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High performance super-capacitive behaviour of deposited manganese oxide/nickel oxide binary electrode system

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ABSTRACT

The chrono-potentiometry technique was used to deposit MnO_2-NiO binary metal oxide film on a stainless steel substrate at room temperature. During the electrodeposition process, the concentration of nickel acetate is varied in the fixed 0.01 M manganese acetate solution. The products were characterised by X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDX) and field emission scanning electron microscopy (FESEM). Their capacitive behaviour was studied by cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance spectroscopy in two different alkaline electrolytes using a three electrode set-up. The MnO_2-NiO binary metal oxide electrode deposited from $Ni(CH_3COO)_2.4H_2O:Mn(CH_3COO)_2.4H_2O$ at a molar ratio of 0.25:0.01 (molar:molar) was found to be the best electrode with the lowest transfer resistance based on the Nyquist plots. The specific capacitance of the best electrode, NiO-25, exhibited a specific capacitance of 435 Fg^{-1} and 681 Fg^{-1} with an energy density of 242 $Whkg^{-1}$ and 213 $Whkg^{-1}$ in 0.5 M Na_2SO_4 and 0.5 M KOH electrolyte, respectively.

1. Introduction

Electrochemical supercapacitors (EC) are considered to be the most promising approach to meeting the requirements of versatile energy storage devices because they can provide a higher energy density than conventional capacitors, along with higher power and longer cycle life compared to batteries. The stored energy originates from either ion adsorption in the case of electrochemical double layer capacitors or fast surface redox reactions for pseudo-capacitors [1–4]. Several metal oxides are used as electrode materials for pseudocapacitors, including titanium dioxide (TiO_2), manganese dioxide (MnO_2), ruthenium oxide (RuO_2), nickel oxide (NiO) and vanadium oxide (V_2O_5) [3–5]. MnO_2 is considered as an alternative electrode material for EC owing to its specific capacitance in aqueous electrolytes, cost effectiveness, natural abundance, environmental compatibility and wide potential window [5,6]. In order to maximise pseudocapacitance, there are many approaches can be applied to improve the drawbacks of MnO_2 such as incorporating/compositing MnO_2 with conductive carbon materials [2,7–9], conducting polymers [5,10,11], and transition metal oxides [2,5,12]. In the latter case, binary metal oxide-MnO_2 based electrode materials have been reported to offer a greater surface area which enhances the electronic conductivity and contributes to a better charge storage capability with good electrode cycle stability [5].

Passed researches on the incorporation of manganese dioxide and nickel oxide have shown an enhancement in energy, power density and improvements in cycle stability [2,5,12,13]. It is presumed that the synergistic effect of active nickel oxide on the positive potential range and activity of MnO_2 in the negative discharge potential range is beneficial to optimise electrochemical performance of MnO_2 based electrode. The lack of porosity and surface area of a manganese oxide electrode can be also improved by porous nickel oxide which is good for electrolyte penetration [13–15]. There are several techniques that have been used to incorporate nickel oxide with manganese dioxide as an electrode film for pseudocapacitors, such as the hydrothermal [12], sol-gel method [2] and co-precipitation method [16]. However, based on the literature, most of the prepared MnO_2 based electrode materials are synthesised in powder form; therefore the addition of additives and binders is necessary to prepare the active materials as an electrode. This procedure requires several preparation steps, starting from the preparation of a slurry mixture containing the active materials, the binder (e.g. polyvinylidene fluoride (PVDF)/polyvinylpyrrolidone (PVP)) and a conductivity enhancer (e.g. carbon black), followed by slurry coating on a current collector (spin/dip coating, doctor blade techniques). The electrodes are ready for use after heat treatment and a pressurisation process

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to eliminate the solvent and prevent irregularities on the surface. The addition of insulating binders can cause a blocking effect on some parts of the active surface and reduce the specific capacitance of cells. This also contributes to additional resistance of the contact area between the electrical conductor (i.e. the current collector and/or conductivity enhancer) and the active materials, thus resulting in reduced power density [17,18]. Therefore a more effective method to synthesize manganese oxide based electrodes for electrochemical capacitor applications such as electrodeposition is important to explore in which the oxide films is directly deposit of on the current collector. In the work of Chen and Hu [19], Mn-Ni oxide was successfully deposited from a solution containing a high Ni^{2+}/Mn^{2+} ratio of 10:1 using the anodic electrodeposition method due to differences in the reduction potential of Mn^{2+} (-1.18 V) and Ni^{+} (-0.25 V). Other electrodeposition techniques, such as potentiodynamics, have been used by Parasad and Muira to deposit microporous manganese oxide based electrodes on stainless steel. They have obtained a high specific capacitance of 621 Fg^{-1} and 377 Fg^{-1} at a scan rate of 10 mVs^{-1} and 200 mVs^{-1} in a 1 M Na_2SO_4 electrolyte [20].

Here, we report on a MnO_2-NiO electrode prepared using a simple chronopotentiometry technique where the suitable concentration ratio between manganese and nickel ions in the deposition solution was determined. The choronopotentiometry is also known as galvanostatic (constant current) technique where this technique provides some advantages such as low cost and effective control of synthesis parameters (type of deposition electrolyte solution, current density, temperature and pH). The thickness of deposition film and particles distribution uniformity with good repeatability can be also controlled through the charge consumed during the deposition process [21–23]. The structural and morphological studies of the prepared samples were carried out using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and transmission electron microscopy (TEM). The electrochemical performance of the MnO_2-NiO electrodes was investigated using cyclic voltammetry, charge-discharge and electrical impedance spectroscopy.

