

Study of Ruthenium Oxide, Manganese Oxide and Composite (Ru:Mn)O₂ thin film Electrodes Assembled by Layer by Layer Spin Coating Method

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ABSTRACT

Ruthenium oxide, Manganese oxide and (Ru:Mn)O₂ composite thin films have been prepared by 0.02M Ruthenium chloride and Manganese acetate solutions respectively on stainless steel substrates by sol-gel spin coating method. Layer by layer deposition of RuO₂ and MnO₂ was done for composite films. RuO₂:MnO₂ composite thin films have been demonstrated to be an excellent material for Supercapacitor application when evaluated with RuO₂ and MnO₂ thin film electrodes with respect to XRD, SEM, CV, CP and EIS studies. As a result, high specific capacitance of 515 F/g at 10 mV/s with excellent stability and long cycle life was obtained, where specific power and energy were as high as 15.38 Wh/kg and 4.06 KW/kg respectively with loading weight of 0.13 mg/cm². Composite films showed changes in structural and morphological features which was admiring for supercapacitor applications. The electrochemical impedance measurement was carried out in 0.1M KOH in the frequency range 10 to 105 Hz. From the analysis it can be concluded that mixed oxide composites have superior capacitive performance to single transition metal oxides as electrodes.

Keywords: (Ru:Mn)O₂ composite thin films, Sol-gel, Cyclic voltammetry, Chronopotentiometry, Electrochemical Impedance Spectroscopy.

INTRODUCTION

The development of energy storage devices is extremely important to store the harvested energy for wide applications. Batteries, conventional capacitors and supercapacitors are the commonly used energy storage devices. Nowadays, supercapacitors are exhibiting wide applications in electric vehicles, consumer electronic devices, pacemakers and so on. Supercapacitor offers the ability to store or release energy in timescales of a few seconds with extended cycle life^{1,2}. A number of transition metal oxides with various oxidation states represent a type of attractive materials for supercapacitors owing to outstanding structural

flexibility and high specific capacitance. The major drawback is the high cost due to limited availability of ruthenium. With an aim to lower cost while improving the utilization, composite materials have been prepared by combining ruthenium oxide with cheap metal oxides, such as MnO₂. Manganese oxide has been considered a very promising electrode material for supercapacitors because of low price, natural profusion along with good electrochemical behavior and environmental compatibility³. The aim of this work is to develop Ruthenium oxide and Manganese oxide composite thin films for application in advanced supercapacitors by utilizing the cost as well as quantity of Ruthenium with a cost-effective sol-gel spin coating deposition technique.

EXPERIMENTAL

All solutions were prepared by using Analytical grade chemicals and Double distilled water. Firstly, 0.02M Ruthenium trichloride solution was prepared in double distilled water. Isopropyl alcohol was added then the solution was continuously and thoroughly stirred for 3 hours by magnetic stirrer. The gel was formed after aging the solution for 24 hrs. at room temperature. A stainless steel substrate having grade of 304 was used for deposition. After polishing by zero grade polish paper, (2cm X 2cm) strips were cut out of the sheet. A proper cleaning of the substrates was done. After that deposition was taken on cleaned SS substrates in spin coater

