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Synthesis and Characterization of (Ru-Sn)O_2 Nanoparticles for Supercapacitors

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ABSTRACT

The electrode materials SnO_2, RuO_2 *and* (Sn-Ru)O_2 *were synthesized through precipitation method from* $SnCl_2\cdot 2H_2O$ *and* $RuCl_2\cdot 2H_2O$ *solutions. The obtained nano-sized pristine products were characterized using X-ray diffractometry, Scanning Electron Microscopy* (*SEM*), *differential scanning calorimetry* (*DSC*)-*thermogravimetric analysis* (*TGA*) *and cyclic voltammetry* (*CV*). *The Debye–Scherrer formula was used to estimate the average size of the nanoparticles* SnO_2 (36 *nm*), RuO_2(24 *nm*), *and* (Sn-Ru)O_2 (19 *nm*). *Electrochemical studies were carried out to examine the capacitance of* SnO_2, RuO_2, (Sn-Ru)O_2 *electrodes in* 0.5 *M* H_2SO_4 *at various scan rates. The estimated electrode capacitance was determined to decrease with an increase of scan rate.*

Keywords: *Precipitation Synthesis*, (*Ru-Sn*)O_2 *Nanocomposities*, *Supercapacitor*

1. Introduction

Electrochemical capacitors (ECs) offer greater power density than well-known batteries and can be quickly discharged with no deleterious effect on lifetime. They offer greater energy densities than electrostatic dielectric capacitors, making them a better option for backup applications. ECs are becoming attractive energy storage systems, particularly for applications involving high power requirements. They are also being studied as a means to improve battery performance when combined as a hybrid power source. For instance, hybrid systems consisting of batteries and electrochemical capacitors are being pursued for electric vehicle momentum. In such hybrid systems, ECs can provide the peak power during acceleration and therefore, the batteries must be optimized primarily for higher energy density and better cycle life.

ECs are also attractive for other applications such as power sources for lasers, pulsed light generators, digital single lens reflex (SLR) camera and video flash equipment, backup power sources for computer memory and as appropriate sources to power quality applications like Statcons and DVRs [1-3]. Power can be quickly injected or absorbed to help minimize voltage fluctuations in distribution systems.

Energy storage mechanisms of electrochemical capacitors are of two types; first, double-layer capacitance arising from the charge separation at the electrode/electrolyte interface and second, pseudocapacitance arising from fast, reversible faradaic reactions occurring at or near a solid electrode surface. Carbon materials which offer high surface area are extensively used for double-layer capacitors [4]. On the other hand, transition metal oxides with relatively high surface area, such as hydrous RuO_2 [5], porous NiO_x [6-8], CoO_x. [9], and MnO_2 [10-12] have been acknowledged as possible electrode materials for pseudocapacitors.

Tin oxide has been considered as one of the potential electrode materials for pseudocapacitors. The sol–gel process, hydrothermal synthesis and sonication methods have been reported as methods for fabricating porous SnO_2 as an electrode material of ECs [13-16]. These process methods are highly sophisticated and difficult to employ in a controlled manner. For instance, the sol–gel technique is a complicated multi-step process and it is not easy to precisely control film thickness. The chemical co-precipitation method is a simple and easy way to pre-

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pare electroactive materials. Electrode materials for electrochemical capacitors should exhibit high surface area along with electrochemical activity in the given potential range and high electric conductivity. The power loss of ECs is essentially determined by the *ohmic IR* drop at high power rate. The conductivity of stoichiometric tin oxide is very low and pseudo capacitors fabricated by SnO_2 electrodes have low power and energy density. However, materials mixed with conductive oxides of transition metals (e.g., RuO_2) and characterized by a high surface area, have a high pseudocapacitive behavior and a wider potential window of 1V between the anodic and cathodic solvent discharge [14].

