

Studies on preparation and performances of carbon aerogel electrodes for the application of supercapacitor

Jun Li^a, Xianyou Wang^{a,*}, Qinghua Huang^a, Sergio Gamboa^b, P.J. Sebastian^b

^a College of Chemistry and Chemical Engineering, Xiangtan University, Hunan 411105, China

^b Solar-Hydrogen-Fuel Cell Group, CIE-UNAM, Temixco 62580, Morelos, Mexico

Received 17 August 2005; accepted 19 September 2005

Available online 29 November 2005

Abstract

Carbon aerogel was prepared by the polycondensation of resorcinol (*R*) with formaldehyde (*F*), and sodium carbonate was added as a catalyst (*C*). Physical properties of carbon aerogel were characterized by infrared spectrometer (IR), X-ray diffraction (XRD) and scanning electron microscopy (SEM). It is found that carbon aerogel is an amorphous material with a pearly network structure, and it consists of one or two diffuse X-ray peaks. The results of cyclic voltammetry indicated that the specific capacitance of a carbon aerogel electrode in 6 M KOH electrolyte was approximately 110.06 F g^{-1} . Through the galvanostatic charge/discharge measurement, it was found that the electrode is stable in KOH electrolyte, the maximum capacitance of the supercapacitor with carbon aerogel as the electrode active material was 28 F g^{-1} . Besides, the supercapacitor has long cycle life. Thus, it was thought that the carbon aerogel is an excellent electrode material for a supercapacitor.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Supercapacitor; Electrode material; Carbon aerogel; Specific capacitance

1. Introduction

The supercapacitor is an emerging power source that plays an important role in meeting the demands of new energy storage devices and systems both now and in the future [1]. It has much lower energy density, higher power and much longer shelf and cycle life than batteries [2]. Great attention has been focused on electrochemical supercapacitor energy-storage systems in recent years on account of the application to electric vehicles, pulse power, and backup sources [3]. For these applications, the development of high energy density supercapacitors has been undertaken by various groups all over the world.

In supercapacitors, energy is stored in the double-layer and as, pseudo-capacitance separately. In all the electrode materials of supercapacitors, carbon material has been the widely used recently. Double-layer capacitor electrodes have been fabricated using activated carbon, carbon black and aerogel particulates and carbon cloth [4–6]. In contrast, carbon aerogels, which are highly porous material, represent a promising and inno-

vative material because of their attractive properties such as a high electrical conductivity ($25\text{--}100 \text{ S cm}^{-1}$), a high porosity (80–98%), controllable pore structure and highly surface area (up to $1100 \text{ m}^2 \text{ g}^{-1}$) thus making the monolithic porous carbon aerogels very suitable for supercapacitor and rechargeable batteries [7–10].

In this paper, carbon aerogel was prepared by the polycondensation of resorcinol (*R*) with formaldehyde (*F*). There are four steps in the preparation of carbon aerogels, namely sol–gel formation, solvent exchange, atmospheric drying and pyrolysis all of which affect the porosity of carbon aerogels. And the electrochemical characteristics of carbon aerogel electrodes for the application of supercapacitor have been studied.

2. Experimental

2.1. Preparation of carbon aerogel

Carbon aerogel was derived from pyrolysis of a resorcinol–formaldehyde (RF) gel. The molar ratio of formaldehyde to resorcinol was held at a constant value of 2. They were dissolved in distilled ion-exchanged water, the mass percentage of the reactants in solution was set at RF = 40%, and the molar ratio

* Corresponding author. Tel.: +86 732 8293371; fax: +86 732 8292061.
E-mail address: wxianyou@yahoo.com (X. Wang).

of resorcinol to catalyst (C) was set at $R/C = 500, 1000, 1500$. Na_2CO_3 was used as the catalyst for a fine pore structure and a high specific surface area [7]. Sol-gel polymerization of the mixture was carried out in a sealed glass cylinder by holding the mixture at 298 K for 24 h, at 333 K for 72 h, and at 353 K for 48 h. Acetone was selected as the drying solvent for ambient drying because of its low surface tension ($20.66 \text{ dyn cm}^{-1}$) and its low boiling point (56.5°C) which reduces the shrinkage of RF gels of during drying [7]. The wet gels were performed at 50°C for 6 days, and then RF gels were dried completely at ambient conditions for 3 days. After the ambient drying process, the carbon aerogels were obtained by carbonization at 1073 K for 3 h under a flow of pure Ar gas.

