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Electrochemically Deposited Nanograin Ruthenium Oxide as a Pseudocapacitive Electrode

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Crystalline structure of ruthenium oxide (RuO_2) was electrochemically deposited onto tin doped indium oxide (ITO) electrode and used as electrodes to form a supercapacitor in a 0.5M H_2SO_4 electrolyte. The structural and surface morphological observations revealed the formation of nanograins of RuO_2 of tetragonal crystal structure. For electrochemical supercapacitor application, electrochemically prepared crystalline RuO_2 was found to be stable for large number of cycles with the specific capacitance 498 F/g at a scan rate of 5 mV/s. The specific capacitance is found to be dependent on the scan rate and the capacitance values varied inversely with scan rate.

Keywords: Ruthenium oxide; Electrodeposition; Surface morphology; Supercapacitor

1. INTRODUCTION

RuO_2 in both crystalline and amorphous forms is of crucial importance for theoretical as well as practical purposes, due to the unique combination of characteristics, such as metallic conductivity, high chemical and thermal stability, catalytic activities, electrochemical redox properties, and field emitting behavior. Due to such properties, RuO_2 finds great promise in various applications, for example, in electronic applications, in integrated circuit development, thick or thin film resistors, ferroelectric films and a buffer layer for the high-temperature superconducting thin films. In catalysis, RuO_2 is the active component in dimensionally stable anodes for chlorine generation in the chlor-alkali industry, oxygen or hydrogen evolution in water electrolysis, CO_2 reduction in photocatalysis, and CO oxidation in sensors [1]. The well-known application of RuO_2 is as an electrode in energy storage electrochemical supercapacitors [2]. Electrochemical supercapacitors are the novel energy-storage devices that possess high power density, exhibit excellent pulse charge–discharge property and very long cycle life. During the last decade, supercapacitors have received significant attention to their potential applications in many fields including surge-power delivery devices for electric vehicles, backup-power storage for calculators, starting power for fuel cells, digital mobile telecommunication and memory back-up devices. Supercapacitors are maintenance-free substitutes for batteries in these applications [2–5].

Among the many transition metal oxides, such as RuO_x, NiO_x and IrO_x, that have been used as an electrode materials for supercapacitors, the most success has been achieved using ruthenium oxide due to its advantages of a wide potential window of highly reversible redox reactions [6], remarkably high specific capacitance [7, 8], and a very long cycle life and metallic type conductivity. Galizzioli et al. [9] first recognized that the current response of thermally prepared anhydrous ruthenium oxide film was similar to that of an ideal capacitor. In recent years, [10] the use of hydrous ruthenium oxide as an electrode material was investigated. It was found that powder form of amorphous and hydrous ruthenium oxide formed by the sol-gel method was a promising for electrochemical capacitor with high power density and energy density [11, 12].

Though the hydrous ruthenium oxide exhibits excellent pseudocapacitive behavior with large specific capacitance and good reversibility, the low abundance and high cost of the precious metal are major limitations to commercial application [13]. This has caused the researchers to find new materials like transition metal oxides, or loading of small amount of Ru in other transition metal oxides or in carbon electrode. Alternatively one can fabricate the RuO_2 electrode by a method having high yield, i. e by a method that can deposit material of large area at expense of small quantity of initial ingredients. Electrodeposition is a powerful and interesting process that can be applied in numerous fields. Films and powders can be synthesized at a low temperature by electrodeposition because of high energy density accumulated in solution near the electrode surface. The advantages of electrodeposition compared with other techniques include low process temperature, low equipment cost, a negligible waste of material, control capability of composition and morphology, and ability to deposit films on a complex surface. Electricity accomplishes the oxidation and reduction, so that there are no by-product species. Today this is a very important feature of electrochemical processes from the viewpoint of environmental protection and materials conservation. This is probably the easiest, low cost, non-vacuum and suitable method to prepare large area thin films. Electrodeposition has been used for the preparation of thin and thick films of metals, magnetic materials, supercapacitive materials and chalcogenides.

In the present investigation, RuO_2 electrodes have been obtained using electrochemical deposition method from an aqueous medium. Their structural, surface morphological and electrochemical supercapacitor properties have been studied.

