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Structure evolutions and high electrochemical performances of carbon aerogels prepared from the pyrolysis of phenolic resin gels containing $ZnCl_2$

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ABSTRACT

Carbon aerogels (CAs) were prepared via the pyrolysis of phenolic resin gels (PRGs) containing $ZnCl_2$. The pyrolysis of PRGs and the activation of resulted amorphous carbons in CAs can be carried out in one step. Structure characterizations of CAs were performed by X-ray diffraction, Raman spectrum and gas adsorption-desorption method. Electrochemical performances of CAs were investigated by cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance spectroscopy. CAs with specific surface area of $2846\,m^2\,g^{-1}$ can display its specific capacitance of $246\,F\,g^{-1}$ at $1\,A\,g^{-1}$ and $219\,F\,g^{-1}$ at $10\,A\,g^{-1}$. The addition of $ZnCl_2$ in matrix of PRGs by a hydrothermal treatment can effectively avoid its serious volatilization at higher temperatures and enhance its activation efficiency. A series of structure evolutions in CAs including their specific surface areas, pore volumes and accumulation states of laminar carbon molecules can be caused by changing the content of $ZnCl_2$ in PRGs. High electrochemical performances of CAs are resulted from their adjusted carbon structures. The relation between the structure evolutions in CAs and their improved electrochemical performances is also discussed.

1. Introduction

Electric double layer capacitors (EDLCs) based on porous carbon materials exhibit their attractive applications in various fields [1–5]. Electric energy storage abilities of EDLCs are decided by the formation of electric double layers (EDLs) on carbon surfaces during the charge process and their electric energy release abilities are decided by the transmission of electrolyte ions from carbon surfaces to their solution body and the transmission of electrons in carbon matrix during the discharge process. Because laminar carbon molecules (LCMs) as the matrix of amorphous carbons act as sites for the formation of EDLs, their structures certainly affect transmissions both of electrolyte ions and electrons in carbon matrix and greatly decide electrochemical performances of EDLCs. So, the structure optimization about amorphous carbons is always a hot topic in the field of EDLCs.

In view of the working mechanism of EDLCs, carbons with high specific surface area (SSA) values can display higher electrochemical performances because they can provide more carbon surfaces for the formation of EDLs, so, any effective activation treatments about amorphous carbons are still worth to being carried out. Up till now, physical and chemical activation treatments have been developed, however, many relative investigations reveal that these activated carbons can usually display their higher electrochemical performances at smaller charge-discharge current densities [6–10]. It is because there are larger transmission resistances both of electrons and electrolyte ions in activated carbons, moreover, these activation treatments usually result in large amount of micro-pores and lack effective measures to adjust structures of resulted activated carbons. On the other hand, most of these activation treatments are mainly focused on as-prepared carbons at high temperatures, so, the efficiencies of activation agents should be investigated. A lot of amorphous carbons are prepared by paralysis treatments of organic materials as carbon precursors because they possess extra structure characters [11–15]. However, the pyrolysis of organic precursors for carbons is in fact the formation of LCMs, which greatly decides structure characters of resulted carbons. So, a chemical agent to be added into the matrix of organic precursors in advance should have a different effect on the formation of LCMs and result in activated carbons with different structure characters. Although there are some investigations to be reported, they are more focused on the

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production of carbons from some natural precursors and less focused on their carbon structure adjustments [16–18].

Carbon aerogels (CAs) as one kind of porous carbon materials possess rich micro-pores in their carbon matrix and meso-pores in their skeletons, moreover, they can be conveniently and economically prepared from the pyrolysis of phenolic resin gels (PRGs) at ambient conditions. So, CAs become one of alternative carbon materials for carbon electrodes in EDLCs. But, relative researches exhibit their unsatisfied electrochemical performances, for example, their specific capacitances are not large enough especially at fast charge-discharge rates or large current densities [19–22]. It is mainly attributed to the fact that the pyrolysis of PRGs usually results in amorphous carbons in CAs with lower SSA values and small pore volumes. Such structural features are not favor to the formation of EDLs, resulting in their poor electrochemical performances at large charge-discharge current densities. Traditional activation treatments, for example, the heating of CAs with KOH at a high temperature, are usually carried out in order to optimize their carbon surfaces [23–27]. However, a large amount of micro-pores are mainly formed in them, in which electrolyte ions cannot be fluently transported at fast rates and large current densities. This is why they usually display deteriorative electrochemical behaviors at fast charge-discharge rates and large current densities [28,29].

In this paper, various CAs are prepared by the pyrolysis of PRGs containing $ZnCl_2$. The decomposition of organic precursor and the activation of resulted amorphous carbons are carried out in one step. Structure characterizations of various CAs are performed by X-ray diffraction (XRD), Raman spectrum (Raman) and gas adsorption-desorption methods and their electrochemical performances are investigated by cyclic voltammetry (CV), galvanostatic charge-discharge (GC) and electrochemical impedance spectroscopy (EIS). Structural evolutions in CAs caused by various $ZnCl_2$ in PRGs are investigated. It is the structure adjustment that makes them display higher electrochemical performances at large charge-discharge current densities. Such a activation treatment of CAs can be used to optimize structures and improve electrochemical performances of other amorphous carbons.

