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Ion transport and capacitive properties of RuO_2-SnO_2 binary films

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ABSTRACT

This paper reports the RuO_2-SnO_2 binary film synthesis and the influence of the SnO_2 composition increase in the ion transport and pseudocapacitive properties of RuO_2. The binary oxide was synthesized by polymeric precursors method followed deposition on a titanium substrate. XRD analysis showed the phases formed and the crystallites size of the samples. SEM allowed studying the morphology variation of the films with the addition of SnO_2. The material obtained was evaluated by electrochemical techniques in 1 M H_2SO_4 electrolyte solution. The voltammograms showed that the pseudocapacitive characteristic of the RuO_2 – SnO_2 binary film remained even for greater amount of SnO_2 in the binary mixture. The electrochemical impedance spectroscopy results are discussed in terms of complex capacitance and complex power. The relaxation time constant of the systems and capacitance values at low frequency, were determinate from complex capacitance plots.

1. Introduction

Electrochemical capacitors are energy storage devices which combine the power of the conventional capacitors and the energy of the batteries. These system can be used in electric vehicles, mobile phones and digital cameras [1,2]. Electrochemical capacitors can store energy in two ways, direct and indirect. In the direct form, electrochemical capacitors are constituted of large area porous materials that storage electric charge on the surface. Carbon-based materials are the most applied in direct storage [3,4]. In an indirect form, the storage occurs through quick faradaic reactions at the electrode/electrolyte interface by a mechanism known as pseudocapacitance [2]. Materials such as conductive polymers [5,6] as well as transition metal oxides are used in this case [7–9].

Ruthenium oxide has been one of the most studied as electrode material for pseudocapacitors [10–12]. This is a very attractive material due to its high specific capacitance value, wide window of potential, reversible redox reactions involving three oxidation states in 1.2 V and good thermal stability [10]. The pseudocapacitive behavior of this material depends on several factors. Among them the surface area is fundamental. Another decisive factor in the redox behavior of ruthenium oxide is the hydration degree. The reversible redox transitions in this material depend on the proton/cation exchange and electron-hopping processes. In this sense, the cations diffusion in hydrated species can occur via hopping of alkaline ions and H^+ ions between H_2O and OH^- sites, suggesting that the hydration degree improves the cations diffusion in the electrode material [10]. In spite of its great advantages, the use of RuO_2 is limited by its little abundance and consequently its high price [10,11].

One possible approach to optimize the use of RuO_2 consists of obtaining composites and/or binary oxides [13–15]. In these materials, the RuO_2 particles are homogeneously dispersed in another cheaper material, increasing the utilization of the active surface and reducing costs. For example, Chi-Chang Hu et al. [12], study the heat treatment influence in the morphological properties and crystallinity of the $RuO_x.nH_2O$ and $(Ru + Ir)O_y.mH_2O$. It was observed that the thermally treated oxides at 200 °C show a close performance to an ideal capacitor. Pusawale et al. [16] used the modified chemical deposition method to prepare films of SnO_2-RuO_2. The best result, 150 F g^{-1}, was obtained using 15% of $RuCl_3$ in the deposition bath. The work of Too et al. [17] compared the effect of deposit RuO_2 and Ru-Co binary oxide on single wall carbon nanotubes. The cobalt oxide addition improved the specific capacitance result. Chang et al. [18] prepare RuO_2-TiO_2 powder using the hydrothermal method. They observed that $Ru_{0.4}Ti_{0.6}O_2$ composition calcined at 200 °C showed the best results. RuO_2-SnO_2 films were prepared by sputtering method. Choi et al. [19] have shown that the $Sn_{0.75}Ru_{0.25}O_{1.9}$ presents the highest specific

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capacitance, about 88 F g^{-1}. It is clear, from those papers, that the synthesis method, synthesis experimental conditions, and molar composition used to prepare the RuO_2 drastically influence the results obtained.

Considering these aspects, in this work we carry out an investigation of the influence of RuO_2/SnO_2 ratio in the transport of ions and capacitive behavior of RuO_2. For this, RuO_2/SnO_2 were synthesized using the polymeric precursor's method. Considering that the capacitive behavior in RuO_2 is directly associated to the material hydration degree, in the present work during the process of obtaining, a thermal treatment was carried out at 400 °C. This treatment had as objective to effects minimize of the hydration degree to study more directly what is the influence of SnO_2 content on the capacitive behavior and ions transport of the RuO_2.

2. Experimental

2.1. Solution preparation

Different compositions of the RuO_2-SnO_2 electrodes were prepared using polymeric precursors method. In a beaker, citric acid (CA) was dissolved in ethylene glycol (EG), under vigorous stirring, at 60 °C. Then the two metal precursors, $RuCl_3$ e $SnCl_2$, were added to this mixture in sequence. The molar ratio of the reactants were M:CA:EG 1:3:12 where M is the molar percentage of the metal precursors %Ru:%Sn, CA is citric acid, and EG is ethylene glycol. The molar rations studied were: Ru25:Sn75, Ru50:Sn50, Ru75:Sn25 and Ru100:Sn0 which were named Ru25, Ru50, Ru75 and Ru100, respectively.

