



Synergistic enhancement in the capacitance of nickel and cobalt based mixed oxide supercapacitor prepared by electrodeposition



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ABSTRACT

A simple and versatile electrodeposition method was adopted to prepare nickel oxide (NiO) and cobalt oxide (Co₂O₃) based mixed oxide supercapacitor material. The mixed electrode was fabricated by electrodeposition of Co₂O₃ on to NiO substrate at various potentials of 0.8, 1.0 and 1.2 V vs Ag/AgCl reference electrode. The NiO substrate was prepared by simple air oxidation of Ni foil at two temperatures of 500 and 700 °C for 2 and 6 h. Ni-foil/Co₂O₃ electrode materials were also synthesized by electrodeposition of Co₂O₃ on to Ni foil under similar deposition conditions for comparative study. The morphology, phase and oxidation states of the composite electrodes were studied using SEM, EDAX and XPS methods. The overall emphasis of this work is to demonstrate the effect of mixed transition oxides in their bulk forms on the supercapacitance behavior of the electrode material. It was indeed observed that NiO/Co₂O₃ composite electrode showed significant improvement in supercapacitance behavior in their mixed oxide architecture. Cyclic voltammetric (CV) studies revealed that the NiO/Co₂O₃ composite electrode could attain a very high level of specific capacitance (>400 F g⁻¹) at a scan rate of 20 mV s⁻¹, together with excellent rate capabilities. More than 50% retention in capacitance was also observed after 200 continuous CV cycles demonstrating promising stability of the electrode material. On the other hand, specific capacitance observed in the case of Ni-foil/Co₂O₃ electrodes was drastically reduced compared to the NiO/Co₂O₃ electrodes. It has been emphasized that the synergistic effect, due to the presence of multiple transition oxides, enhanced the overall capacitance behavior of the electrode material. Further, it was also observed that higher the oxidation temperature of the Ni substrates, lower was the specific capacitance for the NiO/Co₂O₃ electrode. The oxidation time, however, did not alter the capacitance significantly for the electrode material.

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1. Introduction

As alternative energy storage device, electrochemical capacitors (EC), also known as supercapacitors observe precedence over conventional capacitors because of their higher power density and longer cycle life [1]. Based on the charge storage mechanism, two broad categories of electrochemical capacitors were studied extensively, electric double layer capacitor (EDLC) and pseudocapacitor (also known as supercapacitor). The level of capacitance achievable in EDLC depends on the non-faradic charge separations at the interface between a solid electrode (typically materials with very high surface area such as carbon) and an electrolyte [2–4]. On the other hand, in the case of supercapacitors, the primary component that contributes toward the capacitance is the fast and reversible

redox reaction that occurs near the electrode/electrolyte interface within a specific potential window [2,3]. Recently, much attention has been focused to develop efficient materials for supercapacitors/pseudocapacitor due to some inherent problems associated with carbon-based materials, such as deterioration by oxidation and high internal resistance [4].

A good candidate material for supercapacitor must display two most important properties, efficient electronic/ionic conductivity and effective charge storage capability. Various transition metals oxide such as, TiO₂ [5], RuO₂ [6], MnO₂ [7], NiO [8], Co₂O₃ [9–11], MoO₃ [12], V₂O₅ [13], Fe₂O₃-based [14,15] were studied for supercapacitor application. The presence of multiple valence states in the transition metals can lead to efficient redox-based reaction with the electrolyte, thereby enhancing the specific capacitance in this class of material. Although the specific capacitance and the energy density of RuO₂ based supercapacitor was found to be very high, its scarcity limits the cost effectiveness in real life application [6]. On the other hand, oxides such as NiO and Co₂O₃ are the most commonly studied ones because of their ease of abundance and high

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specific capacitance [16]. Generally, the specific capacitance of NiO electrode lies between 50 and 300 F g^{-1} [17]. For example, flake like morphology of NiO prepared hydrothermally by Zheng and co-workers imparted a specific capacitance of 138 F g^{-1} [8]. Likewise, specific capacitance of bulk Co_2O_3 is also similar to that of NiO [4]. Electrode, prepared by electrodeposition of cobalt oxide on to copper produced a specific capacitance of 165 F g^{-1} at a scan rate of 10 mV s^{-1} [11]. Various synthesis techniques, such as sol–gel [18], thermal decomposition [19], Anodization [20–26], chemical bath deposition [10] as well as electrodeposition [11,26] were investigated for preparation of these oxide electrodes. Among these processes, electrodeposition method imparts unique advantages, for example controlled mass and thicknesses as well as various morphologies of the oxide deposits can readily be achieved [2].

More recently, emphasis has been given to develop supercapacitor electrode consisting of multiple transition metal oxide/hydroxide phases, specifically binary and ternary phases [17–19,27–30]. In many cases, it has been reported that the synergistic effect of multiple oxide phases in an electrode significantly enhanced the capacitance than that generally observed in a single phase electrode. Electrode fabricated of nonporous network structure of mixed Ni and Co oxides on carbon nanotube produced a capacitance of 840 F g^{-1} [17]. In a different study [28], NiCo_2O_4 electrode (spinel phase), was synthesized by sequential crystallization process that offered a promisingly high supercapacitance value ($\sim 660 \text{ F g}^{-1}$). Recently, Lu et al. [30] showed that a 2D porous network of mixed Ni and Co oxide electrode demonstrated better supercapacitance properties compared to a single phase oxide electrode. They showed that with suitable adjustment of the volume fractions of Co and Ni oxides, the mixed oxide electrode could attain a capacitance value that was 50% more than that of single phase Ni or Co oxide electrode.