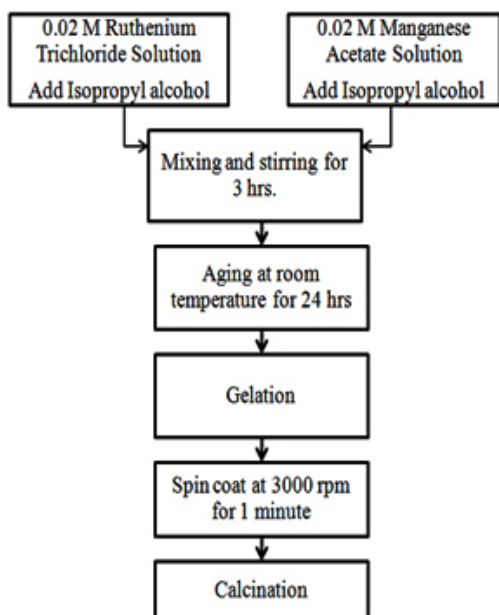


Fig. 1: Flow chart of thin film preparation by the sol-gel spin coat route

unit at a speed of 3000 rpm. Then after calcinations at 900°C, uniform thin films of RuO_2 were formed. The procedure was repeated for multiple coats. Same procedure was repeated by using 0.02 M Mn Acetate solution for deposition of MnO_2 . Layer-by-layer spin deposition is done for deposition of composite $(\text{Ru:Mn})\text{O}_2$ thin films. First two layers of RuO_2 and then two layers of MnO_2 were deposited. All the films studied here are of 4 coats. The schematic presentation of the procedure is given in figure 1.

The films were weighed before and after deposition. The electrodes were weighed by Contech Analytical electronic balance having 0.1mg sensitivity. Morphology of the RuO_2 films of SS substrates was examined by SEM JEOLJSM 6360 and XRD was recorded using a X-ray diffractometer D2 PHASER using $\text{CuK}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). As deposited films were used as electrodes so cyclic voltammetry and chronopotentiometry, EIS analysis were done by a electrochemical workstation CH Instruments CH1608E.

The area of 1 cm^2 at an end of the strip was open in the electrolyte and the remaining was used as current collector. 0.1 M KOH electrolyte solution was used for electrochemical characterization of RuO_2/SS electrodes and a three – electrode cell employing Pt auxiliary electrode and a saturated Calomel electrode as reference electrode.

RESULTS AND DISCUSSIONS

Structural Properties

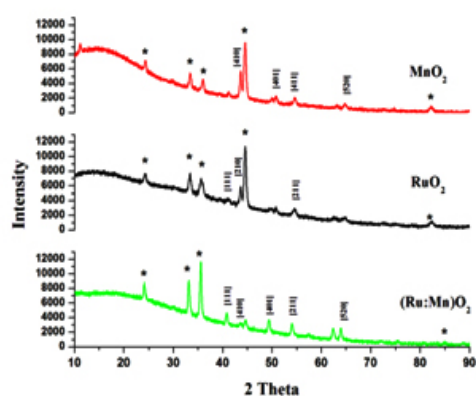
The X-ray Diffractogram of as deposited MnO_2 , RuO_2 , $(\text{Ru:Mn})\text{O}_2$ thin films is shown in Fig. 2.

Table 1: 2θ and d-value variation for MnO_2 , RuO_2 , $(\text{Ru:Mn})\text{O}_2$ thin films

Peak no.	Plane	MnO_2		Composite $(\text{Ru:Mn})\text{O}_2$	
		2θ	d	2θ	d
1	[410]	43.71	2.06	43.28	2.08
2	[401]	51.09	1.79	49.38	1.84
3	[520]	64.86	1.43	63.73	1.45
		RuO_2		Composite $(\text{Ru:Mn})\text{O}_2$	
5	[111]	40.92	2.20	40.57	2.22
6	[211]	54.49	1.68	53.92	1.69

Table 2: Increase in lattice constants of MnO₂, RuO₂, (Ru: Mn)O₂ thin film

Lattice constants (Å°)			Thin Films
a	b	c	
9.31	4.51	2.79	MnO ₂
9.34	4.67	3.00	(Ru:Mn)O ₂
4.51	4.51	3.05	RuO ₂
4.57	4.57	3.03	(Ru:Mn)O ₂