2.2. Film deposition

The solution were painted over the substrates (metallic titanium 99,7% from Ti Brazil), and treated, initially, at 110 °C for 30 min, to promote the polymerization, then at 250 °C for 20 min, to increase the adhesion of the material to substrate, and, finally, at 400 °C for 10 min, to complete burn the organic portion of the polymer. The thermal treatment of the electrodes was adopted according to other reports in the literature [20,21]. The exposed area of the electrodes was 1 cm^2. This procedure was repeated 5 times to increase the mass of active material.

2.3. Characterization

The oxide films were characterized using a Rigaku 120 X-ray diffraction (XRD) with Cu(Kα) (λ = 1,54056 Å) and the data acquisition was made in the range $2\theta = 20°$ - 70°. The sample morphology was analyzed using Scanning Electron Microscopy (SEM), ZEISS model 940a equipment. Cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance spectroscopy were used for electrochemical characterization. The experiments were carried out in a conventional three-electrode cell using an Autolab Potentiostat (PGSTAT 302 N). A saturated calomel electrode (SCE) was used as reference electrode an acid solution 1 M H_2SO_4. Cyclic voltammograms were recorded at 20 mV s^{-1} in the potential range of 0.1–1.1 V, at room temperature. The tests of electrochemical impedance spectroscopy were carried out with the aid of a frequency response analyzer module coupled to the model AUTOLAB FRA. After 300 s polarization, spectra were obtained in the frequency range of 10 mHz to 10 kHz which an alternating disturbance 10 mV peak to peak was applied.

3. Results and discussion

3.1. Structural and morphological study

Fig. 1 shows the XRD pattern of the thin films deposited on the titanium substrate. The main diffraction peaks for tin oxide are centered 2θ values at 26.7°, 34.0°, 52.0°, 54.7°, 61.9°, 64.7° and 66.0° and are in agreement with standard spectrum for SnO_2 (JCPDS 41-1445). For the ruthenium oxide, the diffraction peaks are centered 2θ values at 28.0°, 35.1° and 52.9° also in agreement with standard spectrum for RuO_2 (JCPDS 40-1290). The crystallite size of the thin film was determined by Scherrer's equation [22]:

$$d = \frac{k\lambda}{\beta cos\theta} \quad (1)$$

where d is the crystallite size, k is a shape coefficient (assuming $k = 0.9$), λ is the X-ray wavelength (1.542 Å), β is related to the width of the half height of the Bragg angle and θ is Bragg diffraction angle. The crystallites average size calculated for the Ru100 sample was 9 nm. It was observed that with the increase of the amount of Sn in the composition of the binary oxide, an increase in the crystallites average size also occurred. The calculated values were 9.0 nm, 15.8 nm, 18.5 nm, 18.8 nm and 19.0 nm for Ru100, Ru75, Ru50, Ru25 and Sn100 respectively.

The morphology of the RuO_2-SnO_2 films was characterized using SEM measurements. Fig. 2a–d presents micrographs for different composition. SEM images reveled that, for the lowest proportion of SnO_2 in the mixture (Ru75), the formation of SnO_2 100 nm agglomerates containing rounded and irregular shapes dispersed in the RuO_2 matrix. For (Ru25), there was apparently an increase in the amount of SnO_2 agglomerates observed by the smaller spacing among then in the RuO_2 matrix. The framed figures show that, at the microscopic level, the film presents cracked structure characteristics. Of all compositions, the Ru25 was the one that presented the deepest and widest cracks. In agreement with Trasatti, such structure comes from the material mechanical stress as well as the effect of temperature quenching which occur during the sample calcination [23,24]. According to Terezo and Pereira [25], this morphology is commonly found in Dimensionally Stable Anode (DSA), electrodes with metal oxides adhered to an inert substrate.

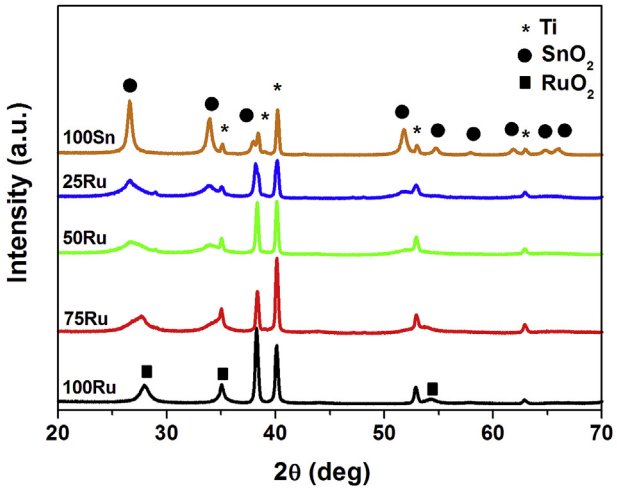

Fig. 1. XRD patterns of RuO_2-SnO_2 binary oxide thin-film electrodes at different routes.