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Investigation of polyaniline films doped with Ni^{2+} as the electrode material for electrochemical supercapacitors

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ABSTRACT

Polyaniline (PANI) films doped with Ni^{2+} (PANI/Ni^{2+}) were synthesized by cyclic voltammetry (CV) on stainless steel (SS) substrates in 0.2 mol/L aniline (An) and 0.5 mol/L sulfuric acid (H_2SO_4) electrolyte with various concentration of nickel sulfate ($NiSO_4$). The structure and morphology of PANI/Ni^{2+} films were characterized by Fourier transform infrared (FTIR), X-ray diffraction (XRD), Scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) techniques. The electrochemical properties of PANI/Ni^{2+} films were investigated by cyclic voltammetry, galvanostatic charge–discharge test and electrochemical impedance spectroscopy (EIS) in 0.5 mol/L H_2SO_4 electrolyte in three-electrode system. The results suggest that the growth rate of PANI was greatly increased, which may arise from the interactions between PANI chain and Ni^{2+}. The PANI/Ni^{2+} films show a larger specific capacitance of 658.3 F/g at a current density of 5 mA/cm^2 and lower resistance compared with the pure PANI film. The results indicate that the PANI/Ni^{2+} films are promising material for supercapacitors.

1. Introduction

Electrochemical supercapacitors are a kind of energy storage devices between conventional capacitors and batteries, which have various applications in electric vehicles, cellular communication devices, portable computers and nanoelectronics [1–3]. Supercapacitors can be divided into two basic types based on the charge-storage mechanism: (1) electrochemical double-layer capacitors composed of carbon materials, in which the capacitance is derived from charge separation at electrode/electrolyte interface, and it is determined by the effective surface area and the dielectric constant of the electrolyte; (2) redox supercapacitors consisting of transition metal oxides and conducting polymers, in which the capacitance is generated from fast faradic reactions of the electrode material. Pseudocapacitance is produced from a bulk process whereas the double-layer capacitance is produced from a surface process [4,5]. Among all these materials investigated, conducting polymers are the most promising material as they possess redox pseudocapacitance in addition to double-layer capacitance. Conducting polymers offer the advantages of low production cost compared with noble metal oxides and high charge capacity compared with carbon materials [6]. In the case of conducting polymers, polyaniline (PANI) has attracted much attention and been intensively studied as electrode material owing to its unique proton doping mechanism [7,8], ease of synthesis, good environmental stability, controllable electrical conductivity and high specific capacitance [9–13].

PANI films are generally synthesized by different electrochemical methods in acid solutions containing aniline [14–16]. Usually the protonic acid dopants are inorganic acids (such as HCl, H_2SO_4, $HClO_4$) [17–19] or organic acids (such as p-toluene sulfonic acid) [20]. The effect of anions on the properties of PANI films has been extensively investigated [21–23]. However, little attention has been given to the role of cations (other than protons) on the rate of PANI growth and on its electrochemical properties. Recently, PANI doped with metal ions has attracted much attention due to its potential practical applications such as redox-active catalyst [24], corrosion inhibitor [25], etc. Previous works [26,27] have demonstrated that alkaline cations, similarly to anions but to a smaller degree, affect the rate of PANI electropolymerization when it is performed by continuous potential cycling. On the contrary, there were rare studies with respect to PANI doped with transition metal salts as electrode material for supercapacitor.

In this research, the PANI/Ni^{2+} films were synthesized in H_2SO_4 solution containing $NiSO_4$ by cyclic voltammetry (CV) on low cost stainless steel (SS) substrates. The electrochemical properties of the PANI/Ni^{2+} films were investigated by cyclic voltammetry, galvanostatic charge–discharge test and electrochemical impedance spectroscopy (EIS) in three-electrode system. The structure and morphology of PANI/Ni^{2+} films were characterized by Fourier

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transform infrared (FTIR), X-ray diffraction (XRD) and Scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) techniques, respectively.

2. Experimental

2.1. Materials

Aniline was vacuum-distilled at 120 °C and stored in refrigerator before use. Analytical-grade reagents, ethanol, H_2SO_4 and $NiSO_4 \cdot 6H_2O$ were used as received without any pretreatment. Double-distilled water was used for the preparation of solutions.

2.2. Synthesis of the PANI/Ni^{2+} films

All electropolymerization were carried out in a classic one-compartment cell using three-electrode configuration on CHI660B electrochemical work station. SS electrodes (type 201, 25 mm × 10 mm × 0.5 mm) were used as working electrode (WE) for PANI deposition. The deposited area was 1 cm^2 (1 cm × 1 cm) with other area insulated by a PTFE coating. SS electrodes (type 304, 25 mm × 15 mm × 0.5 mm) and saturated calomel electrode (SCE) were used as the counter electrode (CE) and reference electrode (RE), respectively. SS electrodes were polished to a mirror surface successively with emery papers (600#, 1500#, 2000#), rinsed with double-distilled water and immersed in ethanol ultrasonically for 10 min, then immersed in double-distilled water ultrasonically for 10 min, last air-dried for use.