2. Experimental methods

2.1. Preparation of electrodes

All the chemicals were of analytical grade and used without any purification. Commercial manganese acetate tetrahydrate, $Mn(CH_3COO)_2.4H_2O$, and nickel acetate tetrahydrate, $Ni(CH_3COO)_2.4H_2O$, were purchased from Fluka. Sulphuric acid, H_2SO_4, was purchased from Friendemann Schmidt. The binary metal oxide electrodes were electrodeposited using 20 mL of aqueous 0.01 M $Mn(CH_3COO)_2.4H_2O$, 20 mL of different concentrations (0.15 M, 0.2 M, 0.25 M, 0.3 M, 0.35 M, and 0.4 M) of $Ni(CH_3COO)_2.4H_2O$ and 4 mL of 0.8 M H_2SO_4 onto 4 cm^2 of stainless steel (SS) using galvanostatic mode (PGSTAT30) for 10 min at a current of 8 mA. The prepared samples were denoted as NiO-15, NiO-20, NiO-25, NiO-30, NiO-35, and NiO-40. For example, NiO-15 denotes the MnO_2-NiO binary deposited from a solution containing 0.01 M $Mn(CH_3COO)_2.4H_2O$ and 0.15 M $Ni(CH_3COO)_2.4H_2O$. The electrochemical cell consisted of the steel substrate as the working electrode, a carbon rod as the counter electrode and Ag/AgCl as the reference electrode. Before electrodeposition, the electrolyte was sonicated for 10 minutes and the stainless steel was washed using acetone three times and allowed to dry. The deposited electrodes were heated at 300 °C for 6 h and allowed to cool to room temperature to obtain binary metal oxide before the characterisation step.

2.2. Characterisation

The X-ray diffraction patterns (XRD) of the as-prepared nickel-manganese oxide electrodes and the powders were obtained using a D8 Advance X-Ray diffractometer-Bruker AXS with CuK_α monochromatised radiation at 40 kV and 40 mA. The FESEM and TEM images of the electrodes were captured using a Jeol JSM 7600 and Jeol JEM 2100F, respectively. The Energy Dispersive X-ray (EDX) spectrum was collected using an Oxford Instruments apparatus for the elemental analysis of the electrode sample.

2.3. Electrochemical characterisation

The cyclic voltammetry (CV), galvanostatic charge-discharge charge-discharge and electrochemical impedance (EIS) methods were used to characterise the electrochemical behaviour of the electrode and were performed using a PGSTAT30 (FRA) equipment at room temperature. The tests were carried out with a three electrode system where the nickel-manganese oxide electrode was the working electrode, platinum was the counter electrode and Ag/AgCl was the reference electrode. The electrochemical behaviour of the electrodes was studied in two aqueous electrolytes: 0.5 M Na_2SO_4 and 0.5 M KOH. The impedance spectra were measured in the frequency range from 0.01 Hz to 100 kHz. Meanwhile the impedance of electrochemical capacitors (ECs) were carried out using two electrodes set-up. The distance between two identical deposit electrodes was measured using a digital micrometer and used in converting the resistance into conductivity. The area of contact is 4 cm^2.

3. Results and Discussion

The comparative XRD patterns of pure SS and binary MnO_2-NiO deposited on the SS substrate at various nickel ion concentrations are presented in Fig. 1(a). The diffractogram reveals that there was no change or additional new peaks in the stainless steel which can be assigned to the deposited nickel manganese oxide films after Ni/Mn electrodeposition. This suggests that a thin layer of the nickel-manganese oxide had homogenously adhered on the SS surface. Prior to determining the elements in the binary MnO_2-NiO electrode, this thin layer deposit was scraped from the stainless steel surface; the XRD pattern of the powder is shown in Fig. 1(b). The pronounced diffraction peaks in the XRD pattern located at $2\theta = 27.24^\circ$, 50.52° are correspond to the (310) and (411) diffraction planes of α-MnO_2 and $2\theta = 36.26^\circ$, 43.67° refers to the (111) and (200) diffraction planes of NiO. The standard diffraction peaks confirmed the formation of NiO and MnO_2 on SS, which is in accordance with the standard Joint Committee for Powder Diffraction Standards (JCPDS) card no. 04-0835 and (JCPDS) card no. 44-0141, respectively [24–26]. Furthermore, no impurity peaks were observed, implying that MnO_2-NiO was effectively deposited on the SS surface. The broad and low intensity diffraction peaks suggest that the deposited sample was amorphous with nano-scale dimensionality, which was confirmed by the FESEM and TEM images [25–27]. The EDX spectrum of binary MnO_2-NiO deposited on the SS substrate shown in Fig. 1(b) confirms the presence of Ni, Mn and O in the electrode sample. The nature of binary metal oxides has been well-studied, and we speculate that the formation of MnO_2-NiO began when the electric current passed through the electrolyte. Then, water molecules were separated into hydrogen gas and hydroxide ions. The cations in the deposition solution commonly have high binding affinity for oxygen-containing groups (hydroxide ions), leading to the nucleation of manganese or nickel hydroxide particles. The metal oxide particles settle onto the substrate during the annealing process after the hydroxide was efficiently oxidised