Short communication

Synthesis and properties of ternary mixture of nickel/cobalt/tin oxides for supercapacitors

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HIGHLIGHTS

- Synthesis of Ni–Co–Sn ternary oxide thin-film by Pechini method on titanium substrate.
- Nanostructured Ni–Co–Sn ternary oxide was obtained at the temperature of 400 °C.
- The electrochemical tests exhibited a maximum specific capacitance of 328 F g^{-1}.

ARTICLE INFO

ABSTRACT

The present study reports the synthesis and morphological, structural and electrochemical characterization of ternary oxides mixture containing nickel, cobalt and tin. The ternary oxide is synthesized by Pechini method with subsequent deposition onto a titanium substrate in a thin-film form. XRD and EDS analysis confirm the formation of ternary film with amorphous nature. SEM analysis show that cracks on the film favor the gain of the surface area that is an interesting feature for electrochemical capacitors. The ternary film is investigated in KOH electrolyte solution using cyclic voltammetry and charge–discharge study with a specific capacitance of 328 F g^{-1}, and a capacitance retention of 86% over 600 cycles. The values of specific power and specific energy was 345.7 W kg^{-1} and 18.92 Wh kg^{-1}, respectively.

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1. Introduction

Energy storage devices such as electrochemical capacitors (ECs) offer broad applications in several systems that require a large amount of electrical charge provided in a short time, such as laser, full cells, cellular phones, digital cameras and power hybrid electric vehicles [1]. Considering its high power density and fast recharge capability [2], ECs have attracted the attention of researchers worldwide [3] and fills a gap between conventional capacitors and batteries [4].

The electrode material for ECs must have characteristics such as high surface area, long-term stability, cyclability and high rate of electrochemical oxidation/reduction [5]. Materials such as activated carbon, conductive polymers and transition metal oxides are widely used in ECs electrodes [6,7]. Among the transition metal oxides with different redox states, ruthenium oxide has high electrochemical response as electrode material [8] and a high specific capacitance [9]. However, due to high cost it is still limited in industrial applications [10]. Besides ruthenium oxide, ECs

employ others transition metal oxides such as MnO_2 [11], Co_3O_4 [12], NiO [13], SnO_2 [14] and Fe_3O_4 [15] that present low-cost [16] and good capacitive characteristics [17]. Moreover, the good performance of transition metal oxides leads to study of binary or ternary systems, such as Ni–Co [18], Mn–Co [19], Mn–Fe [20], Sn–Al [21], Mn–Ni–Co [22], Co–Ni–Cu [23] and Mn–Ni–Cu [24] for several applications. Mixtures of oxides are applied to oxygen reduction reactions [25], as catalyst for many organic reactions [26], Ph-sensors [27], anode for lithium-ion batteries [28], as well as material for ECs [29].

Deposition of thin-films on a substrate is widely used for evaluates electrochemical characteristics of transition metal oxides. The methods that have been used for prepare thin-films include thermal decomposition [30], sputtering [31], electrodeposition [32] and sol–gel method [33], that is widely used and employs several routes. Among them, the Pechini method [34] allows obtain nanostructured materials with excellent homogeneity, composition control and low processing temperatures, even for oxide mixtures [35] and for a variety of metal oxides using inorganic salts as precursors [36]. The procedure consists in prepare a polymer mixing ethylene glycol (EG), citric acid (CA) and a metal salt precursor, which after calcination forms an oxide.

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In the present communication, we report, for first time, the synthesis of Ni–Co–Sn ternary oxide thin-film by Pechini method on titanium substrate to employ it in ECs material electrodes. The films were physically characterized by X-ray diffraction (XRD) and Scanning Electron Microscope (SEM) techniques and electrochemically by cyclic voltammetry (CV) and galvanostatic charge–discharge process in 6 M KOH.

2. Experimental

2.1. Preparation of solution

A precursor solution of Ni–Co–Sn (50–25–25 wt%) was prepared by Pechini method. In a beaker under magnetic stirring CA (Merck, p.a.) was dissolved in EG (molar ratio of 3:12, respectively) at 60 °C. After that, the three precursor salts were successively added with intervals of 30 min for each one, following this order: $CoCl_2 \cdot 6H_2O$ (Aldrich, p.a.), $SnCl_2 \cdot 2H_2O$ (Aldrich, p.a.) and then $NiCl_2 \cdot 6H_2O$ (Merck, p.a.).

