

Electrochemical properties of Ni(OH)₂/polypyrrole composite electrode prepared by electrodeposition for pseudo-capacitor

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Nickel hydroxide/polypyrrole composite electrodes were prepared by an electrolytic deposition and their electrochemical behaviors were evaluated by using cyclic voltammetry, electrochemical impedance spectroscopy and galvanostatic charge-discharge cycling techniques. Deposition of composite electrodes were carried out in the potentiostatic mode at -0.85 V versus Ag/AgCl and compared with the nickel hydroxide film electrode. The electrolyte solution for electrodeposition consisted of 0.1 M aqueous Ni(NO₃)₂ (50 mL) and various vol.% of polypyrrole with 0, 0.05, 0.1 and 0.5 ml. The specific capacitance measured at the scan rate of 10 mV s⁻¹ was found to be 1975 (0 ml), 2141 (0.05 ml), 1565 (0.1 ml) and 1171 F g⁻¹ (0.5 ml) for deposited weights of 30, 30, 35 and 55 μg cm⁻², respectively. The adequate use of polypyrrole improves the dispersion of nickel hydroxide. Therefore, the intercalation and/or absorption of diffusing ions from electrolyte and proton insertion from water may also easily gain access to the available sites reducing the degradation of the electrochemical performance in cyclic redox reactions.

Key words: Ni(OH)₂/polypyrrole composite, Electrodeposition, Pseudo-Capacitor, Electrochemical properties.

Introduction

Electrochemical capacitors (EC) based on hydrous ruthenium oxides exhibit much higher specific capacitance than conventional carbon materials with remarkably high specific capacitance values ranging from 658 to 760 F g⁻¹ (from a single electrode) [1-2]. However, the high cost of this noble metal material limits practical use. Therefore, much effort has been aimed at searching for alternative inexpensive electrode materials with good capacitive characteristics. Materials investigated include NiO [3, 4], CoO_x [5], MnO₂ [6], Ni(OH)₂ [7], and Co(OH)₂ [8]. Amongst these electrode materials, Ni(OH)₂ is considered to be the most promising for applications in energy/power storage devices, due to its low cost and well-defined electrochemical redox activity [9, 10]. To date, only limited reports on the capacitive behavior of Ni(OH)₂ have appeared [11, 12]. The use of electrochemical techniques to produce Ni(OH)₂ provides control over the structure and morphology of the films deposited [13, 14]. But electrical conductivity of the nickel hydroxide electrode is very low and insufficient for high-rate charge/discharge.

Conducting polymers have attracted lots of research interest due to their high electrical conductivity, low cost, and high redox active properties. Polythiophene, polyaniline, polypyrrole and their derivatives are the most promising and widely studied conducting

polymers [15-17]. Although they have good electrical properties, conducting polymers suffer from poor cyclability. This is ascribed to their poor mechanical properties [18, 19] and the chemical instability during repeated redox processes [14, 20]. In addition to these drawbacks, the poor sustainability of conducting polymers towards over-oxidation aggravates the situation. In the search for new materials, the composites play an important role. As a multi-component system, the composites combine the properties of their constituents, which make it possible to overcome the drawbacks of the individual substances [19, 21].

In this work, the electrochemically deposited nickel hydroxide film was investigated in the effects of adding the polypyrrole on the electrochemical capacitive behavior of nickel hydroxide electrodes by means of cyclic voltammetry and cycle stability.

