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Short communication

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

C.S. Ferreira, R.R. Passos, L.A. Pocrifka*

GEMATA – LEEN, Departamento de Química, Universidade Federal do Amazonas, CEP 69077-000 Manaus, AM, Brazil

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}.

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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.

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.

* Corresponding author.
E-mail address: pocrifka@gmail.com (L.A. Pocrifka).

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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:

$$SC = \frac{\Delta Q}{\Delta V m} = \frac{I \Delta t}{\Delta V m} \quad (1)$$

$$\eta\% = \frac{\Delta t_d}{\Delta t_c} \times 100 \quad (2)$$

$$SP = \frac{I \Delta V}{2m} \quad (3)$$

$$SE = \frac{I \Delta V t_d}{2m} \quad (4)$$

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:

$$d = \frac{0.89\lambda}{\beta \cos\theta} \quad (5)$$

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

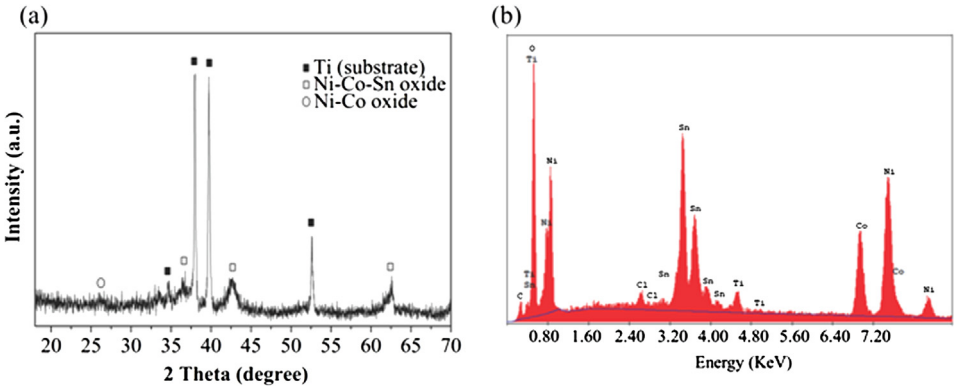

Fig. 1. (a) XRD patterns and (b) EDS spectrum of Ni–Co–Sn ternary oxide thin-film deposited on titanium substrate.

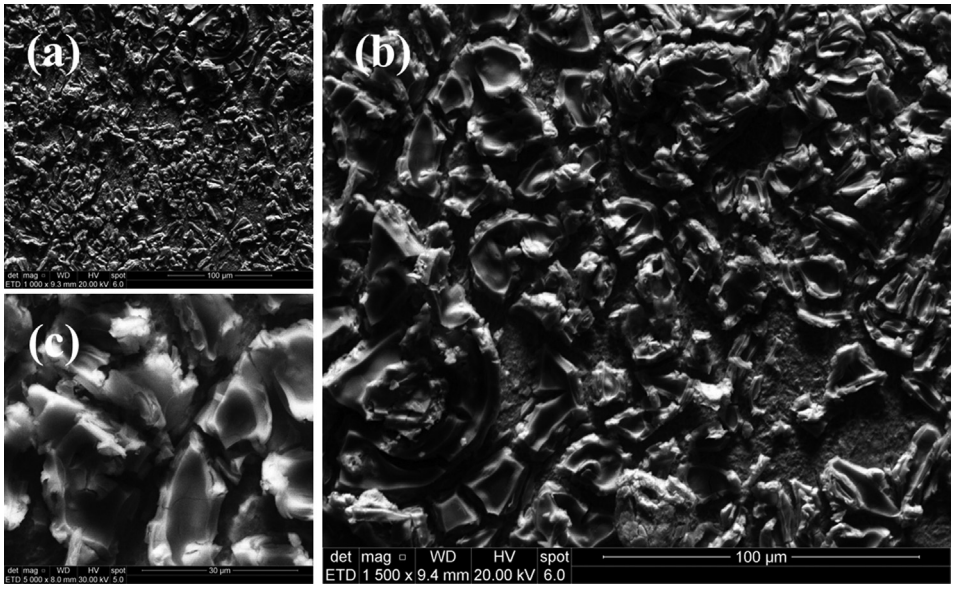

Fig. 2. SEM Images magnified: (a) 1000, (b) 1500 and (c) 5000 times.

peak at half height. The crystallite size based on peak $2\theta = 42.7^{\circ}$ gives an average crystallite of 7.4 nm. The component elements (Ni, Co, Sn and O) of ternary film oxide are confirmed from EDS spectrum (Fig. 1b).

3.2. Morphological study

The morphological study of Ni–Co–Sn thin-film at different magnifications (1000, 1500 and 5000 times) is shown in Fig. 2(a–c).

