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Effect of Nafion on the preparation and capacitance performance of polyaniline

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ABSTRACT

With manganese dioxide (MnO_2) as the oxidant, perfluorinated sulfonic acid ion exchange resin (Nafion) as the doping agent and emulsifier, Nafion doped polyaniline (PANI-Nafion) was prepared by emulsion polymerization method. Scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) were carried out to characterize the structure and morphology of PANI-Nafion. Symmetric redox supercapacitor was assembled with PANI-Nafion as active electrode material and 1.0 mol L^{-1} H_2SO_4 aqueous solution as electrolyte. The electrochemical characteristics of these supercapacitors were investigated by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) and galvanostatic charge/discharge tests. These results show that the diameter of PANI-Nafion nanofiber is about 30 ~ 40 nm and the pores between PANI-Nafion composite materials are distributed uniformly. The specific capacitance of PANI-Nafion electrode is about 385.3 F g^{-1}, which is higher than that of undoped PANI (235.8 F g^{-1}). After 1000 charge/discharge cycles the specific capacitance of PANI-Nafion electrode is 272.4 F g^{-1}, its capacity retention is 70.7%, which is significantly better than that of PANI electrode materials.

Introduction

Supercapacitors have the advantages of high power density, high rates of charge -discharge, excellent cyclic stability, safe, wide operation temperature range and reliable. These characteristics make them to be an ideal choice for energy storage [1–2]. Supercapacitors may be classified as double electric layer capacitor and pseudo-capacitors according to their mechanism of charge energy storage. Pseudo-capacitors are capable of storing higher charge than double electric layer capacitor due to the availability of double-layer and faradaic pseudocapacitive sites. Numerous transition metal oxides and conducting polymers as electrode materials of pseudo-capacitors have attracted great attention [3].

Nevertheless conducting polymer is a research hot spot owing to its many advantages, such as low cost, high conductivity, wide voltage window, and high specific capacitance [4–5]. Polyaniline (PANI), polythiophene (PTh), polypyrrole (PPy) and their derivatives were applied for the electrode materials of supercapacitor [4–8]. Among these conducting

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polymers, PANI has been considered as one of the most promising electrode material in many electrochemical fields due to its chemical stability, environmental stability, easy processability, good redox reversibility, and relatively low cost [9–12].

At present, there are many reports on the preparation and properties of PANI or its composite materials. Among these various syntheses of conducting PANI, emulsion polymerization is known to be one of the most effective methods. Emulsifier generally works as both surfactant and protonic agent. It directly affects the initiation of emulsification, chain growth, size and distribution of polymer particles. Recently, nano-PANI was synthesized by emulsion polymerization with sulfonate as dopant and emulsifier, such as sodium alkylarylsulphonate (DBSA) [13], camphorsulfonic acid (L-CSA) [14], polystyrene sulfonic acid [15], sodium dodecylsulfate (SDS) [16] and p-toluene sulphonic acid (PTS) [17]. The electrical conductivity or supercapacitive performance of the doping PANI was enhanced. Nafion is an environmentally friendly superacid [18–19] in which the sulfonic acid group can provide proton-exchange, and was applied for the preparation of electrode in supercapacitors [20–21]. Nafion is affirmed to be beneficial to the improvement of capacitance. To the best of our knowledge, Nafion was used for the electrodeposition of PPy and was doped into PPy [22], but few reports on Nafion as a dopant and emulsifier used for the chemical preparation of PANI nanomaterial for supercapacitor.

In this paper, PANI was prepared by oxidative emulsion polymerization at ambient temperature, using Nafion as dopant and emulsifier and MnO_2 as oxidant. The effect of Nafion on PANI morphology and phases composition was investigated by Fourier transform infrared spectrometry (FTIR), scanning electron microscope (SEM) and X-ray diffraction (XRD). Electrochemical performances were evaluated by using two-electrode electrochemical capacitor cells with the electrolyte of 1.0 mol L^{-1} H_2SO_4 aqueous solution.