2.2. Measurement techniques of structural characterization

- (1) The IR measurements of different samples were performed with a Fourier transform infrared (FTIR) spectrometer (Perkin-Elmer Spectrum one) in the wavelength range from 4000 to 500 cm^{-1} , using the KBr disk method.
- (2) X-ray diffraction (XRD) of the carbon aerogel was performed in a diffractometer (D/MAX-3C) with Cu $\text{K}\alpha$ radiation and a graphite monochromator at 50 kV 100 mA. A peak corresponding to the carbon (002) reflection is included in this range.
- (3) Scanning electron microscopy (SEM) was also used to study the surface structure of the samples.

2.3. Evaluation of electrochemical properties

The mass ratio of carbon aerogel/graphite was 9:1, the powder mixture was mixed with 5 wt.% polytetrafluoroethylene (PTFE) (60%) used as a binder, then pressed to make a disk-like working electrode. A typical three-electrode test cell in electrolyte at room temperature was used for all electrochemical measurements. Carbon aerogels as electrode materials in supercapacitors were characterized using cyclic voltammetry. Cyclic voltammograms were obtained at different scan rates in various electrolytes. Galvanostatic charge/discharge behavior was performed under the application of a constant current in the voltage range between 0 and 1.0 V. All the measurements were carried out at room temperature.

3. Results and discussion

Energy storage in supercapacitors is the accumulation of ionic charges in the double-layer at the electrode/electrolyte interface, the high surface area and the porosity of the carbon aerogels are the basic requirements to achieve the rapid formation of a double-layer. Carbon aerogels are novel mesoporous carbon materials with an electrically conductive carbon network, a low mass density, and other interesting properties [11–16]. The structure and property of aerogels are affected mainly by the amount of reactant and catalyst. As a result, the structure, the pore size and the particle size can be controlled by operating the sol-gel process, R/C ratio plays a important role in the process [17–22].

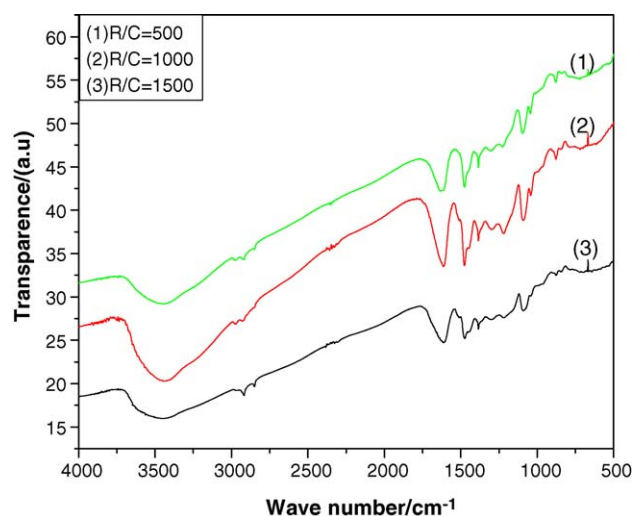


Fig. 1. IR transmittance spectra of samples.

The infrared optical transmittance spectra of organic aerogels prepared with different R/C ratios are shown in Fig. 1. It can be seen from Fig. 1 that there are no obvious changes in stretching vibration with the change of R/C ratios. The broad band in 3440 cm^{-1} is assigned to $-\text{OH}$ stretching vibration. This bond may be attributed to the adsorbed water in the pores of aerogels. In addition, hydrogen bonds may have some contribution. The $2850, 2918 \text{ cm}^{-1}$ absorption bands, respectively, belong to the CH_2 - and CH_3 -stretching vibrations and the 1475 cm^{-1} band is assigned to CH_2 -scissor vibration and CH_3 -flexural vibration. The band 1614 cm^{-1} is assigned to the stretching vibration of aromatic rings. The absorption peak of methylene-ether ($\text{CH}_2-\text{O}-\text{CH}_2$) is observed at 1055 and 1220 cm^{-1} . The $\text{CH}_2-\text{O}-\text{CH}_2$ bridge is a cross-linking bond formed between aromatic rings due to polycondensation [11]. IR measurements do establish the structure of organic aerogels.