In this work, (Sn-Ru)O_2 oxide nanocomposite electrodes were prepared as a candidate for capacitors. A mixed oxide composition containing 30 wt.% RuO_2 was chosen as it is adequate to modulate the conductive properties of the system. The effect of the introduction of RuO_2 on the main physiochemical properties was analyzed.

2. Experimental

The $SnCl_2·2H_2O$ powder (28 mM) was dissolved in 100 mL distilled water at room temperature. The pH of the solution was adjusted to 9 by adding a 3 M NH_4OH solution and stirred for 24 h. The pH-adjusted solution was placed in an oven at 90˚C for 2 days to obtain dense colloid suspension. The obtained colloid suspension was dried at 60˚C under static-air conditions, for 6 h. The product was filtered, washed with distilled water, and dried in air. Calcination was performed at 400˚C for 24 h. A similar procedure was applied to prepare both RuO_2 and (Sn-Ru)O_2 nanomaterials.

Crystallographic information of the samples was obtained using an X-ray powder diffractometer (D8 Advanced Brucker) equipped with graphite monochromatized Cu Kα radiation (λ = 1.54187 Å). Diffraction data was collected over the 2θ range of 20˚ to 80˚. Micrographs of the nanoproducts were obtained by using a JEOL Scanning Electron microscope (JSM6390F). For the TGA measurements, a TA 600 operating in dynamic mode (heating rate = 10˚C/min), was used. Samples of 5mg weight were placed in an alumina crucible. The electrochemical properties of the SnO_2, (Sn-Ru)O_2 and RuO_2 nanoparticles were analyzed by using a three-electrode cell with a platinum counter electrode and a silver wire in the 0.1 mol/L AgCl solution as the reference electrode. The working electrode, prepared by mixing 80 wt% of active material, 15 wt% of acetylene black and 5 wt% of polytetrafluoroethylene (PTFE), was then coated on a 1.0 cm^2 ITO glass. A 0.5 mol/L solution of H_2SO_4 was used as the electrolyte. Cyclic voltammetric (CV) measurements were carried out between the potential limits of –0.2 and 1.0 V against Ag/AgCl using a potentiostat/galvanostat (PRA 273). The CV curves were recorded at scan rates of 10, 50 and 100 $m·Vs^{-1}$.

3. Results and Discussion

The phase purity and crystal structure of the samples have been examined by powder XRD (**Figure 1**). Samples are identified as SnO_2 and RuO_2. The sample prepared from the solution $SnCl_2·2H_2O$ was SnO_2 and all of the reflection peaks are indexed to tetragonal SnO_2 (JCPDS No: 01-088-0287) with lattice parameters a = 4.73735 Å and c = 3.18640 Å. The diffraction peaks of the sample prepared from $RuCl_2.2H_2O$ solution are indexed to the tetragonal RuO_2 (JCPDS No: 00-43-1027) with lattice parameters of a = 4.49940 Å and c = 3.10710 Å. However, in the (Sn-Ru)O_2 nanocomposite, peak intensities are decreased and FWHM (broadness) of the peaks is increased. The broadness of the peaks indicates either particles of very small crystalline size or particles which are semicrystalline in nature [15]. Sizes of the SnO_2, RuO_2, (Sn-Ru)O_2 crystallites were estimated using the Debye-Scherrer formula to the first peak in the XRD patterns. The size of SnO_2, RuO_2 and (Sn-Ru)O_2 nanoparticles is 36 nm, 24 nm and 19 nm, respectively.

The thermal data of the SnO_2, RuO_2 and (Sn-Ru)O_2 were measured using the thermogravimetric/differential scanning calorimeters (TGA/DSC). Typical TGA curves of the SnO_2, RuO_2 and (Sn-Ru)O_2 measured from room temperature to 700˚C with heating rate of 10˚C/min are shown in **Figure 2**. The total weight loss of SnO_2, RuO_2 and (Sn-Ru)O_2 is 2.7, 3.5 and 4.6 wt%, respectively. The weight loss of water at temperatures above 300˚C was due to dehydration of hydroxide groups on the surface of the oxides. Compared to SnO_2 and RuO_2, the (Sn-Ru)O_2 has more weight loss due to having more water involved during the formation of composite Sn-Ru oxides.