Experimental

Ni(OH)₂/polypyrrole composite preparation

All chemical reagents were of analytical grade chemicals (Ni(NO₃)₂·6H₂O, Polypyrrole and 1M KOH, Aldrich). A research grade stainless steel (SS) sheet (grade 304, t = 0.2 mm) was used as the current collector. The SS sheet was cut into the required size (10 mm × 30 mm). The SS foil was polished with emery paper to a rough finish and then washed in acetone, ethyl alcohol and distilled water in turn for 10 minutes. A three-electrode electrochemical cell was assembled in which the SS foil, Pt plate (20 mm × 20 mm) and a Ag/AgCl (in 1M KCl) were used as

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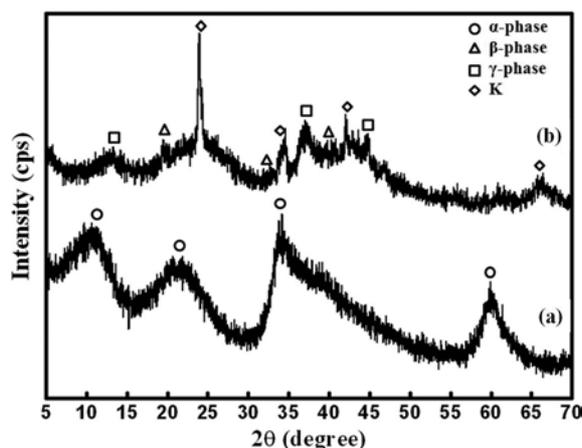


Fig. 1. XRD patterns of (a) before CV test and (b) after CV test of Ni(OH)₂.

the working, counter and reference electrode, respectively. All electrochemical depositions of Ni(OH)₂/polypyrrole composite were performed by using a potentiostat (Zennium, Zhaner Elektrik, Germany). Deposition of composite electrodes were carried out in potentiostatic mode at -0.85 V versus Ag/AgCl and compared with nickel hydroxide electrode. The electrolyte solution for electrodeposition consisted of 0.1 M aqueous Ni(NO₃)₂ (50 mL) and various vol. % of polypyrrole with 0, 0.05, 0.1 and 0.5 ml. The deposited electrodes were washed in distilled water and then dried at room temperature for 24 hrs. The weight of the electrode was determined by means of a micro-balance. Deposited weight was calculated by weighing the substrate before and after deposition experiments, and after by drying at room temperature for 24 hrs.

Characterizations

The microstructures of the specimens were evaluated by a field emission scanning electron microscopy (FE-SEM, S-4700, Hitachi, Japan). All electrochemical measurements were tested in a three-electrode arrangement. The working electrode was characterized in 1M KOH solution by cyclic voltammetry using Ag/AgCl as reference electrode and a platinum plate (20 mm × 20 mm) as counter electrode. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were carried out using a Zennium electrochemical workstation (Zennium, Zhaner Elektrik, Germany) at room temperature. The impedance measurements were conducted by means of a Zennium Instrument and AC perturbation amplitude of 5 mV at OCV was applied in the frequency range between 100 mHz and 100 kHz. The long-term stability of deposited electrode upon cycling was characterized by cyclic charge-discharge test between 0 and 0.43 V (versus Ag/AgCl) over 1000 cycles.