The PANI/Ni^{2+} films were electrodeposited on SS substrates potentiodynamically in 0.2 mol/L aniline and 0.5 mol/L H_2SO_4 electrolyte with different concentrations of 0.2, 0.5, and 0.8 mol/L Ni^{2+}. The deposition was carried out for two-steps: first between −0.2 and 1.2 V *vs.* SCE for 2 cycles, then between −0.2 and 0.9 V *vs.* SCE for 25 cycles at a scan rate of 50 mV/s. After deposition, the coated PANI/Ni^{2+} films were rinsed with 0.5 mol/L H_2SO_4 in order to remove soluble monomeric species, and then dried under vacuum for 12 h at 60 °C. The pure PANI film was prepared following the above process in H_2SO_4 solution, without Ni^{2+}, and a fine dark green film was obtained.

2.3. Structure characterizations

The samples used for structure characterizations were the powers scraped from PANI and PANI/Ni^{2+} films on SS substrates. The structure was characterized by FTIR (Nicolet, type 210, America). FTIR spectrometer in the range of 4000–400 cm^{-1}. The XRD patterns were characterized by D/MAX-2400X X-ray diffractometer with CuKα radiation ($\lambda = 0.154056$ nm), employing a scanning rate of 10° min^{-1} in the 2θ range of 5–60°. The morphology of PANI and PANI/Ni^{2+} were characterized by SEM (JEOL JSM-6701F). Elemental analysis was performed by EDS (JEOL JSM-5600LV). The XPS data were obtained by a V.G. ESCA Laboratory 210 photoelectron spectrometer with a Mg Kα source, the spectra were acquired with a 30 eV pass energy.

2.4. Electrochemical tests

All electrochemical tests were performed on CHI660B electrochemical work station in a three-electrode glass cell with PANI and PANI/Ni^{2+} films working electrode, a platinum plate counter electrode, and a standard calomel reference electrode. The electrochemical properties were evaluated by cyclic voltammetry, galvanostatic charge–discharge test and electrochemical impedance spectroscopy techniques in 0.5 mol/L H_2SO_4 aqueous solution. Cyclic voltammetry and charge–discharge test were performed in the potential window ranged from 0 to 0.7 V *vs.* SCE. EIS measurements were recorded in the frequency range 10^5–10^{-2} Hz with an excitation signal of 5 mV.

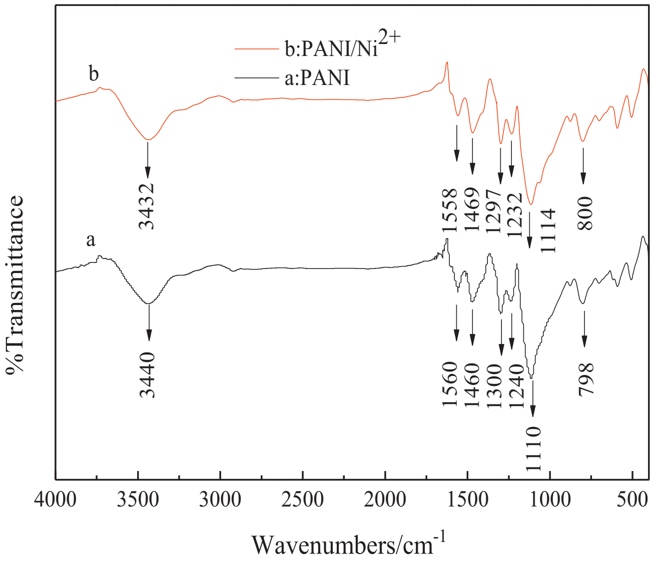

Fig. 1. FT-IR spectra of PANI film and PANI/Ni^{2+} film prepared in the solution with 0.8 mol/L Ni^{2+}.

3. Results and discussion

3.1. FT-IR

Fig. 1 shows the FT-IR spectra of the pure PANI film and PANI/Ni^{2+} film prepared in the solution with 0.8 mol/L Ni^{2+}. The main characteristic peaks of PANI/Ni^{2+} film were assigned as follows: the bands at 1558 and 1469 cm^{-1} were assigned to the N=Q=N stretching (Q represents the quinoid unit) and the N–B–N stretching (B represents the benzenoid unit), respectively. The bands located at 1297 and 1232 cm^{-1} were ascribed to C—N stretching vibration of quinoid rings and benzenoid rings, respectively. While the bands at 1114 and 800 cm^{-1} reflected the C—H in-plane deformation and out-of-plane vibration, respectively. From Fig. 1, we can see that some vibration frequencies of the PANI/Ni^{2+} film are shifted to lower wavenumbers compared with those of the PANI film. The red shift of the IR absorption peaks is referred to be a signature of the conversion of the quinoid rings to the benzenoid rings by proton-induced spin-unpairing mechanism [28], which was considered to be an indication of increasing degree of charge delocalization on the PANI backbone [29]. It implies that PANI doped with Ni^{2+} lead to an increase of charge delocalization on the PANI backbone compared to doping solely with H_2SO_4.

3.2. XRD studies

Fig. 2 depicts the X-ray diffraction patterns of the pure PANI film and PANI/Ni^{2+} film prepared in the solution with 0.8 mol/L Ni^{2+}. The XRD pattern of PANI/Ni^{2+} film exhibited the broad and weak reflection in the range of 20–25°, which were the characteristic peak of amorphous PANI. However, the sharpness of the peak at 23° indicated that the PANI/Ni^{2+} film has lower crystalline in comparison with the pure PANI film.

3.3. SEM characterization

The morphology of PANI film and PANI/Ni^{2+} film prepared in the solution with 0.8 mol/L Ni^{2+} deposited on SS substrate