The SEM observations of the SnO_2, RuO_2 and

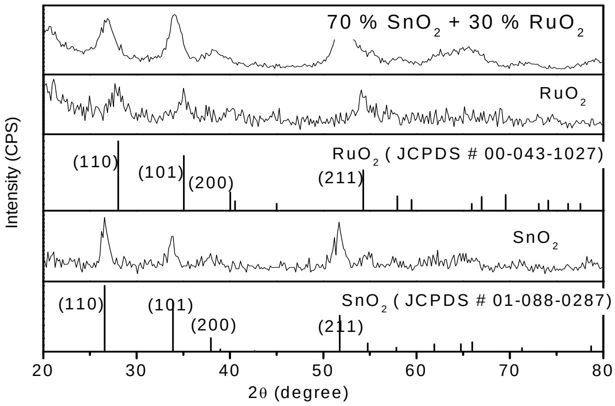

Figure 1. XRD patterns of nanoparticles: SnO_2, RuO_2 and (Sn-Ru)O_2.

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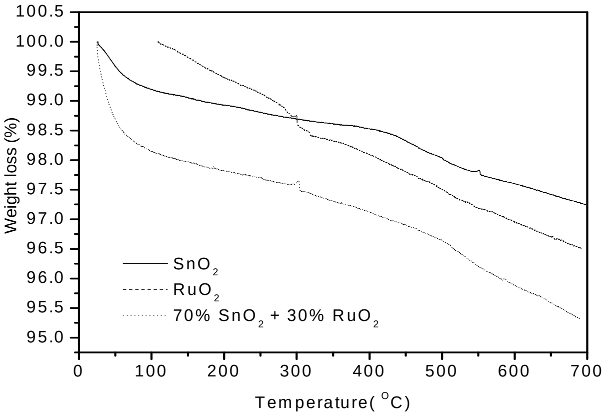
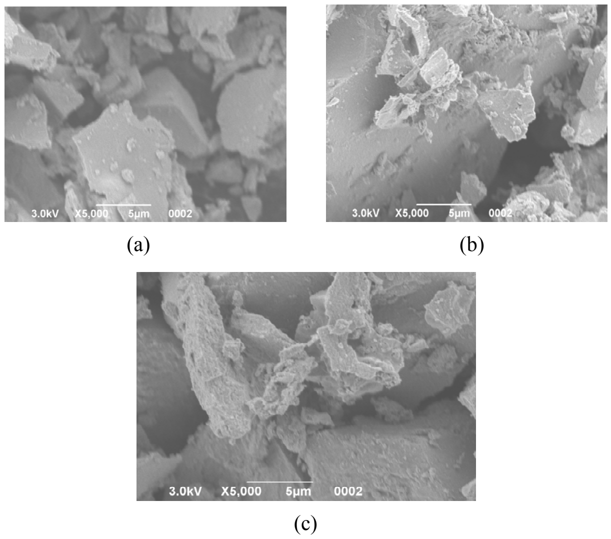


Figure 2. TGA curves of nanoparticles: SnO_2, RuO_2 and (Sn-Ru)O_2.

(Sn-Ru)O_2 nanomaterials are shown in **Figure 3**. It is apparent that the SnO_2, RuO_2 and (Sn-Ru)O_2 nanoparticles are conical and the particles are grown together.

There are several studies available in the literature on RuO_2 complexed as a second component with other oxides [17-22]. The second component RuO_2 includes SnO_2, CaO, Carbon, VO_x, TiO_2, MoO_3 [23]. Over the other complexed oxides, SnO_2-RuO_2 complex shows higher electrochemical performance because of higher conductivity of SnO_2.

