PREPARATION OF POROUS CARBON WITH NANOTUBE-LIKE PORE STRUCTURE AND THEIR ELECTROCHEMICAL PROPERTIES FOR SUPERCAPACITOR

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Introduction

Due to their stable physicochemical properties, high surface area, relatively low cost, and availability, porous carbons are regarded as the most promising supercapacitors electrode materials [1,2]. In particular, mesoporous carbon obtained by template method generally exhibited very good electrochemical performance in this application [3]. Efficient method to obtain mesoporous carbons is using various silica-templates [4–6]. It is difficult to remove the silica in those processes, although the pores with ordered structure and a specific size are easily obtained in carbons. In contrast, a method to prepare porous carbons using metal oxides as template developed by M.Inagaki et al [7-9] seemed to be more attractive. In this work, porous carbons were prepared by carbonizing the soluble starch by using needle-like nano-sized MgO as template. The relationships between the structure and the electrochemical performance for supercapacitors were investigated.

Experimental

The needle-like nano-sized $Mg(OH)_2$ was prepared by the surfactant-mediated solution method according to the literature [10]. 10.0 g $Mg(OH)_2$ was dispersed in 40 ml deionized water for 1 hour with the help of ultrasonic stir. Then 10.0 g soluble starch (30% solution) was added into the $Mg(OH)_2$ suspended solution, and mixed by ultrasonic stir for 1 hour. The mixture was dried at 50°C in vacuum for 12 h. Subsequently, the dried mixture was carbonized at high temperature. The derived products were immersed into 2 mol/L sulfuric acid to dissolve MgO out, and then washed by deionized water. The resulted porous carbons were denoted as SMC-55-X-Y (X and Y corresponding to carbonization temperature and duration, respectively). The soluble starch without $Mg(OH)_2$ was also carbonized at different temperature for comparison, and the derived carbons were denoted as SC-X-Y.

XRD pattern was obtained on a D8 Advance diffractometer with a Cu Kα X-ray source. TEM images were recorded on a JEM2010 electron microscope operating at 200 kV. N_2 sorption isotherms were measured using a Quantachrome Autosorb-1 Adsorption Apparatus at 77 K. Electrochemical measurements were carried out in a 6 mol L^{-1} KOH aqueous electrolyte at room temperature, using a three-electrode cell with the reference electrode and counter electrode of a Hg/HgO and a platinum coil. Solartron Instrument Model 1287 electrochemical interface was used for cyclic voltammetry (CV). Galvanostatic charge/discharge measurements were carried out by Arbin-BT2000 test station.

Results and Discussion

The normalized XRD patterns of the resulting carbons are shown in Fig.1. For the carbons obtained in the presence of needle-like nano-sized $Mg(OH)_2$, peaks appeared at around 2θ = 26.6 °, which can be assigned to the (002) diffraction of the graphitic crystallite. Increasing the heat treatment temperature, those diffraction peaks became stronger, indicating growth of graphitic crystallite. In contrast, for the carbons from pure starch without needle-like nano-sized $Mg(OH)_2$, there were almost no marked (002) diffraction characteristic peak, which is consistent with an amorphous framework.

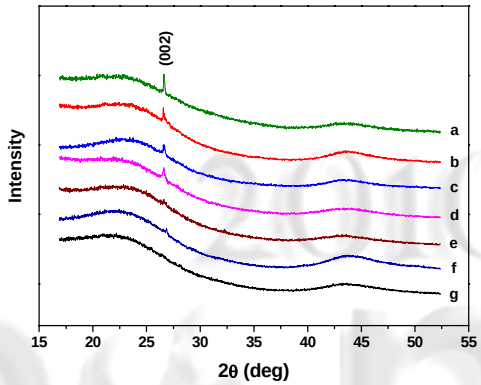


Fig. 1. Normalized XRD patterns: a – SMC-55-950-6, b – SMC-55-950-3, c – SMC-55-950-1,d – SMC-55-850-3, e – SMC-55-750-3 , f – SC-950-6, g – SC-850-3

The TEM images (Fig. 2) show that the pore structure resembled the shape of needle-like nano-sized $Mg(OH)_2$. One dimension nanotube-like structure and disordered pore was obtained in the carbon.

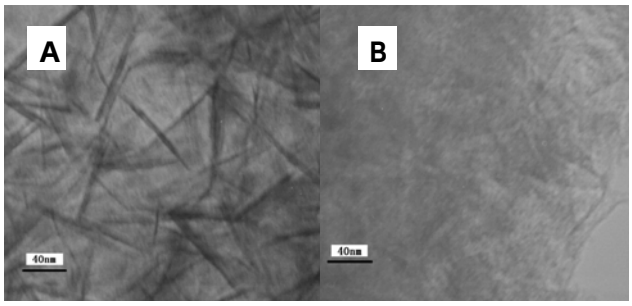


Fig. 2. TEM image of : A—needle-like nano-sized $Mg(OH)_2$ and B—SMC-55-950-3

The adsorption and desorption branches of the isotherm did not coincide, and pronounced adsorption-desorption hysteresis can be seen (Fig. 3). The pronounced hysteresis loop suggested higher amount of mesopores.