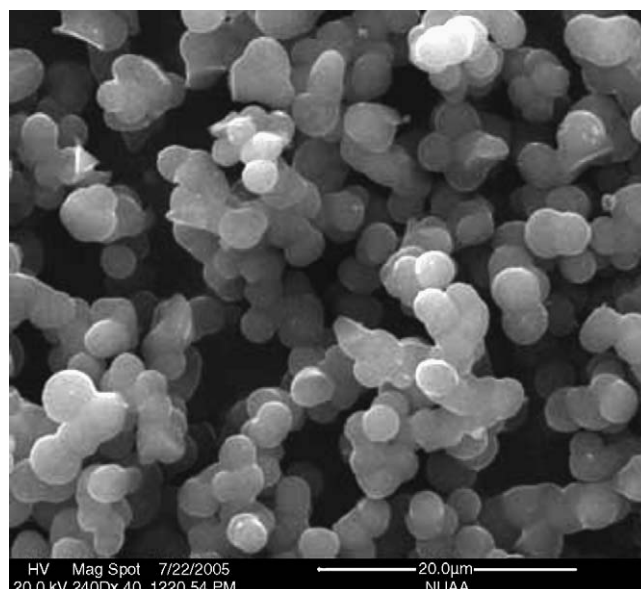


Fig. 2. SEM image of the carbon aerogel ($R/C = 1500$).

To further investigate the structure of carbon aerogels the SEM micrographs of the porous structure of carbon aerogels with R/C ratio 1500 and RF mass concentration 40% is shown in the Fig. 2. As being seen in the Fig. 2, a typical particle size was obtained by ambient drying of wet RF gels instead of conventional supercritical drying. Mesopores and micropores exist in the formation of carbon aerogels, the carbon spheres are all identical with the same diameter. Carbon aerogels consist of a three-dimensional network of interconnected carbon particles [9,10]. The carbon aerogels with a larger percentage of bigger pores are more suitable to high-power supercapacitor applications because the ions transport in to the pores easily. Pore size distribution plays an important role when we chose the ideal carbon material for supercapacitor.

The XRD measurement revealed the structure of the carbon aerogel. It is shown in the Fig. 3. It shows strong C (002) and weak C (101) diffraction lines at 2θ (Cu $K\alpha$) of 23.5° and 43.8° , respectively. The carbon aerogel can be regarded as partly graphitized carbon, though it differs from a graphic carbon.

Cyclic voltammetry was used in the determination of the electrochemical properties of the carbon aerogel electrodes. The experiment was performed in a three-electrode arrangement using 6 M KOH 1 M Na_2SO_4 2 M $(\text{NH}_4)_2\text{SO}_4$ electrolytes respectively. The specific capacitances of the electrodes were estimated from the following equation [23]:

$$C_{s,t} = \frac{I_a + |I_c|}{2W(dV/dt)} \quad (1)$$

where I_a , I_c , W and dV/dt are the current of anodic and cathodic voltammetric curves on positive and negative sweeps, mass of the composite, and the sweep rate, respectively.

Specific capacitances of carbon aerogel electrodes with the normal R/C ratio (500, 1000, 1500) in different electrolytes are given in Table 1 (scan rate: 1 mV s^{-1}), the mass percentage of the reactants in solution was set at 40%. It can be seen from Table 1 that the capacitance measured in the KOH electrolyte solution