The capacitance behavior of SnO_2, RuO_2, (Sn-Ru)O_2 nanoparticles in a 0.5M H_2SO_4 electrolyte with a potential range of –0.2 V to 1.0 V vs. Ag/AgCl at a scan rate of 10 m·Vs^{-1} is shown in **Figure 4**. Specific capacitance of the nanoparticles was calculated from cyclic voltammetric (CV) curves using the following equation: $C = i/sm$, where i is the average cathodic current, s is the scan rate, and m is the mass of the electrode. The shapes of the CV curves looks more or less rectangular, and no redox peaks are observed for SnO_2 electrode. From the CV curve of the (Sn-Ru)O_2 composite electrode, a large current and symmetrical type of voltammogram with a rectangular shape is found in both anodic and cathodic directions compared to the SnO_2 voltammogram. The enhancement in electrochemical performance of the composite electrode can be attributed to surface faradic reactions of the doped Ruthenium oxide phase in addition to the original electrical capacitance of SnO_2 electrode. From the CV curve of the RuO_2 electrode, a pair of oxidation and reduction peaks is clearly found on the positive and negative sweeps at +0.05 V, +0.47 V, +0.41 V and +0.1 V with high current density compare to the SnO_2, (Sn-Ru)O_2 electrodes.



(a) (b)

(c)

Figure 3. SEM photographs of the nanoparticles (a) SnO_2, (b) RuO_2 and (c) (Sn-Ru)O_2.

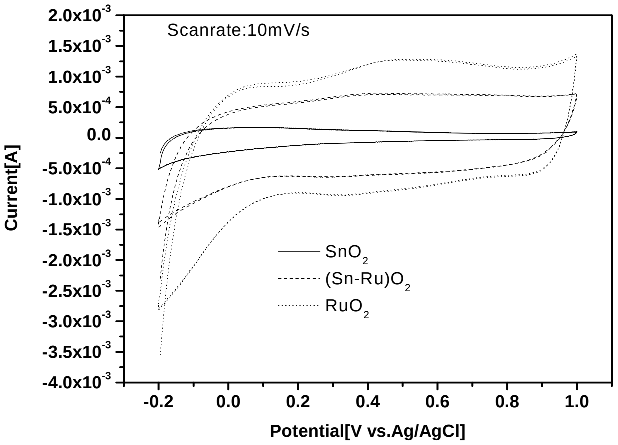


Figure 4. Cyclic voltammograms(CV) of nanoparticles obtained with scan rate 10 mV/s in a 0.5 M H_2SO_4 as an electrolyte.

Figures 5-7 shows the cyclic voltammetric(CV) responses of the SnO_2, (Sn-Ru)O_2, RuO_2 electrodes with scan rates of 10, 50 and 100 m·Vs^{-1}. The current under the curve increased with the increasing scan rate due to the reaction time is shorter and voltammetric current is increased if the reversibility is excellent [16]. The measured specific capacitances were 1.84, 1.63 and 1.46 F·g^{-1} for SnO_2 electrode, 6.08, 4.56 and 3.86 F·g^{-1} for (Sn-Ru)O_2 electrode, 10.19, 5.79 and 4.65 F·g^{-1} for RuO_2 electrode at scan rates 10, 50, 100 m·Vs^{-1}, respectively. The capacitance values decreased with the increase in scan rate. The observed specific capacitance values are comparable with reported values of SnO_2, (Sn-Ru)O_2, and RuO_2 synthesized by other wet chemical methods [14,24]. Literature reports indicate that the factors affecting the capacitance are particle sizes and electrochemical conditions, namely type of electrolyte, concentration of electrolyte, scan rate etc. [14,24]. Some other factors affecting the capacitance are surface activation

