Preparation and characterization of Ni-doped carbon aerogel for supercapacitor

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Abstract. Ni-doped carbon aerogel was prepared by impregnation methods, physical structure, and electrochemical properties were investigated. Electrochemical properties of prepared Ni-doped carbon aerogel and carbon aerogel electrodes were measured by galvanostatic charge/discharge measurements. The results show Ni-doped carbon aerogels maintain the elementary structure of carbon aerogel, but they exhibited higher specific capacitance than carbon aerogel.

1. Introduction
Carbon aerogel can be obtained by sol–gel polycondensation of certain organic monomers such as resorcinol, formaldehyde, and polymerization. Because of the interesting properties such as low density, high surface area, continuous open porosity and electrical conductivity, carbon aerogel has been widely employed as an electrode material of electrochemical capacitors. Supercapacitors are electrochemical energy storage devices that have attracted considerable attention due to their excellent charge and discharge properties and long cycle life [1-2]. Double-layer capacitance and pseudocapacitance are utilized for energy storage. The double-layer capacitance derives from the accumulation of ions on the double-layer at the electrode/electrolyte interface and is dependent on the surface area and the accessibility of the electrolyte to the electrode porosity. Pseudocapacitance derives from eversible faradaic reactions at the electrode/electrolyte interface thanks to the presence of surface functionalities and dopants in the carbon electrodes [3].

In this work, carbon aerogel was prepared by a sol–gel polymerization. To combine the excellent electrochemical performance of carbon aerogel with a pseudo-capacitive property of metal oxide, nickel oxide was doped on carbon aerogel by an incipient wetness impregnation. To evaluate the effect of nickel oxide on the electrochemical properties, the performance of carbon aerogel and Ni-doped carbon aerogel for pseudo-capacitive supercapacitor electrode were investigated.
2. Experimental

2.1. Preparation of Ni-doped carbon aerogel
Carbon aerogel was prepared by a sol-gel formaldehyde, polymerization, and resorcinol according to the method in previous work[4]. To obtain Ni-doped carbon aerogel, after pyrolysis, the PRF (polymerization-resorcinol-formaldehyde) hydrogel was soaked in 0.05 M solution of nickel nitrate hexahydrate for three days (the saline solution was changed after every 24 h). Solvent exchange for acetone was carried out via changing the solution after every 24 h for 3 times. Drying was carried out at ambient pressure. The Ni-doped carbon aerogel was obtained at 900 °C for three hours under a flowing high purity nitrogen atmosphere (100 mL/min).

2.2. Fabrication of carbon aerogel electrode
The prepared Ni-doped carbon aerogels and carbon aerogels were casted respectively using polytetrafluoroethylene (PTFE) as a binder with a weight ratio of 90:10. The resultant was rolled to be 8-10 μm thickness. The electrode material was pressed onto foamed nickel, which was used as a working electrode.

2.3. Characterizations
BET surface area and N₂ adsorption–desorption isotherm were measured with an ASAP 2420 (Micromeritics, America) instrument. The samples were degassed at 350 °C overnight before the adsorption measurements. Pore size distribution was determined by the BJH method applied to the desorption branch of the nitrogen isotherm. XRD patterns on aerogel and carbon aerogel were examined by Ultima IV X-ray diffractometer (Rigaku, Japan) using Cu Kα radiation.

2.4. Measurement of electrochemical property for carbon aerogel
Electrochemical property of Ni-doped carbon aerogel electrode was measured with a conventional three-electrode cell system in 6 M KOH electrolyte. A platinum plate and saturated calomel electrode were used as a counter electrode and a reference electrode, respectively. Galvanostatic charge/discharge measurements were carried out at a constant current of 1 A/g within voltage range of 0–0.8 V.

3. Results and discussion

3.1. Physical characteristics
The pore structure of the carbon aerogels was investigated by low-temperature nitrogen adsorption measurements. The N₂ adsorption/desorption isotherms and the pore size distribution (PSD) curves are showed in Figure 1(a) and Figure 1(b), respectively. The porosity data deduced from the isotherms are listed in Table 1.
Figure 1. (a) Low-temperature nitrogen isotherms and (b) pore size distribution of carbon aerogels.

Table 1. Textural properties of carbon aerogel and Ni-doped carbon aerogel.

|                     | BET surface area (m²/g) | Average pore diameter (nm) | Pore volume (cm³/g) |
|---------------------|-------------------------|----------------------------|---------------------|
| Carbon aerogel      | 658                     | 6.11                       | 0.89                |
| Ni-doped carbon aerogel | 601                     | 6.02                       | 0.83                |

Figure 1(a) compares the N2 adsorption–desorption isotherms and pore size distributions of carbon aerogel and Ni-doped carbon aerogel. Both samples exhibited type IV isotherms with type H2 hysteresis loops. This indicates that porous structure of carbon aerogel was still maintained even after Ni doping. Table 1 shows the textural properties of carbon aerogel and Ni-doped carbon aerogel. Although surface area, average pore diameter, and pore volume of carbon aerogel slightly decreased after the impregnation of Ni(NO₃)₂, Ni-doped carbon aerogel still retained high surface area (601 m²/g), fine average pore diameter (6.02 nm), and large pore volume (0.83 cm³/g). From the results in Figure 1(a) and Figure 1(b), it can be indicated that network structures of carbon aerogel are maintained even after the metal doping.

Figure 2. XRD patterns of carbon aerogels

XRD patterns of carbon aerogels are characterized, as shown in Figure 2. Successful impregnation of metal species on carbon aerogel was confirmed by XRD analysis in Figure 2. Carbon aerogel showed two broad peaks at 23.5° (0 0 2) and 43.8° (1 0 1), which were attributed to the reflections of
graphite carbon, respectively [5]. A mixture of metal and metal oxides was observed in the XRD patterns of Ni-doped carbon aerogels [6]. Considering that metal Ni and metal oxides NiO are closely related to the faradaic redox reactions, it is expected that Ni-doped carbon aerogel would show an enhanced capacitance than carbon aerogel.

3.2. Electrochemical properties of carbon aerogels

| Table 2. Specific capacitance of carbon aerogel electrodes |
|---------------------------------------------------------|
| Carbon aerogel | Ni-doped carbon aerogel |
|----------------|------------------------|
| Specific capacitance (F/g) | 57.5 | 92.6 |

Figure 3 shows the galvanostatic charge/discharge profiles (current density = 1 A/g) of carbon aerogel and Ni-doped carbon aerogel electrodes, and the calculated specific capacitances are summarized in Table 2. Ni-doped carbon aerogel showed higher specific capacitance (92.6 F/g) than carbon aerogel (57.5 F/g). Moreover, inner resistance (IR) drop intensity of Ni-doped carbon aerogels was negligible. This indicates that capacitive property of Ni-doped carbon aerogels was excellent. On the other hand, IR of carbon aerogel was clearly observed. This potential drop derives from the resistance of electrolyte and the IR of ion diffusion in carbon micropores [7-9]. Thus, the specific capacitance of carbon aerogel could be improved by adding pseudocapacitive material.

4. Conclusions

Ni-doped carbon aerogel was prepared by wet impregnation methods to compare the physical structure and electrochemical properties with carbon aerogel. Electrochemical properties of prepared Ni-doped carbon aerogel and carbon aerogel electrodes were investigated by galvanostatic charge/discharge measurements. Ni-doped carbon aerogels exhibited higher specific capacitance than carbon aerogel. The improved performance of Ni-doped carbon aerogels was attributed to pseudocapacitive characteristics of nickel and nickel oxide.

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