2. Experimental

2.1. Preparation of CAs

CAs was prepared at ambient pressure by a modified method. Briefly, resorcinol (5.0 g) and formaldehyde (6.3 mL) and deionized water (7.3 mL) were strongly stirred at room temperature, then, the mixture was sealed in a conical flask and was settled at 85 °C for 5 days, then, it was placed at room temperature for 2 days and PRGs were obtained. One part of PRGs were carbonized at 850 °C and pure CAs were obtained, which was named as CAs-0 in following discussions. The other PRGs were grinded into powder at 120 mesh and each powder (5.0 g) was accordingly mixed with $ZnCl_2$ at various weight ratios including1:1. 1:2, 1:3 and 1:5, then, each mixture was dispersed in deionized water (30 mL) and was strongly stirred for 30 min, after that, it was transferred into teflon-lined stainless steel autoclaves (100 mL) and kept at 160 °C for 2 h, after it being cooled to room temperature, the mixture was dried at 105 °C for 12 h, then, it was annealed at 850 °C in N_2 for 4 h, then, the sample was washed in HCl (aq.6 M) and deionized water with an ultrasonic assistance in order to remove zinc component, then, it was dried at 105 °C, at last, various samples of CAs prepared from PRGs containing various zinc salt were obtained, which are named as CAs-1, 2, 3 and 5, accordingly.

PRGs were mixed with $ZnCl_2$ at the weight ratio of 1:3 and they were treated by above hydrothermal method. Resulted samples were annealed at 500, 850, 1100 and 1300 °C, accordingly and these obtained samples were correspondingly named as CAs-3-500, 850, 1100 and 1300.

2.2. Structure characterization

XRD investigation was carried out by D8 ADVANCE with Cu Kα radiation.

Raman was performed with the test conditions of micro confocal laser including excitation wavelength of 514.5 nm, laser efficiency of 100%, and scanning band of 1000–3200 cm^{-1}.

Nitrogen adsorption and desorption isotherms of samples were measured with a volumetric adsorption system (Micromeritics Tristar 3000). The specific surface area were analyzed by the Brunauer-Emmett- Teller (BET) and pore-width distribution were analyzed by Barette-Joynere-Halenda (BJH) method.

2.3. Electrochemical measurements

In order to prepare the working electrodes, resulted CAs were used as active materials, respectively; pure graphite was used as a conductive filler and polyfluortetraethylene (PTFE) was used as a binder. They were mixed at a mass ratio of sample: graphite: PTFE = 8: 1: 1 in each working electrode and each mixture was wetted by some ethanol to form a slurry. Each working electrode was fabricated by coating the slurry on a nickel mesh and dried under vacuum at 120 °C for 5 hours and weighed. They were all dipped in KOH (6 M) for 24 hours before the electrochemical characterizations.

Investigations about cyclic voltammetry (CV) were performed by using the typical three-electrode system with a voltammetric analyzer (CHI600E) at various scan rates and the voltage was swept from −1.0 to 0 V and back to −1.0 V.CAs were used as working electrodes, the nickel mesh was used as the counter electrode and the Hg/HgO electrode was used as the reference electrode. KOH (6 mol/L) was used as the electrolyte. The electrochemical impedance spectra (EIS) were also recorded on the same electrochemical workstation. The working electrode were conducted in a frequency range 10 mHz to 1 MHz under open circuit potential, with an ac perturbation of 10 mV at a constant potential of 0 V vs. the Hg/HgO electrode and the quite time is 2 s.

3. Results and discussions

3.1. Structure evolution in CAs with changing $ZnCl_2$ in PRGs

XRD patterns of CAs prepared from the pyrolysis of PRGs containing various $ZnCl_2$ are presented in Fig. 1. Widened diffraction peaks (002) at 2θ between 24−26° and (101) between

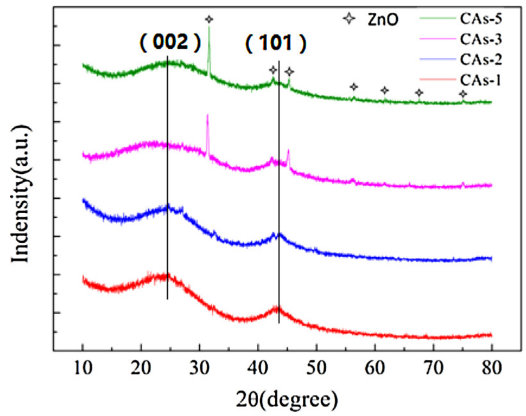

Fig. 1. XRD patterns of CAs containing zinc oxide.