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Nitrogen-containing carbon microspheres for supercapacitor electrodes

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ABSTRACT

Nitrogen-containing carbon microspheres (NCMs) were prepared via directed carbonization of poly(1,5-diaminonapthalene) at different temperatures which was synthesized from 1,5-diaminonapthalene with ammonium persulfate as oxidizing agent. The NCMs were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), N_2 adsorption-desorption analysis, thermogravimetric-differential thermal analysis (TG-DTA) and X-ray photoelectron spectroscopy (XPS). A typical sample (NCM-700) shows a specific surface area of 403 $m^2 g^{-1}$, nitrogen content of 5.94 at.%, and regular spherical geometry (0.2–0.5 μm in diameter). The electrochemical properties of the NCMs electrodes were investigated by cyclic voltanmetry and galvanostatic charge-discharge measurement. NCM-700 electrode shows a high specific capacitance of 228 $F g^{-1}$ at a current density of 1.0 $A g^{-1}$ in 6 M KOH aqueous electrolyte, indicating good capacitive behavior. Besides, the electrode still remains 196 $F g^{-1}$ (with capacitance retention of 86%) after 5000 charge/discharge cycles, suggesting excellent cycling stability.

1. Introduction

In recent years, supercapacitors with excellent reversibility, longer cycle life and higher power density than batteries, higher energy density than conventional physical capacitors, have attracted intensive research interests. Because of these merits, supercapacitors can be used for applications such as electric vehicles, digital telecommunication systems and pulse laser technique [1–4]. According to different charge storage mechanisms, supercapacitors can be classified into two categories [3,5]: one is electric double-layer capacitors (EDLCs) which store electrical energy by electrostatic accumulation of charges at the electrode/solution interface, such as carbon materials [6]. The other is pseudo-capacitors which store the electrical energy by fast and redox reactions occurring at the electrode interface, such as metal oxides [7–9] and conducting polymers [10,11].

Electrode material is a fatal factor to the performance of supercapacitors. Above all materials, carbon materials are usually used as electrode materials for supercapacitors because of their stability in different solutions, non-toxic, low cost and long cycle life, but their specific capacitance is lower than that of metal oxides [12,13]. Carbon microspheres have several advantages, such as regular morphology, adjustable porosity, and particle size, which could decrease the resistance of ion diffusion and result in improved electrochemical performances [14–16]. Moreover, the accumulation of carbon microspheres creates macroporosity that promotes the generation of ion-buffer reservoirs, which is able to minimize the diffusion distances of electrolyte ions to the interior carbon surfaces [17]. Therefore, carbon microspheres have been one of the most promising materials to be used for lithium-ion batteries [18] and supercapacitors [19]. For instance, Ma et al. [20] reported the preparation of mesoporous size controllable carbon microspheres which show a high specific capacitance of 289 $F g^{-1}$ at a current density of 1.0 $A g^{-1}$. Liu et al. [14] synthesized nickel-doped activated mesoporous carbon microspheres by an emulsion-assisted hydrothermal method. The carbon microsphere as supercapacitor electrode has a specific capacitance of 361 $F g^{-1}$ at 1.0 $A g^{-1}$.

On the other hand, the heteroatoms, such as nitrogen and sulfur, have been introduced into carbon materials in order to further improve electrochemical performance of carbon electrodes [21–23]. Nitrogen-containing carbon materials can be prepared by the carbonization of nitrogen-enriched polymers and materials, such

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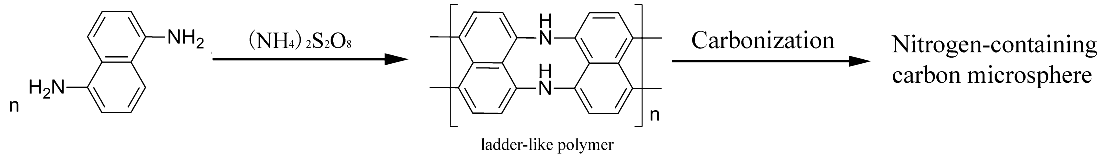

Fig. 1. The schematic synthesis of NCMs.