2. EXPERIMENTAL PART

The ruthenium oxide films were electrodeposited at room temperature from an aqueous solution of 50 mM ruthenium nytril of complexed by ammonia. Ultrasonically cleaned ITO was used as a substrate. Cyclic voltammetry (CV) studies were performed to study the oxidation and reduction mechanisms in the electrolytic bath within the potential range of 0 to −1 V/Ag. All the voltammetric curves were obtained with a scanning potentiostat (Model-273 A EG and G) by forming a conventional three-electrode cell with working electrode as a well-cleaned substrate, a polished platinum plate as the counter electrode and a Ag/AgCl as a reference electrode. The preparative parameters were optimized to obtain feasible films for supercapacitor applications. With optimized parameters, deposition of ruthenium oxide was carried out in galvanostatic mode using chronopotentiometry. The electrode was characterized for their structural, surface morphological and supercapacitive properties. To study the structural property of RuO_2 electrode, X-ray diffraction pattern was obtained by using X-ray diffractometer (RINT/PMAX 2500, Rigaku, Japan) in the range of scanning angle 10–80 (2θ) degree with CuKα radiations. Surface morphological studies were carried out with scanning electron micrographs, obtained with FE-SEM, (SM-6340 F, Jeol, Japan). The electrochemical analysis of the RuO_2 electrode deposited on ITO coated glass substrate was studied by CV using the 273 A EG&G Princeton Applied Research Potentiostat by forming an electrochemical cell comprising platinum as a counter electrode, and Ag/AgCl as a reference electrode in 0.5 M H_2SO_4 electrolyte. The effect of scan rate and number of cycles on the supercapacitor performance of electrochemically deposited RuO_2 was studied.

3. RESULTS AND DISCUSSION

3.1. Cyclic Voltammetry and Film Formation

The CV is a versatile electroanalytical technique for the study of electroactive species. The CV consists of linearly cycling the potential of an electrode immersed in an unstirred solution while measuring the resulting current. Thus, a voltammogram is a display of current versus potential in which the direction of the potential is reversed at the end of the first scan. It is a powerful tool for the determination of formal redox potentials, detection of chemical reactions that precede or follow the electrochemical reaction and evaluation of electron transfer kinetics.

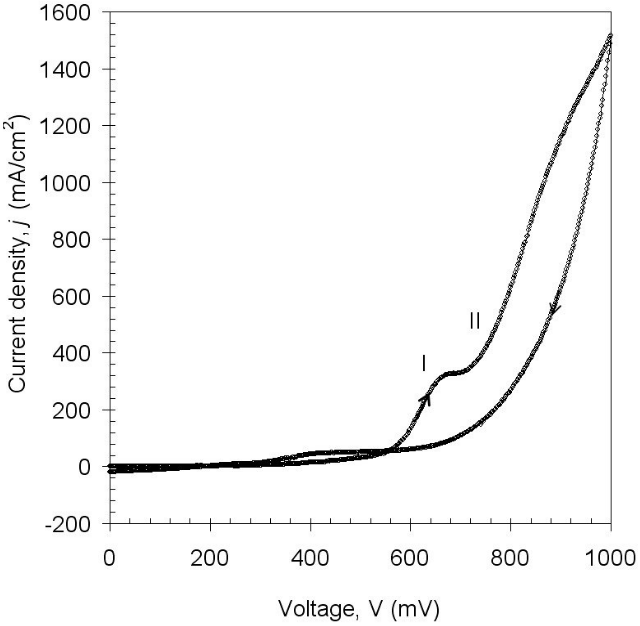

Figure 1. The CV curve for ruthenium oxide from aqueous nitrate bath onto ITO substrate.

The cyclic voltammogram was obtained from the electrolyte bath containing the 50 mM ruthenium nitrosyl complexed with ammonia onto ITO substrate at room temperature. Fig. 1 shows the typical CV in the range of 0 to -1.00 V/Ag/AgCl with the scan rate 20 mV/s onto the ITO substrate. From figure the reduction and oxidation peaks are seen in forward and reverse CV scans, respectively. The hydroxide ions in the solution, produced due to the addition of ammonia and nitrate in the solution, are attracted towards cathode at higher potential and $RuO_2.xH_2O$ get reduced. Thus the reduction peak at 0.8 V/Ag/AgCl corresponds to reduction of RuO_2 onto the ITO substrate. At this peak the higher potential assist the formation of $RuO_2.xH_2O$, which takes place by the following reaction,

$$Ru^{4+} + 4\ OH^- \Rightarrow RuO_2.2H_2O \qquad (1)$$

Thus by analyzing CV plot, the estimated deposition current for the formation of $RuO_x.yH_2O$ films onto ITO substrate is 0.6 mA/cm^2.

3.2. X-ray diffraction studies

The structural analysis of ruthenium oxide films was carried out using X-ray diffractometer varying diffraction angle 2θ from 10 to 80^o. Fig. 2 shows XRD pattern of electrosynthesised ruthenium oxide electrode onto the ITO substrate. It consists of well-defined diffraction peaks of ruthenium oxide and ITO substrate, indicating that very thin crystalline ruthenium oxide is formed onto the ITO. Park *et al.* [14] observed the peaks corresponding to RuO_2 indicating formation of crystalline RuO_2 thin film prepared by electrodeposition on titanium substrate from $RuCl_3$ precursor. On the other hand Hu and co-researchers [15] have reported the formation of amorphous ruthenium oxide by cyclic voltammetric deposition.

