, the carbon aerogel, about 5 g, was heated in tubular furnace as carbonization at 10 °C min^{-1} to 800, 850, 900 °C, respectively, in nitrogen flow rate of 80 ml min^{-1}, and retained at the temperature for 1–3 h under CO_2 flow of 30 ml min^{-1}, then cooled down to the room temperature under nitrogen flow of 80 ml min^{-1}. The CO_2 activated sample was denoted as CmF $-$ T/t, where T and t corresponds to the activated temperature and time, respectively.

2.2. Characterization of carbon aerogels

Nitrogen adsorption isotherms were recorded with an ASAP2010 adsorption analyzer (micromeritics) at 77 K. Prior to measurements, the sample was degassed at 300 °C for 2 h. The BET surface area was calculated from the adsorption data in the relative pressure interval from 0.04 to 0.2. The total pore volume was estimated from the amount adsorbed at the relative pressure of 0.99. And t-plot method was used to determine the micropore surface area and micropore volume.

2.3. Electrochemical measurements

The carbon electrode was prepared by mixing the carbon aerogel with polytetrafluoroethylene in a weight ratio of 95 to 5, using ethanol to wet the mixture. The paste was then rolled into 150 μm thick films. Pieces of film, typical 1 cm^2 size and weight of the carbon active material around 5–10 mg, were then pressed at 10 MPa onto nickel foam. The foam was tabbed using copper wire that was insulated from the electrolyte using epoxy resin. A unit cell for capacitor was fabricated with two electrodes separated by a thin polymer in 30% KOH aqueous solution as electrolyte. The constant current charge/discharge experiment was carried out in a current range of 1–20 mA at room temperature using a PCBT-138-8D battery test instrument (Wuhan Lisun Instruments, China). The cell capacitance was calculated from the slope of discharge. Cyclic voltammetry (CV) experiment was realized by using a Bioanalytical Systems voltammetric analyzer (BAS 100). In CV experiments, one electrode was used as working electrode and another electrode was used as counter and reference electrodes. The experiments were performed within 0–0.8 V versus reference electrode. Electrochemical impedance spectroscopy measurement was performed in a three-electrode arrangement using same electrolyte. Platinum gauze was used as counter electrode and the reference electrode was Ag/AgCl (saturated KCl). The experiment was carried out by 1280 Solartron potentiostat/galvanostat within a frequency range of 20 kHz–0.01 Hz at open circuit potential with an ac-amplitude of 10 mV.

3. Results and discussion

3.1. Physical properties of carbon aerogels

The textural parameters (specific surface area, pore volume and average pore diameter, etc.) of carbon aerogels obtained from N_2 adsorption measurements are listed in Table 1. The non-activated sample CmF shows a lowest specific surface area and pore volume, however a largest average pore diameter. CO_2 activation can dramatically improve the porosity of the carbon aerogels, especially at a high activation temperature of 900 °C. With increasing the CO_2 activation temperature from 800 to 900 °C, both the specific surface area and the pore volume are enhanced from 401 to 908 m^2 g^{-1} and 0.22–0.43 cm^3 g^{-1}, respectively, which is mainly due to the contribution of micropores generated during CO_2 activation process. Moreover, a prolonged activation time to 2 h at fixed activation temperature of 900 °C leads to a remarkable increase of the specific surface area and the pore volume. Sample CmF-900/2 has a high up to 1418 m^2 g^{-1} of surface area and 0.69 cm^3 g^{-1} of total pore volume. Further increase of activation time to 3 h cannot impose much stronger effect on the structural modification of the carbon aerogels.

Compared to the RF carbon aerogel, the non-activated CmF carbon aerogel has lower specific surface area and larger pore size [12,13]. This may be caused by the lower reaction activation of cresol than that of resorcinol, which leads to longer time for gel formation and aerogel particle growth. The acti-

Table 1
Porous textural parameters of carbon materials and their specific capacitance evaluated from the constant current charge–discharge testing[a]

Sample	S_{BET} (m^2 g^{-1})	S_{mic} (m^2 g^{-1})	V_{total} (cm^3 g^{-1})	V_{mic} (cm^3 g^{-1})	D_{max} (nm)	Specific capacitance (F g^{-1})
CmF	245	140	0.17	0.06	27	78
CmF-800/1	401	320	0.22	0.15	6.5	71
CmF-850/1	499	429	0.27	0.20	19.4	97
CmF-900/1	908	823	0.43	0.38	8.7	108
CmF-900/2	1418	1222	0.69	0.57	11.9	146
CmF-900/3	1390	1203	0.67	0.56	9.7	142

The specific capacitance was evaluated from the constant current charge–discharge testing in 30% KOH solution at current density of 1 mA cm^{-2}.