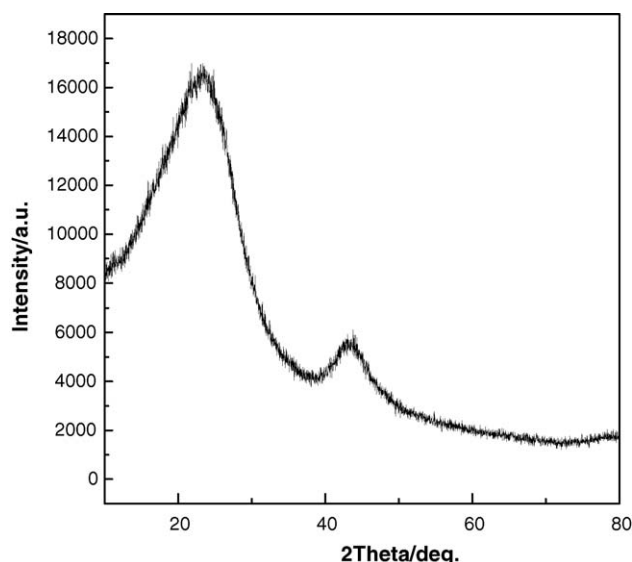


Fig. 3. XRD profiles for carbon aerogel ($R/C=1500$).

Table 1

Specific capacitance of carbon aerogel electrodes in different electrolytes (scan rate: 1 mV s^{-1})

R/C ratio	Electrolytes		
	$6 \text{ mol L}^{-1} \text{ KOH}$ (F g^{-1})	$1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ (F g^{-1})	2 mol L^{-1} $(\text{NH}_4)_2\text{SO}_4$ (F g^{-1})
500	96.26	75.20	50.75
1000	99.28	79.16	57.67
1500	110.06	87.22	69.87

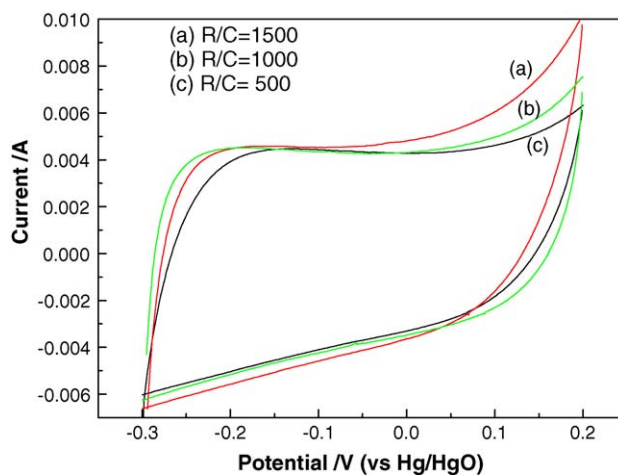


Fig. 4. Cyclic voltammogram of carbon aerogel electrodes with different R/C ratio.

was larger than other electrolytes, since K^+ and OH^- have an effectively electrical and ionic conductivities. It was suggested that the most suitable amount of R/C ratio was about 1500, for which the specific capacitance was approximately 110.06 F g^{-1} .

Fig. 4 shows the typical cyclic voltammograms (CV) for electrodes with different R/C ratios at a 1 mV/s scan rate. The carbon aerogel electrodes exhibited excellent electrochemical behavior in KOH electrolyte solution: they are very symmetric, the charging process is reversible in this potential range, the profiles of the three electrodes have rectangular-like shapes, the CV curves of carbon aerogel the mechanism of electrochemical storage between carbon aerogel electrodes could be described by the electrical double layer theory [11], it is suggested that ions can occupy some pores within the electrode to participate in the formation of the electrochemical double-layer.

To analyze the variation of capacitance with the scan rate, the CV curves were measured in KOH electrolyte, as shown in Fig. 5. The results from Fig. 5 are tabulated in Table 2. The high

Table 2

Specific capacitance of electrode with different scan rates in 6M KOH electrolyte

R/C ratio	Scan rate (mV s^{-1})	Specific capacitance (F g^{-1}) $6 \text{ mol L}^{-1} \text{ KOH}$
1500	1	110.06
	2	97.56
	5	79.18
	10	67.20

