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Study on structural, morphological, electrochemical and corrosion properties of mesoporous RuO_2 thin films prepared by ultrasonic spray pyrolysis for supercapacitor electrode application

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ABSTRACT

RuO_2 samples were deposited on stainless steel at 723 K by an ultrasonic spray pyrolysis technique using 0.005 M $RuCl_3.nH_2O$ as a precursor solution. XRD analysis confirms the amorphous nature of the deposited samples. Raman studies confirm the formation of RuO_2 phase. SEM, AFM and HRTEM morphologies illustrate uniform spherical granular type morphology of hydrophilic nature. BET study confirms mesoporous nature. RuO_2 phase formation is also confirmed by using XPS analysis. All electrochemical characterizations of the as deposited electrodes were carried out in 0.5 M H_2SO_4 electrolyte. Optimized electrode shows maximum specific capacitance 2192 F/g at 2 mV/sec. The achieved maximum values of specific energy (SE) specific power (SP) and columbic efficiency (η) calculated by using galvanostatic charge-discharge method are 61.12 Wh/Kg, 114.94 kW/Kg and 72.34% respectively. The obtained corrosion rate is ~ 0.1171(mm/year) which is very less than reported values.

1. Introduction

In the developed countries, there is a huge need to store the electric energy and transfer it to the power supplies. For the storage purpose supercapacitor offers a very high specific capacitance in a small pack up for the fulfillment of the need of power supplies. It stores energy using faradic (redox) and non faradic (electric double layer) reaction mechanisms. Reported precursor materials which have high potential window should be able to get redox reversibility between various oxidation states [1,2]. Various transition metal oxides (TMO) and conducting polymer materials are the examples of such a materials [3–6]. Among these TMOs, ruthenium oxide is one of the most excellent promising material for supercapacitor electrode application due to its wide potential window, multi oxidation states, mixed electro-protonic conductivity, high porosity [7,8]. As per literature, amorphous ruthenium oxide (RuO_2) exhibits high specific capacitance [9]. Several reports are there to improve the specific capacitance of RuO_2, but not on the reproducibility it for high specific capacitance. The achievement of good reproducibility and high specific capacitance is strongly depends on the method of preparation and surface morphology of the deposited material [10].

Till now, RuO_2 samples have been synthesized by various methods like electro deposition [11], sol-gel [12], e- beam evaporation [13], ultrasonic spray pyrolysis [14,15], etc. Among them, ultrasonic spray pyrolysis (USP) is one capable of producing metal oxide thin films even at low decomposition temperature, useful for large surface area coatings and exhibits high adherency at only one step. USP technique is computer controlled, simple in operation, cost effective, gives reproducibility and have control over various operative parameters such as spray rate, concentration of precursor and decomposition temperature. In the present investigation, RuO_2 samples were prepared by using USP and were analyzed for structural, morphological, electrochemical and corrosion properties to get suited as an electrode material for ultra supercapacitor.

2. Experimental

In the deposition of RuO_2 samples by USP, 50 ml 0.005 M aqueous solution of $Rucl_3:xH_2O$ (Sd Fine, 99.9%) AR grade was prepared in double distilled water. Well-polished (using emery paper) stainless steel (SS-304) plates having dimension 1.5 × 5 cm^2 were used as a substrates. Prepared solution was sprayed at the rate 10 ml/min, using compressed air as a carrier gas at the flow rate of 12 L min^{-1} onto the pre-heated SS substrates kept at 673 K, which was the optimized decomposition temperature in our previous work [16]. The substrate to nozzle distance was kept constant at 22 cm and X-Y movement of nozzle

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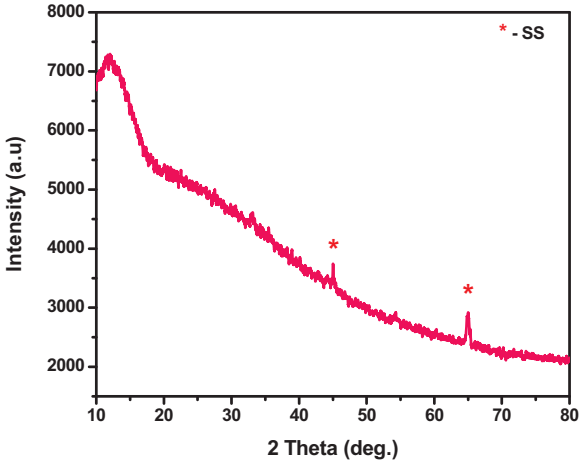

Fig. 1. XRD pattern of RuO_2 deposited at 723 K on SS substrate.