[a] S_{BET}: apparent surface area calculated by BET method; S_{mic}, V_{mic}: micropore surface area and micropore volume calculated by t-plot method; V_{total}: total pore volume at $p/p_0 = 0.99$; D_{max}: pore sizes at maxima of the pore size distribution (from desorption branch).

vated CmF carbon aerogel has higher specific surface area than that of activated RF carbon aerogel. When the cloth-reinforced RF carbon aerogel was activated in CO_2 at 950 °C, the BET surface area increases from 534 to 923 m^2 g^{-1} [14], In our case, when the CmF carbon aerogel was activated in CO_2 at 900 °C for 2 h, the BET surface area increases from 245 up to 1418 m^2 g^{-1}. This illustrates that although the CmF carbon aerogel has low surface area, it is much easy to be modified to increase the surface area by CO_2 activation compared to RF aerogel.

3.2. Constant current charge–discharge

The electrochemical behaviors of the carbon aerogel electrodes for EDLCs were tested under galvanostatic conditions. The charge–discharge curves of samples measured in 30% KOH aqueous solution at a constant current density of 1 mA cm^{-2} are shown in Fig. 1. A sharp change in voltage at the beginning of the discharge is visible, which is associated with the equivalent series resistance (ESR) of the EDLCs [1]. The capacitance of the EDLCs was calculated according to $C = I \times \Delta t / \Delta V$, where I is the current, Δt the discharge-time and ΔV is the voltage. The specific capacitance C_g was evaluated based on equation $C_g = 2 \times C/m$, where m is mass of carbon aerogel in one electrode, because two electrodes are arranged in series within the EDLC. The relevant results are compiled in Table 1. The data reveal that the specific capacitance of non-activated sample CmF is 78 F g^{-1} which is higher than that reported RF based carbon

aerogel when 5 M KOH aqueous solution as electrolyte [13], and similar to that reported cloth-reinforced RF carbon aerogel when 4 M KOH aqueous solution as electrolyte [14], even if the CmF has lower specific surface area. This may be explained from the different pore distribution between the CmF and RF carbon aerogel. The average pore size of CmF carbon aerogel is larger than RF carbon aerogel, it will benefit to quick transportation of electrolyte ions to the bulk of the material when it used as electrode material in EDLC. From Table 1, it can be seen that sample non-activated CmF has a comparable capacitance with sample CmF-800/1 although the surface area of sample CmF is rough half lower than that of sample CmF-800/1. This might be due to a significantly large average pore diameter (27 nm) in sample CmF, which is credibly able to be as a mass transfer path to avail the access of electrolyte molecular to the micropore. The increase of CO_2 activation temperature leads to an obvious enhancement of the specific capacitance of the carbon aerogel electrode, especially for carbon aerogel activated at 900 °C, which seems to be associated with the remarkable increase of specific surface area during the CO_2 activation. The highest specific capacitance (C_g being 146 F g^{-1}) was achieved with sample CmF-900/2, activated with CO_2 at 900 °C for 2 h. Compared the specific capacitance and textural parameter with non-activated sample, the specific surface area increases more than five times but the specific capacitance increases only one time. It illuminates that more fraction of the micropores in CmF-900/2 is not electrochemically accessible when the pore size decreased [14]. Prolonging the activated time to 3 h the specific capacitance of CmF-900/3 is similar to that of CmF-900/2 because of nearly same surface area in between. Associating the capacitance value with the textural parameters of carbon aerogel electrode, one may figure out that a high surface area, essentially micropore surface area, combined a relative large average pore diameter, i.e. a certain amount of mesopore or even macropores presented in carbon aerogel, is the crucial factor to contribute a high capacitance.

