Electrochemical properties of carbon aerogels with freeze-drying

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Abstract. Carbon aerogels (CAs) were prepared via a sol–gel process by polymerization of phloroglucinol, resorcinol and formaldehyde using 2,4-dihydroxybenzoic acid as catalyst with freeze-drying. The electrochemical properties were characterized using cyclic voltammetry, galvanostatic charge–discharge measurements and electrochemical impedance spectroscopy (EIS). The specific capacitance of corresponding CAs was up to 131 F g\(^{-1}\) and 105 F g\(^{-1}\) at the density of 0.5 A g\(^{-1}\) and 1.0 A g\(^{-1}\), respectively.

1 Introduction

Carbon aerogels (CAs) were first synthesized by Pekala in the 1990s, the traditional preparation method was via a sol–gel process by condensation-polymerization of resorcinol and formaldehyde using Na\(_2\)CO\(_3\) as the base catalyst. Because of excellent electrochemical properties, carbon aerogels have attracted wide-spread interest as promising energy storage. These properties of electrochemical double-layer and high electrical conductivity promote the application of CAs in the supercapacitors and batteries fields.

The traditional drying method need acetone solvent exchange and the drying time is lengthy. Because of the high operational pressure, the method of supercritical extraction has some dangers. Freeze-drying method has some advantages: 1) shorten the drying time; 2) improve the specific surface area; 3) increase the operational security. The traditional catalysts are alkaline carbonates and alkaline hydroxides, the pH value is about 8. The gel time is lengthy and the the specific surface area is low with base catalyst.

The effects of freeze-drying method on the electrochemical properties have been few reported. It will be an new field that the electrochemical properties are improved by freeze-drying method. In this paper, carbon aerogels were synthesized via a sol–gel process by condensation-polymerization of phloroglucinol, resorcinol and formaldehyde using 2,4-dihydroxybenzoic acid as catalyst with freeze-drying. Electrochemical properties of the carbon aerogels are investigated with cyclic voltammetry, galvanostatic charge–discharge measurements and electrochemical impedance spectroscopy (EIS). Meanwhile the effects of freeze-drying method on the electrochemical properties were studied.
2 Experimental

2.1 Materials
The chemical reagents used are analytical grade: phloroglucinol, resorcinol, formaldehyde (30%), and 2,4-dihydroxybenzoic acid (C). GAMRY Interface 1000 electrochemical workstation (GAMRY, USA).

2.2 Synthesis of the carbon aerogels
The relevant preparation routes are expressed in Fig. 1, and the reaction mechanism is shown in Fig. 2.

![Reaction mechanism diagram]

Fig. 1 The relevant preparation routes of carbon aerogels

1) addition reaction

2) polycondensation reaction

R = OH or H

Fig. 2 The reaction mechanism

2.3 Measurements of electrochemical properties
The preparation of carbon aerogels electrodes is described as follows. The prepared CAs were ground and filtered through a 200-mesh sieve. The resulting powders were then blended with polytetrafluoroethylene (PTFE), which acted as a binder, and deionized water as the solvent. The CA/PTFE weight ratio was 95:5. The mixture was stirred for 4 h at room temperature, dried at 105°C
for 12 h and then coated onto nickel foam. Next, the mixture electrodes were pressed into thin slices and dried at 105°C for 12 h.

The electrochemical properties were investigated using cyclic voltammetry (CV), galvanostatic charge–discharge and electrochemical impedance spectroscopy (EIS) analysis methods. The experiments were carried out on a GAMRY Interface 1000 electrochemical workstation (GAMRY, USA). The samples were soaked in 6 M KOH for 24 h before the mixture electrodes were characterized. The CV scans were performed over the voltage range from −0.8 to 0.0 V at a scan rate of 0.1 mV s⁻¹. The galvanostatic charge–discharge measurements were conducted at a current density of 0.5 A g⁻¹ and 1.0 A g⁻¹, respectively, over the voltage range from −0.8 to 0.0 V. The investigated frequency range for the Nyquist plots was 100 kHz to 0.1 Hz.

The electrochemical performance was measured with a three-electrode system. The prepared CA electrode was used as the working electrode. A Hg/Hg₂Cl₂ electrode was utilized as the reference electrode, and Pt was used as the counter electrode. The specific capacitances were obtained from the galvanostatic charge–discharge.

3 Results and discussion

![Fig. 3 CV curves of as-prepared CAs samples at a scan rate of 0.01 V s⁻¹](image)

Cyclic voltammetry (CV) measurements are carried out to examine the electrochemical properties of as-prepared CAs samples. The cyclic voltammetry curves of CAs samples at a scan rate of 0.01 V s⁻¹ and the voltage from −0.8 to 0 V are shown in Fig. 3. As shown in Fig. 3, all the curves exhibit a roughly rectangular-like shape, implying the electric doublelayer capacitance behavior of as-prepared CAs samples. 1/250 sample has a near-rectangular shape which indicates that when the dosage of 2,4-dihydroxybenzoic acid is 1/250, the sample exhibits better electric doublelayer capacitance; 1/500 sample exhibits larger electric capacitance than others.