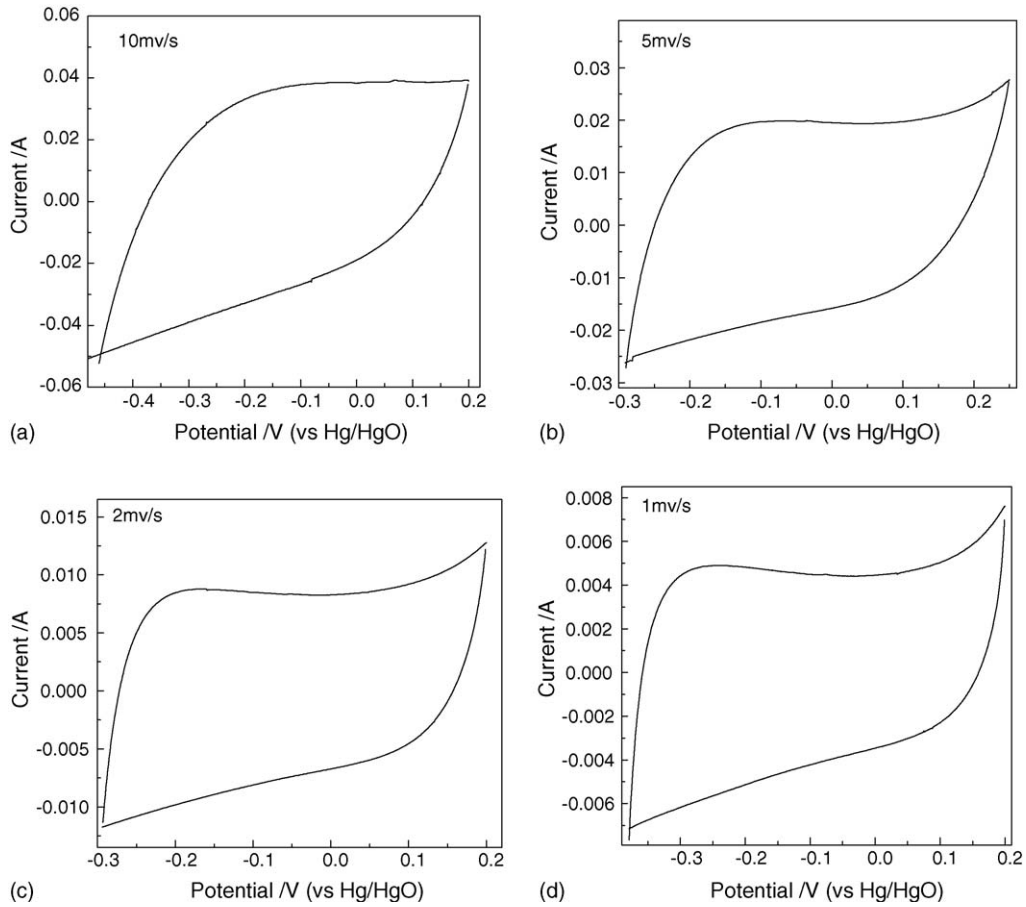


Fig. 5. Cyclic voltammogram of carbon aerogel electrodes depending on the scan rate. (a) 10 mV/s, (b) 5 mV/s, (c) 2 mV/s and (d) 1 mV/s.