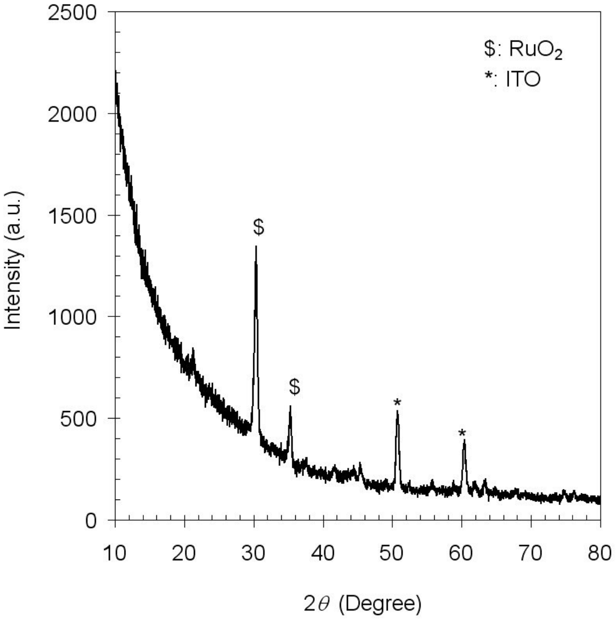

Figure 2. The XRD pattern of as-deposited ruthenium oxide thin film.

3.3. Surface morphological studies

Scanning electron micrographs (SEM) of RuO_2 electrode was studied to evaluate the surface morphology of the electrode. The SEM images of RuO_2 electrode are shown in Fig. 3 at two different magnifications (50 and 100 KX). The micrographs at low magnification (50 KX) showed the total coverage of substrate surface. High magnification (100 KX) micrograph showed the total coverage with habitual shaped nanograin morphology without cracks and pin holes formed by coagulation of many nanoclusters.

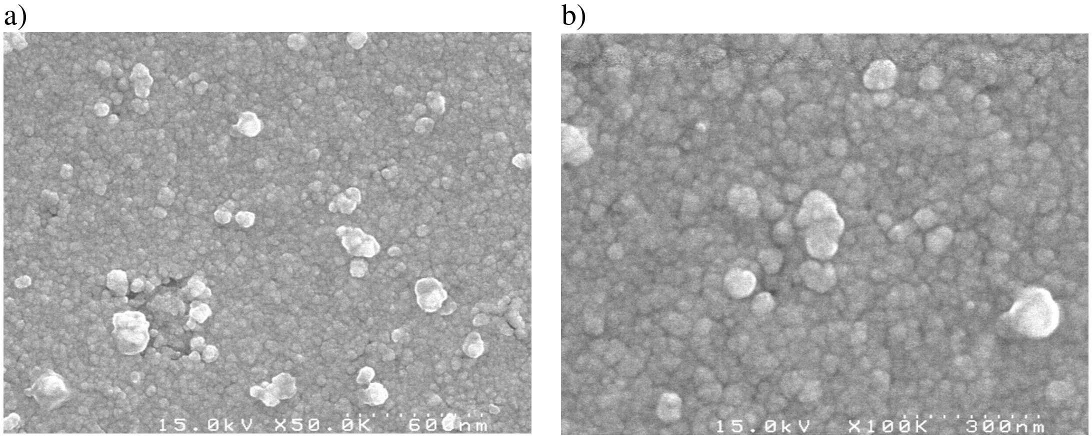

Figure 3. Scanning electron micrographs of electrodeposited ruthenium oxide electrode of magnifications (a) 50 KX and (b) 100 KX.

3.4. Supercapacitive property studies

The electrodeposited ruthenium oxide electrodes were used in the electrochemical supercapacitors and its performance was tested using CV. The effect of scan rate on electrochemical capacitor formed by RuO_2 as an electrode and studied in 0.5 M H_2SO_4 in the voltage range of 0 to -900 mV. Fig. 4 shows the CV with different scan rates of ruthenium oxide electrode. It was found that the current under curve was slowly increased with scan rate. This shows that the voltammetric currents are directly proportional to the scan rates of CV, indicating an ideal capacitive behavior [16]. Further, it can be seen that for each scan rate the shape of the voltamograms is rectangular, even at higher scan rates, which were found to be distorted at high scan rate in case of sol-gel deposited RuO_2 electrode [12, 17].