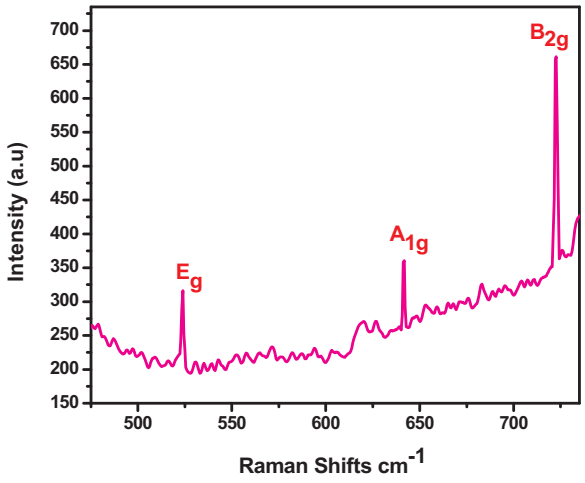

Fig. 2. Raman spectra of RuO_2 deposited at 723 K.

was kept 40 and 70 cm respectively. The prepared electrode shows good adherency and proper decomposition as seen in pilot observations. The possible reaction mechanism of RuO_2 film formation is given below:

$$Rucl_3{:}xH_2O \rightarrow Ru(OH)_2 + 2Cl_3$$

$$Ru(OH)_2 + 2OH^- \rightarrow RuO_2 + 2H_2O$$

Deposited films are black grey in color and they are fully adherent to the SS substrates, these were further used for structural, morphological and electrochemical characterizations.

The structural characterizations were carried out using X-ray diffractometer (Rigaku D/max 2550 Vb^+/pc 18 kW with Cu Kα) by varying the range of diffraction angle (2θ) from 10° to 90°. A Raman spectrum was carried out using Coherent Innova 92 Ar+ ion laser by varying the shift from 450 to 750 cm^{-1}. Morphological observations and Energy-dispersive X-ray spectroscopic (EDX) analysis was taken by using Scanning Electron Microscope (SEM), S-4300 Hitachi, Japan. Powders collected from the surface of the films were analyzed by Transmission Electron Microscope (TEM) (Philips CM 200, Japan). Surface wettability was observed by using Holmarc Opto-Mechatronics (HAM-CAM-01) contact angle meter and BET (Brunauer–Emmett –Teller) surface area measurement of the RuO_2 powder was characterized by BET multipoint N_2 physisorption apparatus (Gemini 2360 Instrument). Surface chemistry of the sample was analyzed by using X-ray Photoelectron Spectroscopy (XPS Thermo Scientific) with Al K alpha X-ray source. Computer controlled potentiostat (CHI 660D instrument, inc. Austin, USA Electrochemical analyzer/workstation) with standard three electrode cell was used for electrochemical characterizations such as cyclic voltammetry (CV), charge/discharge (CD), corrosion study and electrochemical stability. Mass of the deposited material was measured by weight difference method using (1×10^{-5} g) high accuracy microbalance (Tap son's, Model – 100S).

3. Results and discussion

3.1. XRD analysis

Fig. 1 shows the XRD pattern of RuO_2 deposited on SS. Sample depicts amorphous nature without showing any diffracted orientations. Similar observations are reported by others for spray deposited RuO_2 [17,18].

3.1.1. Thickness measurement

Thickness of the deposited RuO_2 sample was measured by weight difference method by using the following relation [19].

$$t = \frac{W}{\rho \times A} \quad (1)$$

where,

t = thickness of the film, W = mass of the deposit

ρ = density of the deposit and A = surface covered by deposit.

The density of the RuO_2 materials is 6.97 g/cm^3. The mass of the deposited RuO_2 sample is 0.20 mg. The observed thickness of RuO_2 sample is found to be 1.21 μm.

3.1.2. Raman studies

The Raman spectrum of the prepared RuO_2 sample is shown in Fig. 2. It depicts the formation of three Raman active vibration modes, namely E_g, A_{1g} and B_{2g} located at 523, 644 and 719 cm^{-1} [20]. B_{1g} vibration mode is not appeared due to very weak intensity in Raman active mode and also no unique data is available in the literature survey for this mode [20,21]. Despite that the lack of any highly intense mode is not appeared in the spectra and XPS studies of the sample also supports the formation of RuO_2.

3.2. SEM and TEM analysis

Fig. 3 shows the SEM and TEM images of deposited RuO_2 sample. Fig. 3(a) shows the formation of 3D, crack free, continuous, spherical porous granular architecture of RuO_2 samples, strongly evidenced by SEM. The growth of RuO_2 grains is mainly due to the nucleation and coalescence process occurring during thermal decomposition. Initially grown spherical grains may increase their size by further deposition process and comes closer to each other. Thus, the larger grain size is appearing due to proper thermal decomposition and solution concentration. Such uniform surface morphology with spherical grains offer increased surface area as evidenced by BET and increasing rate of ionic transportation which is feasible for supercapacitor application [22,23]. Inset of Fig. 3(a) shows the surface wettability of the as deposited RuO_2 sample. The observed angle of contact is 23.28° signifies that the hydrophilic behavior of the deposit is due to proper thermal