INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 41 (2016) 9876–9884

Available online at www.sciencedirect.com

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journal homepage: www.elsevier.com/locate/he

Hydrothermally grown $Ni_{0.7}Zn_{0.3}O$ directly on carbon fiber paper substrate as an electrode material for energy storage applications

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ARTICLE INFO

Article history:
Received 15 November 2015
Received in revised form
14 March 2016
Accepted 17 March 2016
Available online 7 April 2016

Keywords:
Energy storage
Mixed oxides
Long-term performance
Ni–Zn oxides
Annealing

ABSTRACT

Nickel oxides because of their excellent electrochemical performance have been considered attractive materials for electrochemical energy storage. However, their application as active material for redox supercapacitor electrodes has been limited by poor electrical conductivity. In order to improve this property, herein we synthesized a nanonet of Ni–Zn-mixed oxide, by facile hydrothermal route, directly on the substrate. The Zn-modified oxide material showed good electrochemical performance, displaying specific capacitance of 770 F g^{-1} at 1 A g^{-1} and almost 120% capacitance retention after 2000 cycles of charge discharge at 2 A g^{-1} in 2 M KOH. Electrochemical impedance results revealed that the $Ni_{0.7}Zn_{0.3}O$ mixed oxide displayed increased conductivity compared to the single NiO material.

Introduction

Electrochemical capacitors or supercapacitors (SC) have attracted much interest due to their high power density, when compared to batteries, and high energy density compared to conventional capacitors, while maintaining longer cycle life [1,2]. In this context, carbon based materials have been widely studied as electrode materials. Carbon-based electrodes exhibit specific capacitance (Cs) values typically in the range 200–300 F g^{-1}, which limits the energy density of the corresponding SCs. In order to overcome this drawback, without compromising the power density of the SC, hybrid systems combining electrodes with capacitive or pseudocapacitive behavior with electrodes exhibiting faradaic battery-type behavior have been proposed as an interesting alternative.

Numerous studies have been performed to explore the pseudocapacitive behavior of transition metal oxides and hydroxides. RuO_2 presents the most notable pseudocapacitive behavior, but its high cost and toxic nature exclude its commercial application [1,2]. To date, various other transition

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http://dx.doi.org/10.1016/j.ijhydene.2016.03.126

metal oxides, such as MnO_2 [3–5], Co_3O_4 [6,7], ZnO [8], NiO [9–12], MoO_3 [13] and V_2O_5 [14] have been widely studied for application as electrodes in high energy density redox SCs, by taking the advantages of their fast kinetics and quasi-reversible redox processes. Moreover, it has been shown that mixture of transition metallic oxides can exhibit a synergistic behavior contributing to their high performance behavior [15].

Surface area and morphology of the materials are key parameters for improved specific capacitance [15,16]. In this context, one-dimensional (1D) nanostructured materials are advantageous for charge storage applications because the surface area exposed to the electrolyte is maximized, which results in the utilization of more electrochemically active material sites. Moreover, 1D oriented growth favors the diffusion of ions that results in enhanced charge transfer kinetics [17].

High surface area nanostructures composed of two metal oxides have been widely studied mainly due to synergetic effects of mixed metal oxides [15,18,19]. Interesting electrochemical performance has been reported for core/shell Co_3O_4@$CoMoO_4$ nanowires on Ni-foam [20], 3-D tubular arrays of MnO_2–NiO nanoflakes [21], electrodeposited Ni and Co-based mixed oxide [22], Ni–Mn mixed oxides [15] as well as vertically aligned nanotubes arrays of mixed V_2O_5–TiO_2 oxides [23]. NiO is a p-type wide band gap semiconducting transition metal oxide that has received considerable attention due to its environmental compatibility, low cost and high theoretical specific capacitance (2573 F g^{-1} within 0.5 V) [9–11]. However, this material presents poor electronic conductivity, a drawback that can be minimized by combining NiO with other metal oxides such MnO_2 or ZnO [24,25]. ZnO is attractive because it is a semiconductive material displaying chemical stability, conductivity and mechanical flexibility [8].