The discharge curves of sample CmF-900/2 at different current density were shown in Fig. 2a, and the corresponding calculated specific capacitance versus the current density was plotted in Fig. 2b. The specific capacitance decreases slightly from 146 to 131 F g^{-1} with the current density increasing from 1 to 20 mA cm^{-2}, which indicates a good behavior in power, as observed in other carbon [16].
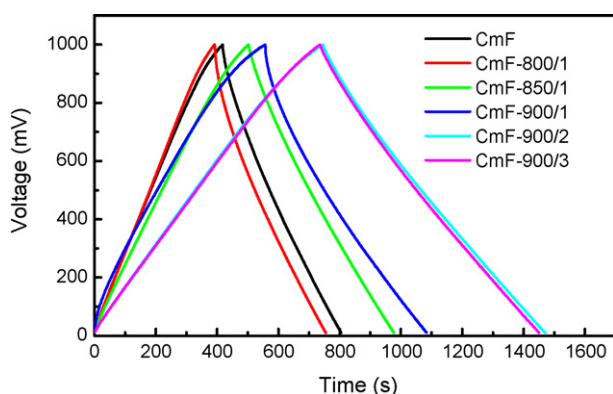

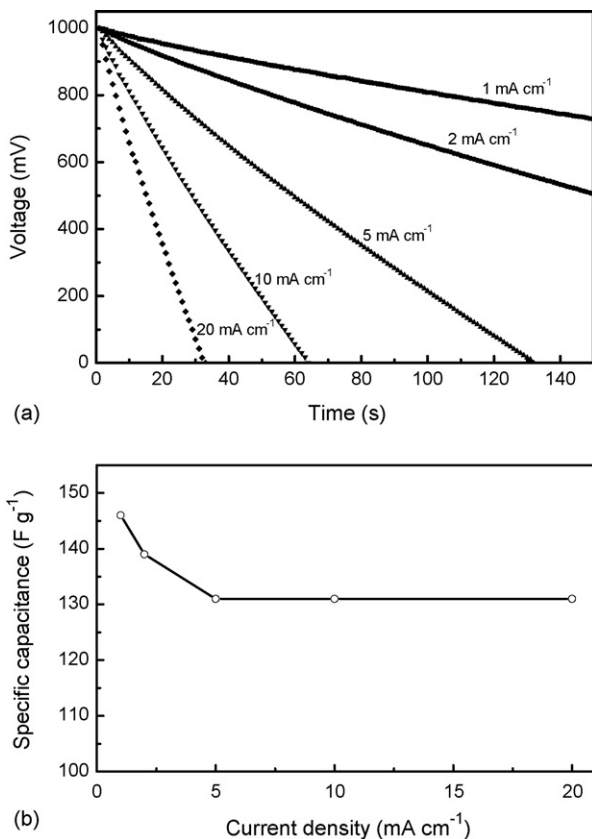Fig. 1. Potential–time curves obtained at current density of 1 mA cm^{-2}.

Fig. 2. (a) Discharge–time curves obtained at 1–20 mA cm^{-2}. (b) Specific capacitance at different current density of sample CmF-900/2.

3.3. Cyclic voltammetric

Cyclic voltammetry (CV) measurement was used to determine the electrochemical properties of the samples. The CV curves were recorded at room temperature in 30% KOH aqueous solution at a potential range of 0–0.8 V with scan rate of 10 mV s^{-1}. Fig. 3 shows two representative CV curves of sample non-activated CmF and CmF-900/2. In both cases a nearly rectangular shapes are observed, and over most of the potential range the currents are nearly constant, which implies the ideal
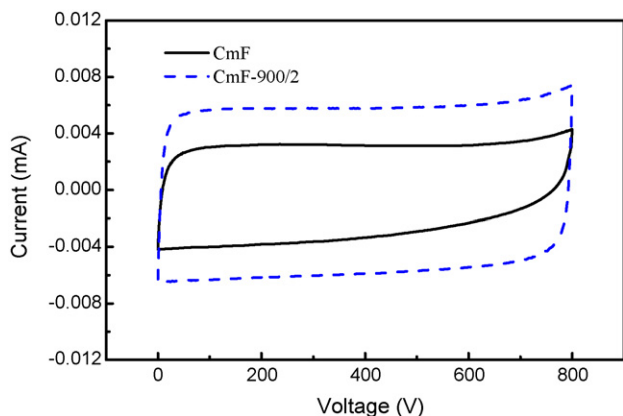