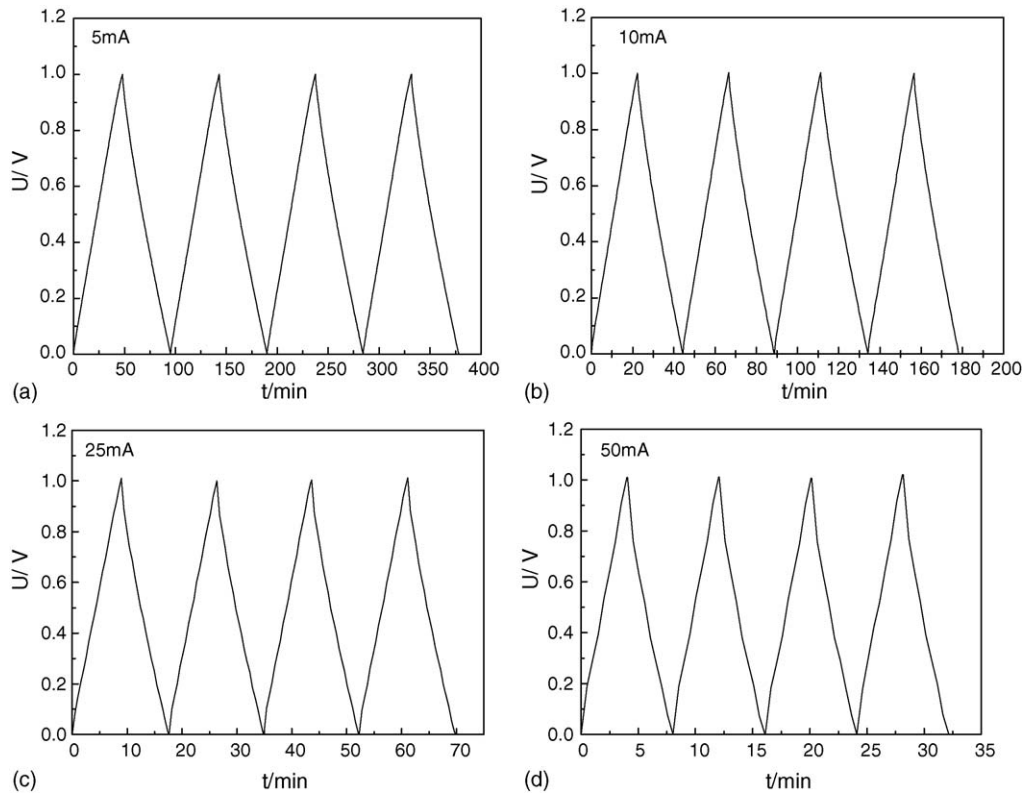


Fig. 6. Charge/discharge curves of aerogel electrodes measured at different current. (a) 5 mA, (b) 10 mA, (c) 25 mA and (d) 50 mA.

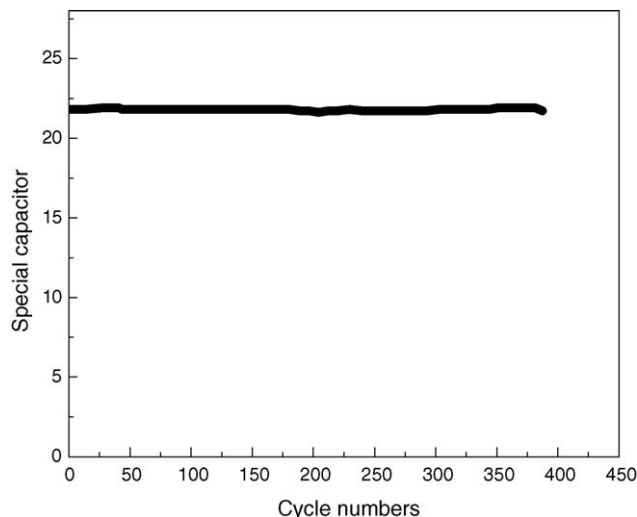


Fig. 7. Cycle life of carbon aerogel supercapacitor.

capacitance is observed at the lowest scan rate (1 mV s^{-1}), the curve is very symmetric. As the scan rate increases, the profiles become gradually depressed. It may be that the ions can transport in pores more easily at the low scan rate, however, ions cannot diffuse into the pores when each fast cycle is completed.

The charge/discharge curves of carbon aerogel electrodes measured in 6 M KOH at 5, 10, 25, and 50 mA are shown in Fig. 6, respectively. The electrodes have a stable electrochemical property in 6 M KOH electrolyte with different currents, the specific capacitance of the supercapacitor can be calculated by the following equation [23]:

$$C = 2 \times \frac{Q}{mV} = 2 \times 3600 \times 0.001 \times \frac{C^*}{mV} = 7.2 \times \frac{C^*}{mV} \quad (2)$$

where C is the specific capacitance of the supercapacitor (F g^{-1}); Q is electric quantity (C); C^* is the capacitance measured (mAh); M is the weight of simple electrode (g); V is the range of the charge/discharge (V).

Based on the experimental results of Fig. 6, it can be found through calculation of Eq. (2) that the highest capacitance of the supercapacitor was up to 28 F g^{-1} . In general, the $E-t$ relationships in these four chronopotentiograms are approximately linear, indicating that the carbon aerogel electrodes behave as a capacitor, and have a good cycling stability. Hence, this material is a suitable electroactive material for supercapacitors.

The cycle life of the carbon aerogel supercapacitor is also illustrated in Fig. 7. The test of cycle life was performed using the 6 M KOH electrolyte at the constant-current (75 mA) condition. It has shown very long cycle life with shallow depth of discharge. Successful recharging and good cyclic behavior can be obtained. So, carbon aerogel electrodes have excellent charge/discharge characteristics in KOH solution.

