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Ni, Co - doped carbon aerogels for Supercapacitors

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Abstract. Metal doping carbon aerogels are prepared via polymerization of glutaraldehyde and chitosan with $Ni(NO_3)_2$ and $Co(NO_3)_2$ doping under freeze - drying method. The as - prepared product are carbonized at 900 °C in a nitrogen atmosphere. The obtained doping carbon aerogels were characterized by means of N_2 - adsorption, X-ray diffraction (XRD), cyclic voltammetry, galvanostatic charge–discharge measurements and electrochemical impedance spectroscopy (EIS). The analysis results shows that doping carbon aerogels exhibit a high specific surface area, up to 387 m^2/g, and a high specific capacitance, up to 105 F/g at a current density of 1.0 $A \cdot g^{-1}$. In a nutshell, this work provides a new method to prepare carbon aerogels with high specific surface area and specific capacitance.

Introduction

Carbon aerogels are considered to be the most efficient and ecofriendly carbon materials in the supercapacitor and adsorbent field because of excellent three-dimensional cross-linked porous structure and electrochemical properties [1-3]. Carbon aerogels are first reported by Pekala and coworkers in the 1990s [4-6], they used resorcinol and formaldehyde to synthesize wet aerogels, then carbonizing in N_2 atmosphere. Because of unusual electrochemical and textural properties, carbon aerogels have been widely used for catalyst supports, adsorption of heavy metal ions, separation of poisonous gas, hydrogen storage, electrodes for supercapacitors and batteries in recent years [7-10]. Carbon aerogels have been synthesized from resorcinol–formaldehyde (RF), phenol–resorcinol–formaldehyde, phenolic–furfural, melamine–formaldehyde, polyurethanes, and polyureas during the development of recent years.

The traditional preparation method is the pyrolysis process of organic precursors which is the phenolic polymerization product. The development of next – generation preparation and modification method of carbon aerogels (CAs) is a key to the success widely application of CAs in the adsorption and energy storage field. Metal atom doping is an efficient method to improve the electrochemical and textural properties. Iron-containing carbon aerogels have been reported by Ave Sarapuu, Fe atoms were added into the precursor and carbonized [11]. The surface area was up to 471 m^2 g^{-1} and the electrocatalytic activity of iron-containing CAs for ORR increased with increasing the Fe content. Filipa Duarte prepared a new carbon aerogels with transition metals (Fe, Co, Ni) doping to degrade azo-dye Orange II [12], metal-doped carbon aerogels not only exhibited

a good textural property but also shown a good degradation efficiency.

In this work, we reported a new method to prepare metal-doped carbon aerogels via polymerization of glutaraldehyde and chitosan with $Ni(NO_3)_2$ and $Co(NO_3)_2$ addition. The result products have a high specific surface area, up to 387 m^2/g, and a high specific capacitance, up to 105 F/g at a current density of 1.0 $A \cdot g^{-1}$. Meanwhile, the electrochemical and textural properties have been investigated through various methods.

Experimental

Synthesis of metal doping carbon aerogels. Carbon aerogels were synthesized by polycondensation of glutaraldehyde(G) and chitosan(C), using $Ni(NO_3)_2$ and $Co(NO_3)_2$ as doping metals and deionized water as the solvent. The molar ratio of G / C was 2, the mass ratio of (G + C) / ($Ni(NO_3)_2$ + $Co(NO_3)_2$) was 10, and the molar ratio of $Co(NO_3)_2$ / $Ni(NO_3)_2$ was 2. The concentration of raw material (G + C) in solution was 45 wt%. This solution was putted into a 100 ml hydrothermal reactor at 120 °C for 10h, then the result hydrogels were freeze-dried. The dried aerogels were carbonized at 600°C and 900°C, respectively, for 3 h with a heating rate of 2°C/min under a flowing nitrogen atmosphere (100 mL/min).