In line with the above discussion, this work has been undertaken to evaluate if the mixture of Ni and Co oxides, in their bulk form could potentially enhance the capacitance behavior of the composite electrode. A simple potentiostatic electrodeposition method has been presented to fabricate $\text{NiO/Co}_2\text{O}_3$, and Ni-foil/ Co_2O_3 composite electrode materials for supercapacitor applications. Electrodeposition of Co_2O_3 was carried out at various potentials (0.8, 1.0, and 1.2 V vs Ag/AgCl) on to Ni foil and thermally oxidized NiO substrates. The preparation method for the composite electrode is rather simple and economical without any complicated, time taking synthesis steps. It has been observed that the composite electrode thus formed exhibited superior supercapacitance properties with excellent rate capabilities and cycle life. Further, $\text{NiO/Co}_2\text{O}_3$ composite electrode demonstrated better capacitance behavior compared to that of the Ni-foil/ Co_2O_3 electrodes. This enhancement in supercapacitance is appeared to be due to the synergistic behavior of the oxide phases present in the electrode material consistent with previously reported work.

2. Experimental

2.1. Cobalt oxide was deposited on Ni-foil and NiO substrates by anodic deposition at room temperature

Electrodeposition of Co_2O_3 was carried out in an aqueous solution of 0.01 M cobalt Acetate ($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$) under constant magnetic stirring during the entire period of deposition. The Ni-foil was polished with SiC paper, washed with DI water followed by degreasing in a mixture of 50/50 vol.% acetone and isopropyl solution for 15 min in an ultrasonicator. The samples were dried overnight at 100 °C. The NiO substrate was synthesized by annealing the dried Ni-foil in a furnace at 500 °C for 2 h in air atmosphere. For electrodeposition, a three-electrode configuration was used

with Ag/AgCl (3 M KCl) as reference, platinum as counter, and the Ni foil and/or NiO as working electrodes. All potential reported in this study were with respect to Ag/AgCl reference electrode. Anodic depositions on Ni as well as NiO substrates were carried out at three different potentials: 0.8, 1.0, and 1.2 V, while the deposition time was maintained constant (20 min) for all potentials. Further, the effect of annealing time/temperature of the Ni foil on the overall capacitance behavior of the $\text{NiO/Co}_2\text{O}_3$ composite electrodes was analyzed. For this purpose, Ni foils were annealed at a temperature of 700 °C for 2 h. Further, samples of Ni were also annealed at 500 °C for 6 h. Depositions of Co_2O_3 were carried out at 1.2 V for 20 min on these two NiO substrates. After deposition, the samples were washed with DI water and dried overnight at 100 °C. For clarity in later explanation, the oxide composite electrodes were named as $\text{NiO}(500^\circ\text{C} - 2\text{h})/\text{Co}_2\text{O}_3$, $\text{NiO}(500^\circ\text{C} - 6\text{h})/\text{Co}_2\text{O}_3$, $\text{NiO}(700^\circ\text{C} - 2\text{h})/\text{Co}_2\text{O}_3$.

2.2. Characterization

Microstructural analysis of $\text{Ni/Co}_2\text{O}_3$ and $\text{NiO}(500^\circ\text{C} - 2\text{h})/\text{Co}_2\text{O}_3$ composites was performed with a scanning electron microscope (S-4800, Hitachi). The phase compositions of the electrode materials were determined by energy dispersed spectroscopy (EDAX), and X-ray photoelectron spectroscopy (XPS). EDS analysis was done using oxford system (X-Max) attached to the Hitachi S-4800 SEM system. X-ray photoelectron spectroscopy (XPS) study was carried out using monochromatic Al K α source (PE=1600 eV) on a Kratos Axis Ultra DLD instrument, with a 300–700 μm spot size. Dwell time was set to 200 ms with three sweeps and a step size of 1 eV (0.1 eV for regional scans). The weight of the deposited Co_2O_3 was determined using a Satorius microbalance with the accuracy of 0.01 mg. The electrochemical behavior of the composite electrodes was evaluated by performing cyclic voltammetric (CV) analysis in 1 M KOH solution at room temperature. A three-electrode set up was adopted for the CV analysis with Ag/AgCl as reference, platinum as counter and $\text{Ni/Co}_2\text{O}_3$ and $\text{NiO/Co}_2\text{O}_3$ as working electrodes. The potential window of the CV analysis was 0–0.5 V.

3. Results and discussions

In order to establish the suitable deposition potential, linear sweep voltammetry (LSV) was performed on Ni-foil and NiO (500 °C/2 h) substrates. Fig. 1 shows the LSV profiles carried out at 20 mV s^{-1} in 0.01 M $\text{Co}(\text{CH}_3\text{COO})_2$ aqueous solution. The figure indicates that the deposition behavior Co_2O_3 on Ni-foil and NiO substrates did not differ significantly. Anodic deposition of Co_2O_3

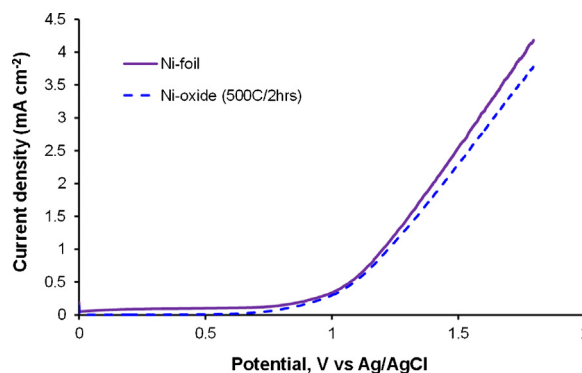


Fig. 1. Linear sweep voltammetry (LSV) profiles for Ni-foil and NiO (500 °C – 2 h) substrates conducted in 0.01 M cobalt acetate ($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$) at a scan rate of 20 mV s^{-1} .

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