Results and discussion

Fig. 1 shows the XRD patterns of as-deposited nickel

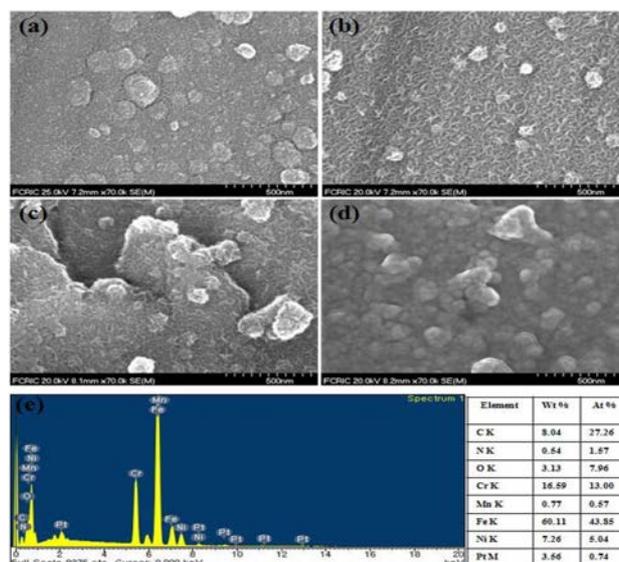


Fig. 2. SEM images and EDX results: (a) Ni(OH)₂ electrode, (b) Ni(OH)₂/polypyrrole (0.05 ml) composite electrode, (c) Ni(OH)₂/polypyrrole (0.1 ml) composite electrode, (d) Ni(OH)₂/polypyrrole (0.5 ml) composite electrode, and (e) EDX result for Ni(OH)₂/polypyrrole (0.5 ml) composite electrode.

hydroxide before and after CV test. These diffraction patterns can be indexed to the diffraction data of the Ni(OH)₂ · 0.75H₂O (JCPDS No. 38-0715, Rhombohedral) (Fig. 1(a)). It can be assigned as the typical reflection of α-type Ni(OH)₂. However, after several cycles, γ-phase (JCPDS No. 84-1459, Orthorhombic) and β-phase (JCPDS No. 74-2075, Hexagonal) appeared (Fig. 1(b)). The XRD results shows that the crystallization of γ-phase induced by the oxidation of Ni(OH)₂ to NiOOH. It implies that the surface state of electrode would not return to its original state under experimental conditions. It follows that the surface state of the electrode will hardly be restored to its original state as the cycling number increases. As well as the XRD results shows that the crystallization of γ-phase induced by the oxidation of Ni(OH)₂ to NiOOH for Ni. According to Ref. [22], the α-type material is firstly oxidized into γ(III) as similar inter-sheet distances characterize both α(II) and γ(III) phase. However, after one cycle, the discharged material shows the β(II) structural type. They have shown that the following sequence occurs during the several first electrochemical cycles:

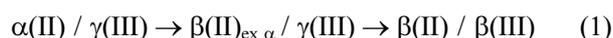


Fig. 2 (a-d) shows the SEM images of the Ni(OH)₂/polypyrrole composite electrodes formed on the amount of polypyrrole. As the amount of polypyrrole increased, the deposited mass and area also increased. At Ni(OH)₂ electrodes without added polypyrrole, deposited particles are shown to have agglomerated (Fig. 2(a)). However, the adequate amount of polypyrrole to improve the dispersion of Ni(OH)₂/polypyrrole

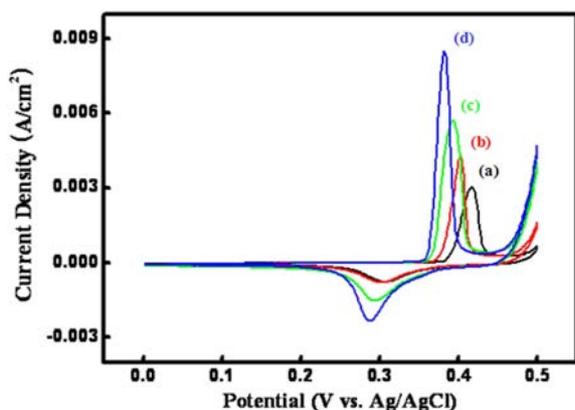


Fig. 3. Cyclic voltammetric behaviors of the Ni(OH)₂/polypyrrole composite electrodes on the amount of polypyrrole at 10 mVs⁻¹ in 1 M KOH solution. (a) Ni(OH)₂ electrode, (b) Ni(OH)₂/polypyrrole (0.05 ml) composite electrode, (c) Ni(OH)₂/ polypyrrole (0.1 ml) composite electrode, (d) Ni(OH)₂/polypyrrole (0.5 ml) composite electrode.