**Fig. 2: X-ray Diffractogram of MnO₂, RuO₂, (Ru:Mn)O₂ thin films**

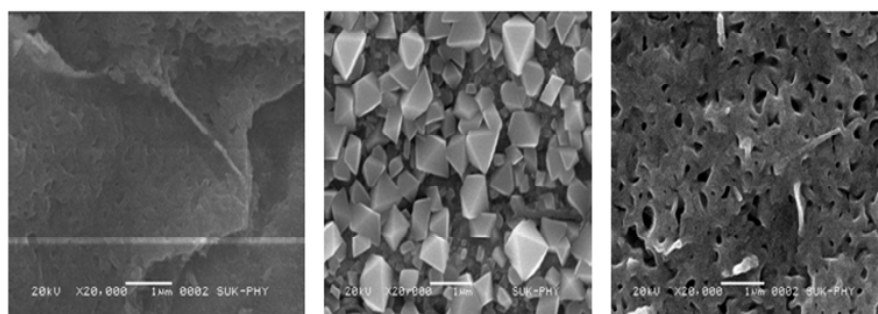
The experimental data showed that tetragonal structure of RuO₂ film (JCPDS Card No.-88-0322) with lattice constants of $a=b=4.51 \text{ Å}$, $c=3.05 \text{ Å}$. The d-values are equal to 2.20 Å and

1.68 Å corresponding to Miller Indices¹¹¹ and ²¹¹ respectively which are nearly same when compared with JCPDS card. Similarly orthorhombic structure of MnO₂ film (JCPDS Card No.-82-2169) with lattice constants $a=9.31 \text{ Å}$, $b=4.67 \text{ Å}$, $c=2.78 \text{ Å}$. The d-values corresponding to Miller indices^{410, 401, 520} are 2.06 Å , 1.78 Å , 1.43 Å respectively. For (Ru: Mn) O₂ films, the peaks for MnO₂ as well as RuO₂ has been observed but with decreased intensity. Also for composite films it was observed that there is a shift in angle 2θ for every peak. Intensity change is related to adsorption on surface while change in theta indicates inter-layer change⁴. Usually on doping, the peak intensity decreases which might be due the change in electron density or might be due to point defects. Very small crystalline size or semicrystalline particles were signified by the broadness of the peaks⁵. The details are given in Table 1.

Shift of Bragg peaks to lower values of the diffraction angle, increases lattice parameter. From Table 2. similar changes are observed. The table gives the comparison of lattice parameters for MnO₂, RuO₂ and the composite films.

Morphological Properties

As the electrochemical performance of electrodes is strongly influenced by particle size, microstructure and porosity, the films were studied by SEM as shown in figure 3. The RuO₂ thin films showed porous, mud-cracked morphology giving rise to high surface roughness. The MnO₂ films showed non-uniformly distributed well developed grains with porosity. Interconnected web-like formation with porous void cavities was observed for (Ru:Mn)O₂ composite film⁶. The porosity of the

**Fig. 3: SEM images of RuO₂, MnO₂, (Ru:Mn)O₂ thin films**

thin film prompts possibility of better electrochemical supercapacitor behaviour of the above discussed thin film electrodes.

Electrochemical Properties

The electrochemical characterization of materials is often carried out using chronopotentiometry, cyclic voltammetry and EIS studies. The cyclic voltammetry graphs of specific capacitance versus scan rates is as shown in Fig.4.

The curves showing characteristic peaks in the given voltage ranges showed the pseudocapacitive activities and are different from the rectangular shape of ideal capacitors. The SC

decreased from 172 to 45 F/g, 310- 140 F/g and 515- 245 F/g with increase in scan rate for MnO_2 , RuO_2 and $(\text{Ru:Mn})\text{O}_2$ electrodes respectively. When the scan rate is low as the inner active sites undergo the redox transitions totally hence specific capacitance is produced and at high scan rate due to the diffusion effect of proton within the electrode. It can also be seen from CV that voltage window is not reliant on scan rate. The voltage window increases as $V_{\text{MnO}_2} < V_{\text{RuO}_2} < V_{(\text{Ru:Mn})\text{O}_2}$ which clearly indicates that the presence of MnO_2 layer increases the voltage window of RuO_2 electrode. Increased voltage window leads to improve the specific energy and power of the thin film electrode⁷. Figure 5. shows the variation of current with respect to voltage for the respective films at 10 mV/Sec scan rate.