4. Conclusions

In this paper, preparation of a carbon aerogel and its electrochemical performance have been studied. It is regarded as a

suitable electrode material for use in supercapacitors. Through XRD patterns and SEM studies, it has been demonstrated that a carbon aerogel, which can be obtained by ambient drying is an amorphous material with a pearly network structure, and can be regarded as partly graphitized carbon. The optimum R/C ratio was determined to be 1500 with the normal concentration (40%) in this work, and the specific capacitance of carbon aerogel electrode in 6 M KOH electrolyte was approximately 110.06 F g^{-1} . The capacitance of the supercapacitor with the carbon aerogel as the electrode active materials was up to 28 F g^{-1} . The supercapacitor has stable electrochemical properties, excellent reversibility and a long cycle life.

Acknowledgements

This project was supported by National Natural Science Foundation of China under grant no. 50472080, Natural Science Foundation of Hunan Province, China under grant no. 04JJ3040, 05JJ20013, the Project of Nature Science Foundation of Jiangsu Province under the grant no. BK2003092 and DGAOA-UNAM (N102100), Mexico.

References

- [1] B.E. Conway, *J. Power Sources* 66 (1997) 1.
- [2] A. Burke, *J. Power Sources* 91 (2000) 37.
- [3] C. Portet, P.L. Taberna, P. Simon, E. Flahaut, C. Laberty-Robert, *Electrochim. Acta* 50 (2005) 4174.
- [4] W.C. Chen, C.C. Hu, C.C. Wang, *J. Power Sources* 125 (2004) 292.
- [5] H.C. Liang, F. Chen, R.G. Li, et al., *Electrochim. Acta* 49 (2004) 3463.
- [6] E. Frackowiak, F. Beguin, *Carbon* 39 (2001) 937.
- [7] Y.Z. Wei, B. Fang, S. Iwasa, M. Kumagai, *J. Power Sources* 141 (2005) 386.
- [8] F. Kirkbir, H. Murata, D. Meyers, et al., *J. Non-Cryst. Solids* 225 (1998) 14.
- [9] S. Gavalda, K.E. Gubbins, Y. Hanzawa, et al., *Langmuir* 18 (2002) 2141.
- [10] T.F. Baumann, J.H. Satcher, *J. Non-Cryst. Solids* 350 (2004) 120.
- [11] W.C. Li, A.H. Lu, S.C. Guo, *Carbon* 39 (2001) 1989.
- [12] S.J. Kim, S.W. Hwang, S.H. Hyun, *J. Mater. Sci.* 40 (2005) 725.
- [13] R. Petricevic, G. Reichenauer, V. Bock, A. Emmerling, J. Fricke, *J. Non-Cryst. Solids* 225 (1998) 41.
- [14] R. Saliger, V. Bock, R. Petricevic, et al., *J. Non-Cryst. Solids* 221 (1997) 144–150.
- [15] R. Saliger, U. Fischer, C. Herta, J. Fricke, *J. Non-Cryst. Solids* 225 (1998) 81.
- [16] C. Schmitt, H. Probstle, J. Fricke, *J. Non-Cryst. Solids* 285 (2001) 277.
- [17] H. Probstle, C. Schmitt, J. Fricke, *J. Power Sources* 105 (2002) 189.
- [18] F.J. Maldonado-Hodar, C. Moreno-Castilla, A.F. Perez-Cadenas, *Microporous Mesoporous Mater.* 69 (2004) 119.
- [19] R.W. Pekala, J.C. Farmer, C.T. Alviso, et al., *J. Non-Cryst. Solids* 225 (1998) 74.
- [20] C. Moreno-Castilla, F.J. Maldonado-Hodar, *Carbon* 43 (2005) 455.
- [21] S.W. Hwang, S.H. Hyun, *J. Non-Cryst. Solids* 347 (2004) 238.
- [22] M. Wiener, G. Reichenauer, T. Scherb, J. Fricke, *J. Non-Cryst. Solids* 350 (2004) 126.
- [23] X.Y. Wang, X.Y. Wang, W.G. Huang, et al., *J. Power Sources* 140 (2005) 211.