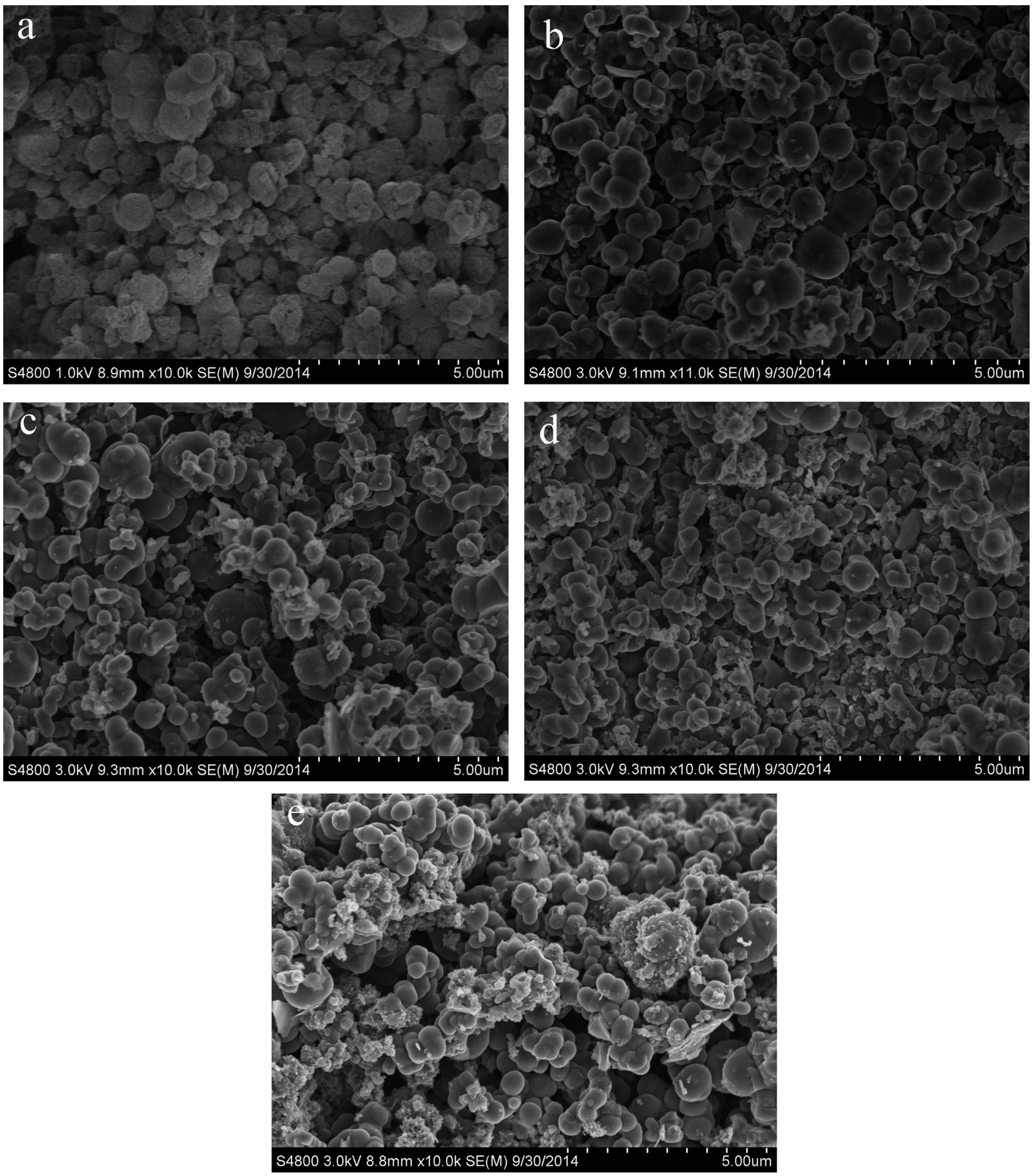

Fig. 2. SEM images of PDAN microspheres (a), NCM-600 (b), NCM-700 (c), NCM-800 (d), NCM-900 (e).