2.2. Thin-film deposition

The thin-film was deposited on a substrate (electrode), a titanium piece with surface area of 1 cm^2 and 99.7% purity (TiBrazil) previously cleaned by sandblasting, followed by a thermal chemical treatment at 10% (w/v) oxalic acid solution during 20 min. These electrodes were washed with Milli-Q water and dried at 105 °C for 12 h. Before deposition, the precursor solution above was stirred and placed in a water bath at ambient temperature and ultrasonic vibration (20 KHz) for 10 min. Then, the precursor solution was painted on the substrate and thermally treated at 110 °C during 30 min, followed by 20 min at 250 °C and finally calcinated at 400 °C for more 10 min. This deposition/calcination procedure was repeated 10 times in order to increase the thickness of the oxide layer deposited.

2.3. Characterization

The morphology of the surface of the thin-film of ternary oxide was examined by SEM (FEI-COMPANY, QUANTA 250 model). XRD data were collected using a Shimadzu XRD-6000 device model (using Kα line of copper [Cu(Kα)] (30 kV and 30 mA)). The data acquisition was made in the range $2\theta = 20°-70°$ at a scan rate of $2°$ min^{-1}. Cyclic voltammograms and chronoamperometric experiments were carried out in a conventional three-electrode cell using an Autolab Potentiostat (PGSTAT 302N). The thin-film prepared on the titanium substrate was used as working electrode and an Ag/AgCl/saturated KCl as reference electrode. An alkaline solution of

6.0 M KOH was used as electrolyte. The specific capacitance (SC), coulombic efficiency (η%), specific power (SP) and specific energy (ES) of the electrodes were calculated according to the equations below:

$$SC = \frac{\Delta Q}{\Delta V m} = \frac{I \Delta t}{\Delta V m} \tag{1}$$

$$\eta\% = \frac{\Delta t_d}{\Delta t_c} \times 100 \tag{2}$$

$$SP = \frac{I \Delta V}{2m} \tag{3}$$

$$SE = \frac{I \Delta V t_d}{2m} \tag{4}$$

where ΔQ is the total amount of charge, ΔV is potential window, I is the charging current, $(\Delta V/\Delta t)$ is the CV scan-rate, m is the mass, t_c is the charge time and t_d is the discharge time.

3. Results and discussion

3.1. Structural study

Identification of phases and the crystallite size of deposited ternary thin-film were analyzed by XRD. Fig. 1a shows that XRD patterns of the thin-film deposited on titanium substrate present little distinctive diffraction peaks, which correspond to amorphous nature [37]. The diffraction peaks were indexed to the sharper peaks centered on 2θ values around of 26.2°, 36.5°, 42.7°, and 62.6°. These peaks have good agreement with the $NiCo_2O_4$ (PDF#01-073-1704), $NiSnO_3$ (PDF#00-028-0711) and Co_2SnO_4 (PDF#00-029-0514) standard spectra. The peak $2\theta = 26.2°$ shows specific agreement with $NiCo_2O_4$ phase and for the other peaks occurs an overlapping of the phases $NiCo_2O_4$, $NiSnO_3$ and Co_2SnO_4, indicating that these peaks are formed by the three oxides. This information is according to Vijayakumar et al. [38] and with the standard spectrum of the $Ni_{0.75}Co_{0.75}Sn_{0.75}$ (PDF#00-027-1119) ternary alloy of crystalline nature.

The crystallite size of the thin-film was determined by Debye–Scherrer equation:

$$d = \frac{0.89\lambda}{\beta \cos \theta} \tag{5}$$

where d is the crystallite size, λ is the X-ray wavelength (1.542 Å), θ is the Bragg diffraction angle and β is the width of the diffraction
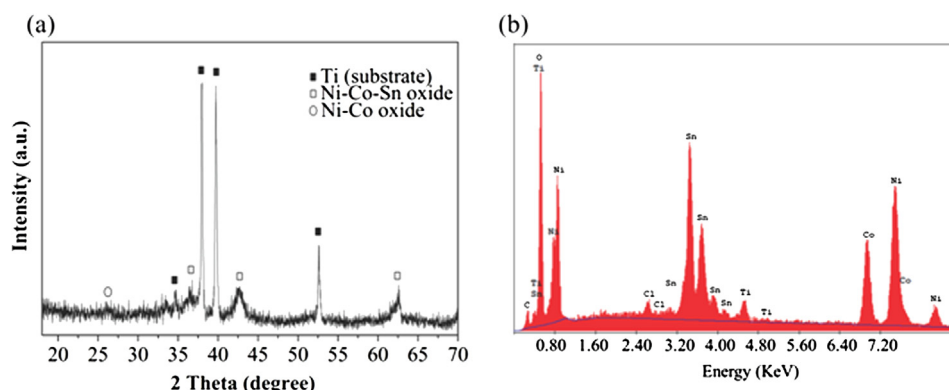

Fig. 1. (a) XRD patterns and (b) EDS spectrum of Ni–Co–Sn ternary oxide thin-film deposited on titanium substrate.