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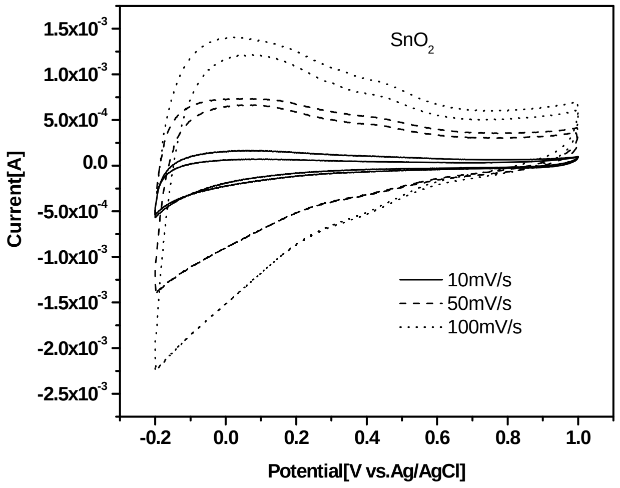

Figure 5. CV of SnO_2 nanoparticles obtained at different scan rates in a 0.5 M H_2SO_4 as an electrolyte.

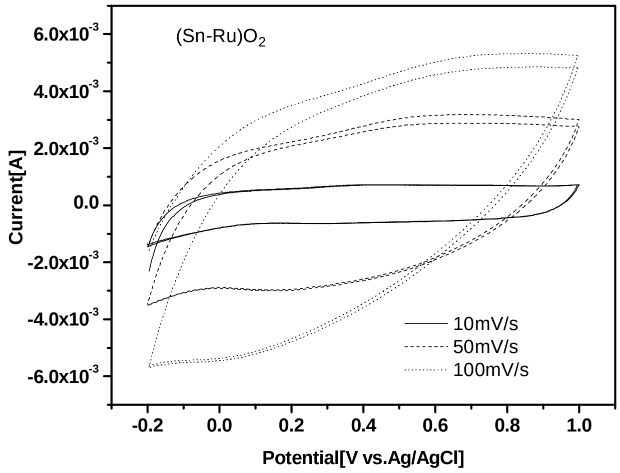

Figure 6. CV of $(Sn\text{-}Ru)O_2$ nanoparticles obtained at different scan rates in a 0.5 M H_2SO_4 as an electrolyte.

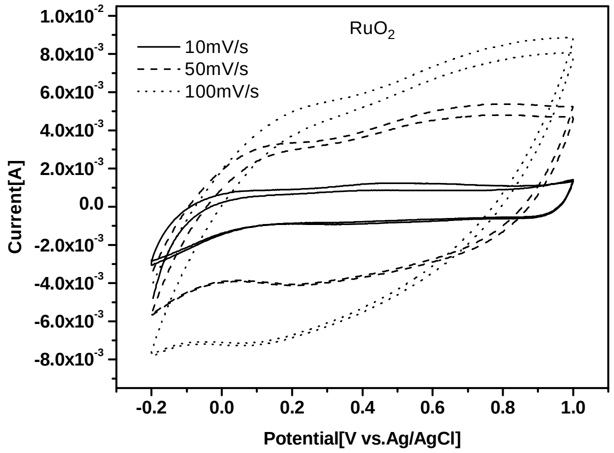

Figure 7. CV of RuO_2 nanoparticles obtained at different scan rates in a 0.5 M H_2SO_4 as an electrolyte.

under the electrochemical conditions, oxygen content on the surface, surface oxides and lattice defects resulting from the method of preparation.

4. Conclusions

The SnO_2, RuO_2 and $(Sn\text{-}Ru)O_2$ nanoparticles were synthesized using a precipitation method. Pristine nanoparticles were characterized using XRD, SEM and TGA techniques. The average size of the $(Sn\text{-}Ru)O_2$ nanoparticles is smaller than that of SnO_2 and RuO_2 nanoparticles. Compared to SnO_2 and RuO_2 nanoparticles, the $(Sn\text{-}Ru)O_2$ nanoparticles have more weight loss. An electrochemical study shows that the RuO_2 electrode exhibits higher capacity than SnO_2 and $(Sn\text{-}Ru)O_2$ electrodes. The capacitances of the electrodes were found to decrease with an increase of the scan rate.

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