Experimental

Materials

Nafion (5 wt.%) was purchased from Sigma–Aldrich. HCl, MnO_2, aniline, acetone, polytetrafluoroethylene, acetylene black were obtained commercially. All chemical reagents used in this experiment were of analytical purity. Additionally, freshly double-distilled water was obtained by experiment.

Preparation of PANI-Nafion nanomaterials

The aniline monomer was distilled under reduced pressure over zinc metal until the solution color turns colorless. 4 mL as-pretreated aniline was dissolved in 100 mL 1.0 mol L^{-1} HCl solution with intense stirring at ambient temperature for 20 min. Then, a certain amount of Nafion was added into this solution. This solution was signed as A. MnO_2 was added slowly into A solution ($n_{AN} : n_{MnO_2} = 1 : 1$). After several minutes, a dark green product was obtained. The mixture was stirred for 10 h at room temperature. The resulting solution was filtered and rinsed with acetone and distilled water several times until Mn^{2+} ion was removed from solution. After rinsing, product was dried in a vacuum oven at 60 °C for 24 h, then was ground and sieved. This as-prepared product was marked with PANI-Nafion. In contrast, the product prepared without Nafion was marked with PANI.

Characterizations of PANI-Nafion nanomaterials

The samples were analyzed by Fourier transform infrared spectroscopy (FTIR, PE Spectrum One, Perkin Elmer). Field-emission-scanning electron microscope (FE-SEM, FEI Quanta 200 FEG) was used to investigate the surface morphology of samples. The elemental composition of the samples was characterized by energy dispersive X-ray spectroscopy (EDS) equipped on SEM. The crystal structures of samples were analyzed by X-ray diffraction (XRD, Rigaku D/max 2500 v/pc, Cu Kα1, λ = 0.15406 nm, the operation voltage and current maintained at 40 kV and 30 mA, respectively).

Electrochemical analysis

The as-prepared PANI-Nafion, polytetrafluoroethylene (PTFE), acetylene black (mass ratio: 80:10:10) were mixed in absolute alcohol, then the slurry was rolled into a film with 0.2 mm thick. The film was cut into disk electrodes with diameter of 10 mm. Subsequently, fastener-type symmetric supercapacitor cells were assembled with a pair of disk electrodes divided by a piece of microporous separator (shown in Fig. 1). Cyclic voltammograms (CV) were performed on an electrochemical workstation (Zahner IM6, Germany) at room temperature, were recorded from −0.2 to 0.8 V at a scan rate of 20 mV s^{-1}. The charge/discharge experiments were conducted in the potential window ranged from 0 to 0.7 V (vs. SCE) with a Battery Tester (Neware, Shenzhen, China) at current density of 0.1 A g^{-1} for 1000 cycles to evaluate the cycle stability.

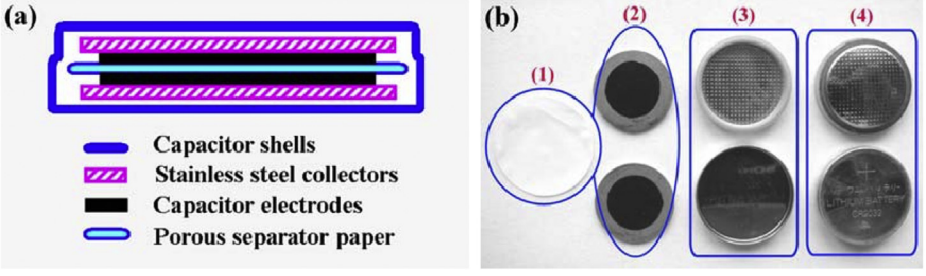

Fig. 1 – (a) Schematic the as-assembled button supercapacitors and (b) full size picture of the supercapacitor cell assembled: (1) porous separator; (2) disk electrodes; (3) electrode shells and (4) fastener-type supercapacitor cell.