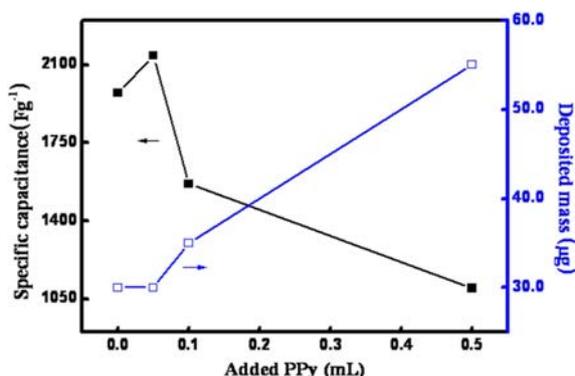


Fig. 4. Plot of specific capacitance and deposited mass for Ni(OH)₂/polypyrrole composite electrodes on the amount of polypyrrole. (a) Ni(OH)₂ electrode, (b) Ni(OH)₂/polypyrrole(0.05 ml) composite electrode, (c) Ni(OH)₂/polypyrrole (0.1 ml) composite electrode, (d) Ni(OH)₂/polypyrrole (0.5 ml) composite electrode.

(0.05 ml) composite electrode as well as the specific surface area is expected to increase (especially Fig. 2(b)). However, as the loading of polypyrrole increased (Fig. 2(c, d)), the Ni(OH)₂ were covered with polypyrrole. This led to poor electrode conductivity because the ion diffusion in the electrode was inhibited. An optimized amount of active material can contribute to capacitance. The EDX-spectrum (Fig. 2(e)) shows the peaks for O (3.13 wt.%), Ni (7.26 wt.%) and N (0.54 wt.%) which proved that the polypyrrole was successfully incorporated into the Ni(OH)₂.

Fig. 3 shows the CVs of the Ni(OH)₂/ polypyrrole composite electrodes depend on the amount of polypyrrole. The cyclic voltammetry measurements were carried out in 1 M KOH electrolyte in the potential range of 0.0 to 0.5 V at a rate of 10 mVs⁻¹. The Ni(OH)₂/ polypyrrole composite electrodes show a higher current density (Fig. 3(b-d)) than the Ni(OH)₂ electrode without added polypyrrole (Fig. 3(a)). As the amount of polypyrrole was increased, the current density of the

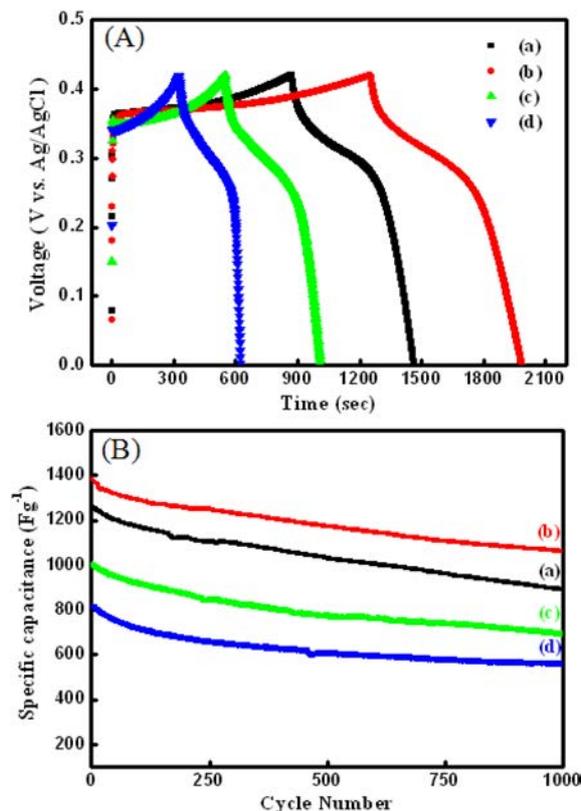


Fig. 5. Galvanostatic charge-discharge curves (A) and Life cycle test (B) of Ni(OH)₂/polypyrrole composite electrodes as a function of the number of charge-discharge cycles. (a) Ni(OH)₂ electrode, (b) Ni(OH)₂/polypyrrole (0.05 ml) composite electrode, (c) Ni(OH)₂/ polypyrrole (0.1 ml) composite electrode, (d) Ni(OH)₂/polypyrrole (0.5 ml) composite electrode.