Fig. 3. Voltammograms obtained at 10 mV s^{-1} for the EDLCs with CmF and CmF-900/2 as electrode material and 30% KOH aqueous solution as electrolyte.
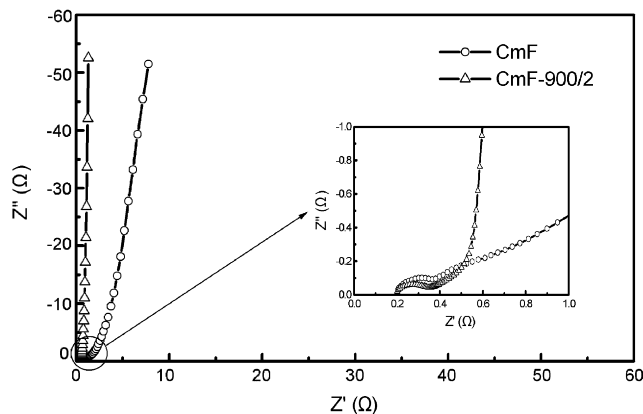

Fig. 4. Impedence plots measured from 20 kHz to 0.01 Hz for sample CmF and CmF-900/2.

capacitive behavior. There is no evidence for any redox currents on both positive and negative sweeps in the chosen potential range, which is the characteristic of EDLCs made from carbon-based electrodes.

3.4. Electrochemical impedance spectroscopy

Impedance spectroscopy is a very useful technique to derive the capacitance and gives complementary frequency dependent information. The Nyquist plots obtained for samples CmF and CmF-900/2 are shown in Fig. 4. A semicircle appears at high frequency with a transition to a sharp increase in the imaginary part of the impedance at lower frequency in the plots, which corresponds to a capacitive behavior. The high frequency intercept on the Z'-axis can be correlated to contact resistances at the interface of the carbon aerogel with current collector and internal contact effects inside the electrode. The semicircle is associated with the porous structure of the carbon, and the diameter of the semicircle is referred to the polarization resistance. Specific capacitances were calculated from impedance plots according to the equation: $C = -(2\pi f \times Z'')^{-1}$, where f and Z'' are frequency and imaginary impedance, respectively. Fig. 5 shows the capacitance of sample CmF and CmF-900/2 on frequency derived from impedance spectroscopy. The capacitance values of both samples derived at 0.01 Hz from impedance is 64 and 139 F g^{-1}, which agree
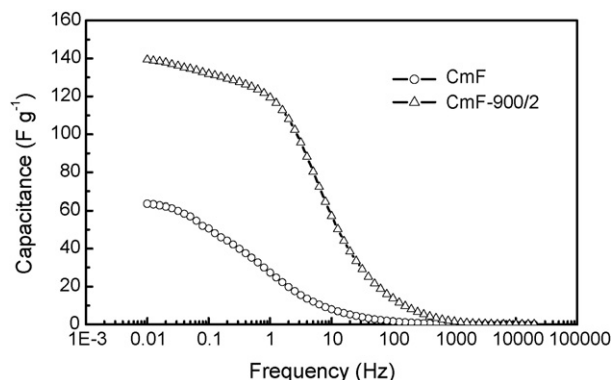

Fig. 5. Capacitance as a function of frequency for sample CmF and CmF-900/2 in 30% KOH.

well with the capacitance values estimated from constant current charge–discharge method. From the plots, it can be seen that the samples exhibit a similar frequency dependency, where the capacitances decrease noticeably at high frequency.

4. Conclusions

The CmF carbon aerogels were successfully synthesized by sol–gel polycondensation of a mixed cresol with formaldehyde under sodium hydroxide via ambient pressure drying to get organic aerogel followed by carbonization of the organic aerogel in an inert atmosphere. The obtained samples are alternative electrode materials for EDLCs, and the specific capacitance of up to 78 F g^{-1} was obtained at current density 1 mA cm^{-2} using 30% KOH aqueous solution as electrolyte. The specific surface area, pore volume and pore size of CmF carbon aerogels can be significantly increased by CO_2 activation. When sample activated 2 h at 900 °C, the highest specific capacitance, up to 146 F g^{-1}, was obtained. When the current density increases from 1 to 20 mA cm^{-2}, only a slight decrease in capacitance from 146 to 131 F g^{-1} has been observed. This trend indicates a good behavior in power. Further increasing of activation time, the physical properties and the specific capacitance changed little.

Acknowledgment

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