The capacitance was calculated from:

$$C = \frac{I}{(dv/dt)} \tag{2}$$

where I is the average current in amperes; d*v*/d*t* is the scanning rate in mV/s. The specific capacitance (F/g) of the electrode was obtained dividing the capacitance by the weight dipped in the electrolyte, which was measured by weight difference method using a sensitive microbalance.

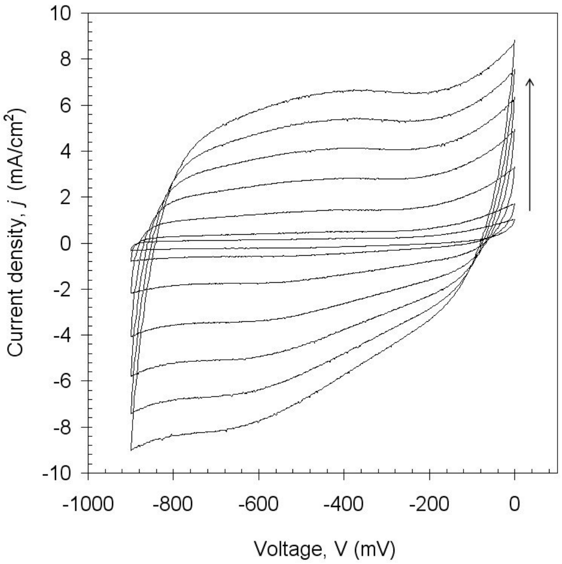

Figure 4. The CV curves of ruthenium oxide electrode at different scanning rates in 0.5 M H_2SO_4 electrolyte.

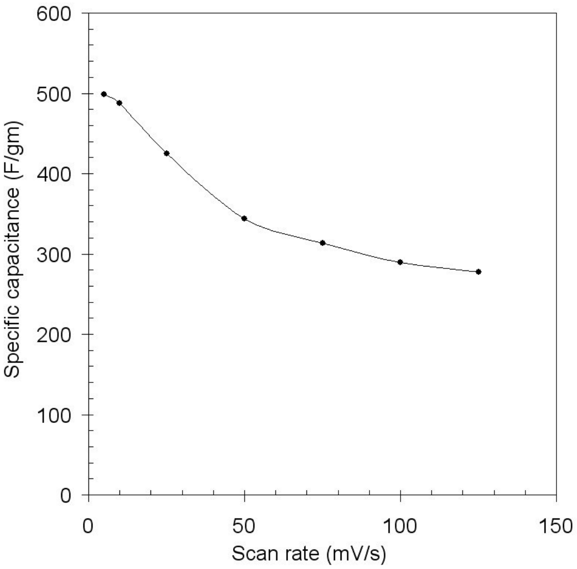

Figure 5. Specific capacitance variation of ruthenium oxide electrode at different scan rate.

Fig. 5 shows the variation of specific capacitance with the scan rate of RuO_2 electrode. From the graph, it is seen that the specific capacitance decreases from 498 to 277 F/g, as the scan rate was increased from 5 to 125 mV/s for RuO_2 electrode. During the oxidation-reduction process in RuO_2, protons are exchanged with the electrolyte and electrode interface. Since this proton transfer process is slow, higher scan rates leads to either depletion or saturation of protons in the electrolyte inside the electrode during the redox process. This mainly results in the increase of ionic resistivity leading to a drop in the capacitance of the electrode [18]. The decreasing trend of the capacitance suggests that parts of the surface of the electrode are inaccessible at high charging–discharging rates. Hence, the specific capacitance obtained at the slowest scan rates is believed to be closest to that of full utilization of the electrode material [19]. The value of specific capacitance is less than the electrodeposited and sol-gel prepared of ruthenium oxide electrodes, one possible reason is the crystalline nature of RuO_2 electrode. However it is note worthy that the capacitance value obtained in this work is definitely better than that obtained for crystalline RuO_2, which was 380 F/g [20]. The possible reason for less value of capacitance for crystalline material is the rigid lattice of crystalline material which causes to a difficulty to expand when the ions are inserted during the redox reaction. However, we claim that due to this rigid lattice, our electrode was very stable for large number of cycles.

4. CONCLUSIONS

In this paper, a simple and environment friendly electrodeposition method of preparation of RuO_2 electrode and its electrochemical performance for supercapacitor have been presented. Through XRD examination it has been demonstrated that crystalline RuO_2 material with tetragonal structure was prepared. The nanograin like crystalline RuO_2 electrodes were synthesized successfully by a electrochemical method. The specific capacitances of RuO_2 electrode decreased with an increase of scan rate and maximum capacitance 498 F/g was observed at 5 mV/s.

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