Ni(OH)₂/polypyrrole composite electrodes increased. During the charge-discharge process of the polypyrrole electrode, the high capacitance arises from a doping process, which, in the simplest case, involves the introduction of positive holes (or polarons) together with charge-balancing anions [23]. It was observed that the deposition of a small amount of polypyrrole contributed to the enhancement of the capacitance of the Ni(OH)₂ electrode, as expected.

Fig. 4 shows the dependence of specific capacitance on the deposited mass and amount of polypyrrole in the Ni(OH)₂/polypyrrole composite. The specific capacitance measured at the scan rate of 10 mV s⁻¹ was found to be 1975 (Fig. 2(a)), 2141 (Fig. 2(b)), 1565 (Fig. 2(c)) and 1171 (Fig. 2(d)) F g⁻¹ for deposited weights of 30, 30, 35 and 55 µg cm⁻², respectively. The specific capacitance increases and peaks at 2141 F · g⁻¹, when the amount of polypyrrole increases at 0.05 ml, and then decreases with increasing amount of polypyrrole. The surface areas of an electrode are important parameters for its capacitance. A larger surface area allows a higher capacitance, because a thin electrode provides a lower ohmic drop and a larger surface area provides a greater contact area with the electrolyte ions. As increasing amount of polypyrrole, the diffusion limitation slows

down the accessibility of ions to the inner regions of the electrode material, except for more accessible outer surface regions where the diffusion of ions is not hampered.

Electrochemical capacitance behavior of the Ni(OH)₂/polypyrrole composite electrode was investigated by chronopotentiometry in 1 M KOH aqueous solution. Fig. 5 shows the charge-discharge curves of the Ni(OH)₂/polypyrrole composite electrode measured at amount of polypyrrole within the potential window of 0 to 0.43 V. It can be noticed that the shape of the charge-discharge curves does not present the characteristic of a pure electric double layer capacitor, but mainly pseudo-capacitance, which corresponds with the result of the CV test. It may be suspected to result from well dispersed structure and conducting improvement of polypyrrole mix. Compared with the CV curve, Ni(OH)₂/polypyrrole electrode shows comparatively good electrochemical capacitance with good cyclic reversibility.

The long-term cycle performance (up to 1000 cycles) of the prepared electrodes at a current density of 10 Ag⁻¹ in 1.0 M KOH electrolyte is shown in Fig. 5. It can be noticed that the specific capacitances fade as the cycle number increases. However, as shown in Fig. 2(b), the adequate addition of polypyrrole can be seen to improve the dispersion of Ni(OH)₂ particles. Therefore, the intercalation and/or absorption of diffusing ions from electrolyte and proton insertion from water may also easily gain access to the available sites reducing the degradation of the electrochemical performance in cyclic redox reactions.

Conclusions

Ni(OH)₂/polypyrrole composite for electrochemical capacitors has been successfully deposited by electrodeposition technique on the SS foil. The Ni(OH)₂ and Ni(OH)₂/polypyrrole composite were used as electrodes in capacitors and their capacitive characteristics were studied. Electrochemical characterization revealed that the specific capacitance of composite electrode deposited from 50 mL : 0.05 mL electrolyte solution was highest than the others. This might be resulted from that the increased capacitance and enhanced response rate at the electrode with added polypyrrole may be attributed to microstructure, morphology and highly electron conductivity. The SEM images and charge-discharge tests show that the Ni(OH)₂/polypyrrole composite electrode (Fig. 2(b)) provides a greater contact area with the electrolyte ions. The Ni(OH)₂/polypyrrole composite electrode with its high surface area and relatively good stable was recognized as a promising

electrode material for the supercapacitor applications.

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