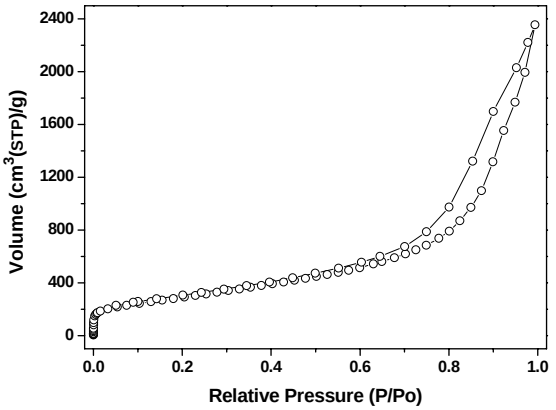
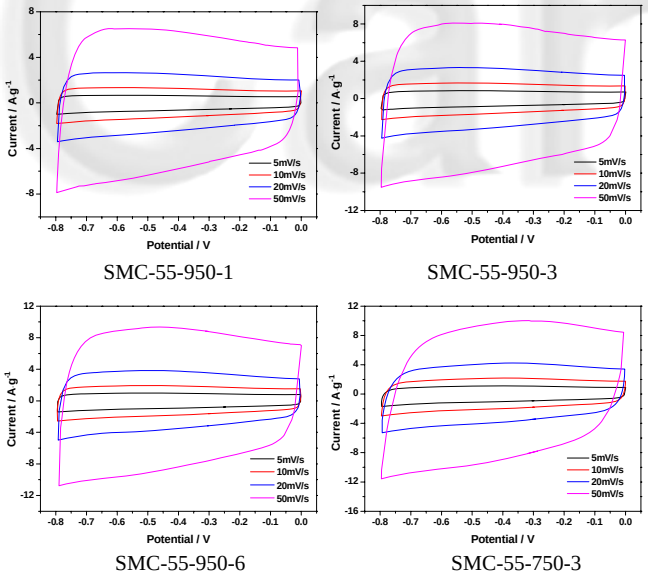


Fig. 3. Nitrogen sorption isotherms of SMC-55-950-3

Fig. 4 shows cyclic voltammogramms at various scan rates from 5mV·s^{-1} to 50mV·s^{-1} at the potential range of -0.8 V to 0 V (vs. Hg/HgO) for porous carbons. All the samples exhibit typical quasi-rectangular curve shapes at low scan rate of 5mV·s^{-1}. With increasing scan rates, rectangular curve shapes of samples treated at high temperature kept well (Fig.4 a, b and c), while the curve shape of SMC-55-750-3, which treated at lower temperature, showed distortion to some extent (Fig.4 d).The nearly 90° change in the CV curves of at the switching potential suggested that they had small time constants as an ideal capacitor, which indicates the excellent capacitive ability of even at high current density for samples treated at high temperature



SMC-55-950-1 SMC-55-950-3

SMC-55-950-6 SMC-55-750-3

Fig. 4. CV curves at various scan rates

The galvanostatic charge/discharge capacitances of porous carbons are shown in Fig.5. With increasing treating temperature, the capacitances of samples decreased at low charge-discharge current density of 0.5 A·g^{-1}. SMC-55-750-3 exhibited a capacitance of as high as 217 F·g^{-1}, while the capacitance of SMC-55-950-3 only reached a lower level of 154 F·g^{-1}. The capacitance of porous carbon treated at relatively lower temperatures (750 °C and 850 °C) decreased rapidly. For samples treated for different durations at high temperature (950 °C), the capacitance decrease tendencies were similar as the applied current increased, and excellent capacitance retainment were exhibited at high current densities. SMC-55-950-6 even retained a capacitance of 103 F·g^{-1} at a current of 50 A·g^{-1}. This could be attributed to the good electron conductivity because of growth of some graphitic crystallite.

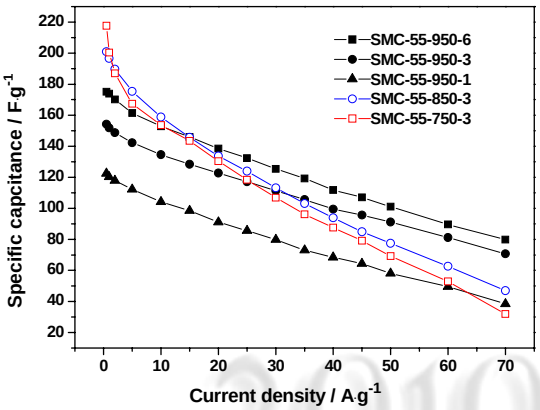


Fig. 5. Charge/discharge capacitances of porous carbons

Conclusions

Porous carbons prepared by carbonizing the starch using needle-like nano-sized $Mg(OH)_2$ as template possesses abundant mesopores. Due to the effect of the template with special shape, the porous carbon exhibited nanotube-like pore structure. The growth of some graphitic crystallite. and the special structure resulted in high capacity and excellent power performance of the materials.

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References

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