Characterization. The specific surface areas were obtained via the Brunauer–Emmett–Teller (BET) method using an ASAP 2420 surface-area analyzer (Micromeritics, USA). Ultima IV X-ray diffraction instrument (XRD, Rigaku, Japan) was used to investigate the textural properties. The electrochemical performance was measured with a three-electrode system. The prepared CA electrode was used as the working electrode. A Hg/Hg_2Cl_2 electrode was utilized as the reference electrode, and Pt was used as the counter electrode.

Results and discussion

Pore structure of metal-doped carbon aerogels

Table 1 Porous properties of metal-doped carbon aerogels

Entry	S_{BET} (m^2/g)	S_{micro} (m^2/g)	$D_{average}$ (nm)	V_{total} (cm^3/g)
CAs-1	289	113	5.96	0.288
CAs-2	387	175	5.14	0.355

CAs-1: carbonization at 600°C; CAs-2: carbonization at 900°C.

Detailed pore structure (BET surface area(S_{BET}), micropore surface area (S_{micro}), average pore diameter ($D_{average}$), mesopore volume (V_{meso}), and total pore volume (V_{total})) of metal-doped carbon aerogels are listed in Table 1. The nitrogen adsorption–desorption isotherms is presented in Fig. 1 (a) and the pore size distribution is shown in Fig. 1 (b). As shown in Table 1, CAs-2 exhibited a higher specific surface area than CAs-1, up to 387 $m^2 \cdot g^{-1}$. As presented in Fig. 1 (a), all curves exhibited a type-IV isotherms, which indicates the existence of well-developed porous structure. As shown in in Fig. 1 (b), metal-doped carbon aerogels show a narrower distribution of pore size, which implies this method is beneficial for the controlled pore size carbon aerogels preparation.

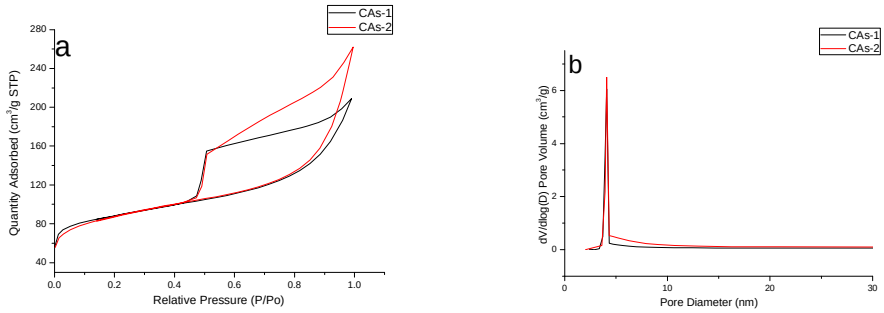

Fig. 1. Nitrogen adsorption–desorption isotherms (a) and Pore size distribution (b). CAs-1: carbonization at 600°C; CAs-2: carbonization at 900°C.

XRD Patterns of metal-doped carbon aerogels

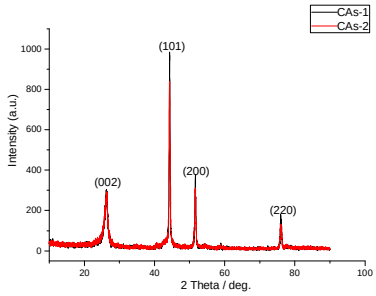

Fig. 2 XRD patterns of metal-doped carbon aerogels
CAs-1: carbonization at 600°C; CAs-2: carbonization at 900°C.

The XRD patterns of metal-doped carbon aerogels under different carbonization temperature are shown in Fig. 2. As shown in Fig. 2, there are two obvious peaks at the 2θ of 24° and 44° , which are the (002) peak of graphite carbon and (101) peak of the crystal plane diffraction, respectively. The (200) peak and (220) peak are vested in nickel-cobalt alloy compound, which illustrates that we have prepared the metal-doped carbon aerogels.