The charge/discharge profiles of as-prepared CAs samples at a current density of 0.5 A g⁻¹ and 1.0 A g⁻¹, respectively, are shown in Fig. 4. The specific capacitances of as-prepared CAs samples which are calculated from charge/discharge measurements are shown in Table 1. As shown in Fig. 4, all samples show a virtually linear shape and triangular distribution. When the current density was 0.5 A g⁻¹, the CAs electrodes exhibited excellent electrochemical properties and had higher specific capacitances as shown in Fig. 4 A. However, the potential drops are very obvious which indicates that the lower current density results in the changing of the resistance. As shown in Fig. 6, 1/500 sample exhibits the maximum specific capacitance, up to 132 F/g and 106 F/g, respectively.
Fig. 4 Galvanostatic charge/discharge curves.

Table 1 Specific capacitance of as-prepared CAs samples calculated by charge/discharge measurements

| Entry      | C (F/g)_{0.5 \text{A.g}^{-1}} | C (F/g)_{1.0 \text{A.g}^{-1}} |
|------------|-------------------------------|-------------------------------|
| blank      | 105                           | 95                            |
| 1/800      | 108                           | 98                            |
| 1/500      | 132                           | 106                           |
| 1/500(RT)  | 112                           | 96                            |
| 1/250      | 117                           | 102                           |

The Nyquist plots of as-prepared CAs samples are shown in Fig. 5, the data were collected by EIS over the frequency range from 100 kHz to 0.1 Hz. The Nyquist plots could examine the resistance to the transport electrolyte ions. As shown in in Fig. 7, the Nyquist plots exhibit two regions, namely high frequency and low frequency regions. The high frequency region exhibits a semi-circle loop, and the low frequency regions exhibits a 45° line. The semi-circle loop indicates the charge transfer resistance, the 45° line indicates the bulk solution resistance. As shown in Fig. 7, 1/500 sample has the lower charge transfer resistance and bulk solution resistance; 1/250 sample has the higher charge transfer resistance and bulk solution resistance.
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References
[1] A. Mirzapour, M.H. Asadollahi, S. Baghshaei, M. Akbari, Effect of nanosilica on the microstructure, thermal properties and bending strength of nanosilica modified carbon fiber/phenolic nanocomposite, Compos. Part A Appl. Sci. vol. 63, 2014, pp. 159-167.
[2] Khezri K, Haddadi-Asl V, Roghani-Mamaqani H, Salami-Kalajahi M Polystyrene- organoclay nanocomposites produced by in situ activators regenerated by electron transfer for atom transfer radical polymerization. J Polym Eng vol. 32, 2012, pp. 235–243.
[3] Sun Z, Yang X, Zhang G, Zheng S, Frost RL A novel method for purification of low grade diatomite powders in centrifugal fields. Int J Miner Process vol. 125, 2013, pp. 18–26.
[4] Zhang J, Kong L-B, Cai J-J, Li H, Luo Y-C, Kang L Hierarchically porous nickel hydroxide/mesoporous carbon composite materials for electrochemical capacitors. Microporous Mesoporous Mater. vol. 132, 2010, pp. 154–162.
[5] A.C. Dillon, K.M. Jones, T.A. Bekkedahl, C.H. Kiang, D.S. Bethune, M.J. Heben, Storage of hydrogen in single-walled carbon nanotubes, Nature vol. 6623, 1997, pp. 377-379.
[6] L.J. Zhang, Z.X. Su, F.L. Jiang, L.L. Yang, J.J. Qian, Y.F. Zhou, W.M. Li, M.C. Hong, Highly graphitized nitrogen-doped porous carbon nanopolyhedra derived from ZIF-8 nanocrystals as efficient electrocatalysts for oxygen reduction reactions, Nanoscale. vol. 6, 2014, pp. 6590 - 6602.
[7] Neimark AV, Lin Y, Ravikovitch PI, Thommes M (2009) Quenched solid density functional theory and pore size analysis of micro-mesoporous carbons. Carbon vol. 7, 2009, pp. 1617–1628.
[8] Nishihara H, Mukai SR, Tamon H (2004) Preparation of, resorcinol- formaldehyde carbon cryogel microhoneycombs. Carbon vol. 42, 2004, pp. 899–901.
[9] S. Mulik, C. Sotiriou-Leventis, in: M.A. Aegerter, L. Leventis, M.M. Koebel (Eds.), Aerogels Handbook – Advances in Sol–Gel Derived Materials and Technologies, Springer, New York, Dordrecht, Heidelberg, London, 2011, pp. 215–234.