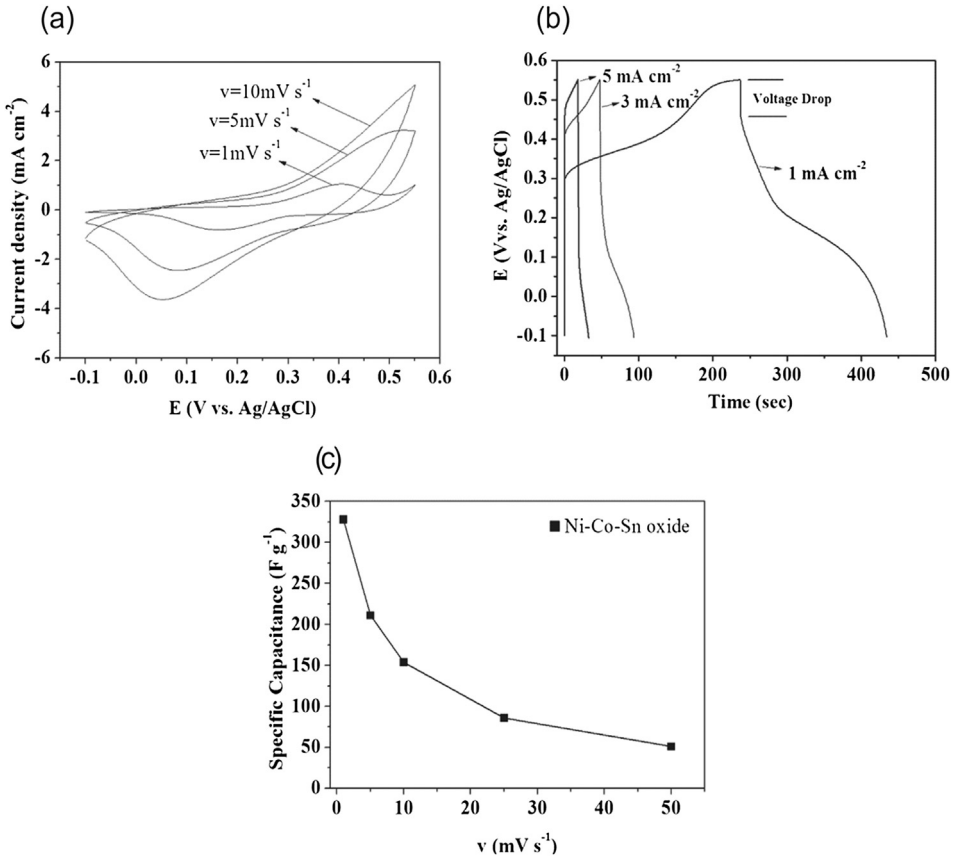

Fig. 3. (a) Cyclic voltammograms in the voltage range of −0.1 to +0.55 V at 1, 5 and 10 mV s^{-1}, (b) galvanostatic charge–discharge curve at 1, 3 and 5 mA cm^{-2} for the Ni–Co–Sn ternary oxide thin-film on substrate and (c) specific capacitance as a functions of scan rate for Ni–Co–Sn ternary oxide.

SEM micrographs revealed cracks on the surface of the samples, resulting in an increase of porosity [39] and provided high surface area and porous volume, which is a requirement in ECs [40] for easy access to redox process [41].

3.3. Electrochemical study

The cyclic voltammetry study, in 6 M KOH with potential window of −0.1 to +0.55 V (vs. Ag/AgCl) at various scan rates, is shown in Fig. 3a. The shape of CV curves in the voltammograms revels the same characteristic from nickel oxide, according to shown in literature [42].

The specific capacitance is associated with the redox mechanism, decreasing rapidly when scan rate is increased from 1 to 10 mV s^{-1}. When the scan rate is 1 mV s^{-1} it can be seen oxidation/reduction peaks well defined, but when scan rate is 10 mV s^{-1} the voltammogram does not presents the oxidation peak clearly defined. This suggests that parts of the active material are inaccessible at high scan rates. In this case, the charge transfer process of redox reactions is associated to resistance of active material [43].

The galvanostatic charge–discharge curves to ternary thin-film for current density of 1, 3 and 5 mA cm^{-2} when potential is ranged from −0.1 to +0.55 V show no symmetric charge–discharge curves, as can be seen in Fig. 3b. The discharge curve has a resistive process, which is indicated by fast voltage drop followed by a capacitive component. This same phenomena is observed for other materials when cobalt is present [5,18]. The voltage drop enhances when the discharge current increases, leading to a decreases of the specific capacitance [17].

The calculated values of specific capacitance are shown in Fig. 3c. It is observed that the higher capacitance value for the ternary thin-film oxide was 328 F g^{-1} for a scan rate of 1 mV s^{-1}. It was observed, however, that for higher scan rates there is a decreasing in the specific capacitance values. When we consider the specific capacitance in terms of percentage of active material on ternary electrode [4,44], we are overestimate the specific capacitance values in 656 F g^{-1} for nickel and 1312 F g^{-1} for cobalt. These specific capacitance values only serve to understand the performance of the material in the electrode.

The stability of the electrode was evaluated considering the coulombic efficiency (η%) for a current density of 3 mA cm^{-2} for 600 cycles, which attained an efficiency of approximately 86%. When we consider the parameters of specific power (SP) and specific energy (SE), the maximum values obtained for the ternary electrode were 345.7 W kg^{-1} and 18.92 Wh kg^{-1}, respectively.

4. Conclusions

The Ni–Co–Sn ternary oxide thin-film was synthesized by Pechini method. The SEM images revealed cracks in the surface of the samples that resulted in an increase in the porosity and a gain on the surface area. The XRD and EDS confirmed formation and composition of Ni–Co–Sn oxide. The electrochemical tests exhibited a maximum specific capacitance of 328 F g^{-1} for the ternary oxide thin-film. The calculated values for specific power and specific energy were 345.7 W kg^{-1} and 18.92 Wh kg^{-1}, respectively, and the capacitance retention was kept at 86% of its initial value after 600 cycles.

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