Electrochemical properties of metal-doped carbon aerogels

Cyclic voltammetry (CV) measurements are carried out to examine the electrochemical properties of the result carbon aerogels. The cyclic voltammetry curves at a scan rate of 0.002 V s^{-1} and the voltage from − 0.8 to 0 V are shown in Fig. 3 (a), the Galvanostatic charge–discharge (GCD) curves are present in Fig. 3 (b) and the electrochemical impedance curves are shown in Fig. 3 (c). The specific capacitances of metal-doped carbon aerogels which are calculated from charge/discharge measurements are shown in Table 2. As shown in Fig. 3 (a), the redox peaks are very obviously observed in the curves, which are caused by the presence of metal pseudocapacitance. All the curves exhibit a roughly rectangular-like shape, which indicates that the samples show a general electric double-layer capacitance behavior. As presented in Fig. 3 (b), the curves of metal-doped carbon aerogels show a virtually linear shape and triangular distribution. CAs-2 exhibits a higher specific capacitance, up to 105 F/g, which implies the optimal carbonization temperature is 900 °C. As shown in Fig. 3 (c), 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. CAs-2 has the lower charge transfer resistance and bulk solution resistance.

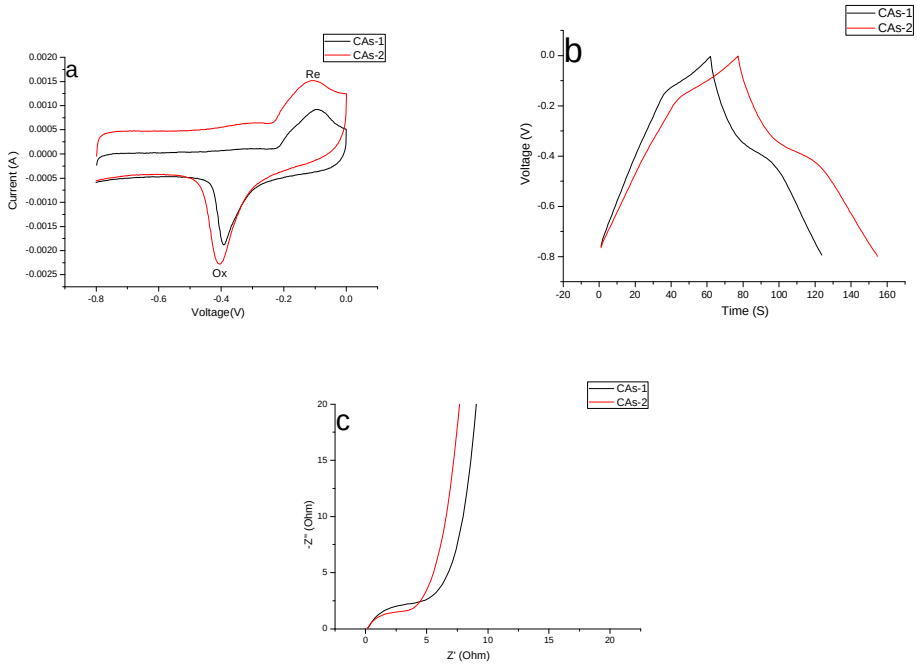

Fig. 3 CV curves at a scan rate of 2 mV s^{-1} (a), Galvanostatic charge–discharge (GCD) curves of all carbon aerogels at a current density of 1.0 A g^{-1} (b) and Nyquist plots(c).
CAs-1: carbonization at 600°C; CAs-2: carbonization at 900°C.

Table 2 Specific capacitance of metal-doped carbon aerogels

Entry	C (F / g)$_{1.0\ A\ g^{-1}}$
CAs-1	84
CAs-2	105

CAs-1: carbonization at 600°C; CAs-2: carbonization at 900°C.

Conclusions

Metal-doped carbon aerogels were prepared through polycondensation of glutaraldehyde and chitosan using $Ni(NO_3)_2$ and $Co(NO_3)_2$ as doping metals with free - drying method. The result carbon aerogels shows high specific surface area and specific capacitance, which illustrates this method is beneficial for the preparation of carbon aerogels.

Acknowledgements

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