In this work, we report the fabrication of a mixed metal oxide by depositing $Ni_{0.7}Zn_{0.3}O$ directly on carbon paper by a facile hydrothermal process followed by heat treatment. By using this simple method, the $Ni_{0.7}Zn_{0.3}O$ nanostructures have direct electrical contact with the conducting substrate, thereby enhancing the electron transfer kinetics. Carbon fiber paper was selected as substrate due to its lightweight, high conductivity, porosity and chemical inertness towards the electrolyte [26,27]. The process ensures good adhesion to the substrate and eliminates the use of binders and other additives that introduce unwanted resistances in the material.

Experimental

Material preparation

2 mmol $Zn(NO_3)_2.6H_2O$, 4 mmol $Ni(NO_3)_2.6H_2O$, and 7.5 mmol urea were dissolved in 75 ml deionized water under vigorous stirring for 30 min. The resulting mixture solution was transferred into a 100 ml autoclave. The carbon fiber paper (Toray®) was supported on glass slide and placed vertically in the autoclave. The autoclave was sealed and kept in an oven at 130 °C for 5 h. After normal cooling to room temperature, the carbon paper was washed with deionized water and ethanol and kept at 70 °C overnight for drying. Then, the samples were annealed at 250 °C for 2 h at the rate of 1 °C min^{-1}. For comparison, NiO on carbon paper was synthesized by the same procedure mentioned above using a 4 mmol $Ni(NO_3)_2 \cdot 6H_2O$ and 7.5 mmol urea solution and then subjected to heat treatment as above.

Material characterization

The morphology of the films was studied by scanning electron microscope (SEM) using a JEOL model JSM7001 F field emission gun SEM. The elemental analysis was done with energy dispersive X-ray spectroscopy (EDS) attached to SEM. The phase analysis of the films was performed by X-Ray diffraction (XRD) using Cu Kα radiation (1.5418 Å) in a Bruker AXSD8 advance instrument. Transmission electron microscopy (TEM) analysis was carried out in a Hitachi H8100 electron microscope using LaB6 gun working at 200 keV.

Electrochemical characterization

$Ni_{0.7}Zn_{0.3}O$ mixed oxide and single NiO on carbon paper were characterized by cyclic voltammetry (CV) and galvanostatic charge–discharge curves (chronopotentiometry) in a freshly prepared 2 M KOH solution using a three-electrode assembly by Voltalab PGZ 100 potentiostat. A saturated calomel electrode (SCE) and a platinum plate were used as reference electrode and counter electrode, respectively. Electrochemical activation of the electrodes were performed by applying 1000 of consecutive CV cycles at the scan rate of 50 mV s^{-1}, in a potential window of 0–0.55 V. The CV curves were performed at different scan rates (5–100 mV s^{-1}) in a potential window of 0–0.55 V and the galvanostatic charge–discharge curves were obtained by varying the current density (1–10 A g^{-1}) in the potential range of 0–0.45 V.

Electrochemical impedance spectroscopy (EIS) experiments were performed by using a Gamry FAS2 Femtostat, in the frequency range from 0.01 Hz to 10^5 Hz at open circuit potential using 10 mV sinusoidal perturbation.

Results and discussion

Physico chemical characterization

The morphology of the carbon substrate and the Ni–Zn mixed oxide on carbon paper, as deposited and after annealing, was investigated by SEM. Fig. 1a shows the typical morphology of the carbon fiber paper substrate where well-connected carbon fibers with typical widths of 5–7 μm were observed. The space between the interconnected carbon fibers allows a facile transportation of ions enabling deposition throughout the substrate. Fig. 1b shows that the mixed oxide grew uniformly on the carbon fibers, completely covering each individual fiber, while maintaining the overall substrate porosity. The deposit is formed of nanostructured clusters of one dimensional (1-D) structures (Fig. 1c and d). After annealing, the nanostructured morphology was maintained (Fig. 1e and f), being more uniform and individual clusters are no longer identifiable. In addition, some refinement in the structure and additional pores could be observed. These features lead to a