Synthesis and properties of Ni-doped carbon aerogel

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Abstract. Ni-doped carbon aerogels were synthesized by impregnation methods, their physical structure and surface morphology were studied. The results show that adding Ni is beneficial to increase the specific surface area of CA, but too much Ni will block some holes. The SEM images possess closer network structure and excellent connectivity. The XRD and Raman patterns show the addition of Ni can enhance the graphitization degree of carbon aerogels.

1. Introduction

Carbon aerogels (CA) with extremely high porosity and highly cross-linked three-dimensional networks are relatively new materials. CA has unique functions, including low density, continuous porosity, high specific surface area, good thermal conductivity and good electrical conductivity. Their ideal energy source is their unique pore structure, which makes them useful in various fields, such as hydrogen fuel storage [1], catalyst carriers [2] and capacitors [3]. CA used for double-layer capacitance usually shows good stability, but has a lower specific capacitance. Generally, the specific capacitance of CA can be improved by introducing transition metal oxide into the electrode material [4]. At the same time, the conductivity and stability of the pseudo-capacitance substance can also be improved by using carbon carriers. Therefore, the composite material of carbon material and metal oxide is the best material for quasi-capacitive behavior and 3D network structure [5].

2. Experimental

2.1 Synthesis

Resorcinol (R), Phloroglucinol (P), and formaldehyde (F) were dissolved in deionized water (W) and Na2CO3 as a catalyst (C). The molar ratios of reagents was set as P/R = 0.15; (P+R)/F = 0.5; (P + R)/C = 800, and R/W = 0.06. The monomer concentration of reactants (P+R+F) in solution was 45%. To ensure a homogeneous mixture, the reagents were shocked by ultrasonic oscillator in sealed glass moulds until gelification. This gel was heated in test tubes at 50°C for 72 h and then 80°C for 24 h and PRF (polymerization-resorcinol-formaldehyde) hydrogels were obtained. Then the PRF hydrogel was soaked in acetone with 3% (volume fraction) trifluoroacetic acid 1 day. The solution was changed 3 times every 24 hours for solvent exchange of acetone. Drying is performed under ambient pressure. Under a flowing high-purity nitrogen atmosphere (100 mL/min), a carbon aerogel was obtained at 900°C for 3 hours. CA was soaked in 1.5 mol/L, 2.5mol/L, 3.5mol/L Ni (NO3)2·6H2O aqueous solution for 6 hours, then dried at 250°C for 5 hours to obtain CA-Ni-1.5, CA-Ni-2.5, CA-Ni-3.5, respectively.
2.1.1. Characterizations. Pore structure parameters was tested by N\textsubscript{2} adsorption-desorption using an ASAP 2460 adsorption analyzer (Micromeritics Instruments Corporation, Norcross, GA, USA). X-ray diffraction (XRD; Rigaku Ultima IV X-ray diffractometer, with a CuK\textalpha radiation of \(\lambda=1.54\ \text{Å}\)) and Raman spectroscopy (Raman; Thermo Fisher DXR Raman spectrometer) were used to examine the structural changes. The surface morphologies of carbon aerogels were observed by S-4800-I (Hitachi, Japan) scanning electron microscopy (SEM).

2.1.2. Results and discussion. The structure parameters of samples was gave using N\textsubscript{2} isotherms (77 K). The size distribution was gave from the BJH method. The pore structure parameters are displayed in Table 2.

![Figure 1](image.png)  
**Figure 1** (a) Low temperature N\textsubscript{2} isotherms of carbon aerogels, (b) size distribution from BJH method.

| Samples     | \(S_{\text{BET}}\) (m\textsuperscript{2}.g\textsuperscript{-1}) | \(V_{\text{tot}}\) (cm\textsuperscript{3}.g\textsuperscript{-1}) | R (nm) |
|-------------|-------------------------------------------------|-------------------------------------------------|--------|
| CA          | 624.1                                           | 0.54                                            | 8.1    |
| CA-Ni-1.5   | 630.5                                           | 0.59                                            | 8.4    |
| CA-Ni-2.5   | 697.8                                           | 0.89                                            | 5.2    |
| CA-Ni-3.5   | 576.3                                           | 0.93                                            | 7.3    |

\(S_{\text{BET}}, \) specific surface area from BET model; \(V_{\text{tot}}, \) pore volume at \(p/p_{0}\to 1;\) R, average pore size.

As shown in Figure 1 (a), all samples exhibited type IV isotherms with type H2 hysteresis loops. This indicates that the structure of obtained carbon aerogels are mainly composed of mesopores. This is consistent with the results in the pore size distribution diagram in Figure 1 (b). In Table 2, as the amount of Ni increases, the specific surface area increases first and then decreases, CA-Ni-2.5 gave the highest surface area (697 m\textsuperscript{2}.g\textsuperscript{-1}). It shows that adding Ni is beneficial to increase the specific surface area of CA, but too much Ni will block some holes and reduce the specific surface area.

SEM images of the surface morphology of 4 samples are depicted in Figure 2 (a)-(d). CA is typical disorder porous material. Compared with CA, samples with Ni possessed closer network structure, the holes between the network are abundant, have excellent connectivity.
X-ray diffraction was tested and the results are shown in Figure 3(a). There are two diffraction peaks around 24° and 44°, corresponding to (002) and (101) diffraction peak of graphitic carbon, respectively [6]. Raman spectra was tested and the results are displayed in Figure 3(b). All samples gave typical features peaks located at 1350 cm\(^{-1}\) (D-band), which is ascribed to disordered carbon and various defects of carbon material, and 1582 cm\(^{-1}\) (G-band), which is assigned to ordered carbon [7]. The relative intensity ratios (R) of D-band to G-band (R = ID/IG) are listed in Fig. 3(b). The ratios reflect the degree of disorder and defects in the carbon material [8]. A low R-value (ID/IG ) implied a high graphitization degree. The high graphite degree of Ni-CA can significantly increase the electric conductivity.

**Figure 2** SEM images of samples

**Figure 3** (a) X-ray diffraction spectra . (b) Raman spectra .
3 Conclusions
Ni-doped carbon aerogel samples were prepared by the sol-gel polymerization method, resorcinol (R), phloroglucinol (P), and formaldehyde (F) were used as reactants. Impregnation methods was introduced to the reactions system.

The results show: (1) The addition of Ni is beneficial to increase the specific surface area of CA; (2) The SEM images possess closer network structure and excellent connectivity; (3) The XRD and Raman patterns show the addition of Ni can enhance the graphitization degree of carbon aerogels.

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