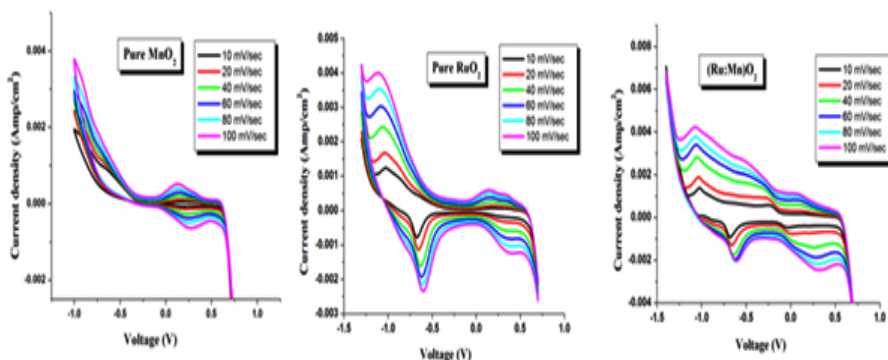


Fig. 4: Cyclic Voltammogram for MnO_2 , RuO_2 , $(\text{Ru:Mn})\text{O}_2$ thin film electrodes at different scan rates

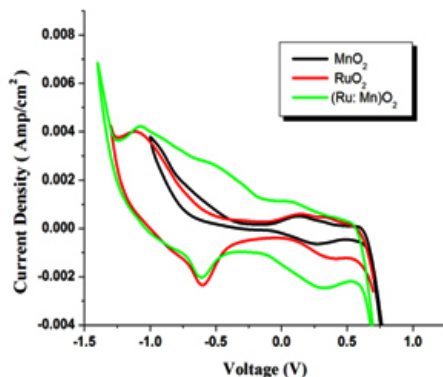


Fig. 5: Cyclic Voltammogram for RuO_2 , MnO_2 , $(\text{Ru:Mn})\text{O}_2$ thin film electrodes at 10 mV/Sec scan rate

The current under the curve is considerably higher for $(\text{Ru:Mn})\text{O}_2$ than for the RuO_2 and MnO_2 electrodes. Relatively high capacitance of $(\text{Ru:Mn})\text{O}_2$ thin film can be attributed to the porous structure which determined the ability of electrolyte ions to enter and to allow local ion transfer process. This indicates the superiority of $(\text{Ru:Mn})\text{O}_2$ as a potential electrode for supercapacitors.

The charge storage properties and stability of the electrodes is studied by chronopotentiometry. Fig.6 shows the Charge/discharge sketch of RuO_2 , MnO_2 and $(\text{Ru:Mn})\text{O}_2$ electrodes at 0.001 A/g of constant discharge current density. All the electrodes show nearly triangular shape indicating linear variation of the voltage linear variation of the potential through charging and discharging

processes. Coulombic efficiency, power density and energy density are calculated by selecting a common voltage window for all the electrodes.

Table 3 shows the variation of coulombic efficiency, power density and energy density of MnO_2 , RuO_2 and $(\text{Ru:Mn})\text{O}_2$ thin film electrodes respectively. It could be seen that the performance of composite film had been increased than individual oxide thin film.

Mass and charge transfer process that take place at the interface of electrode/electrolyte and in electrode can be obtained by EIS. The Nyquist plots were plotted using frequency from 10^{-10} to 10^5 Hz in 0.1 M KOH electrolyte for MnO_2 , RuO_2 and $(\text{Ru:Mn})\text{O}_2$ composite thin films shown in figure 7.

The complex plane plot is divided into high and low frequency regions. The left intercept of Z'' at Z' axis corresponds to the series resistance

R_s of the electrolyte in contact with the current collector and electrode. The right intercept of Z'' at the Z' axis represents parallel resistance R_p giving internal resistance of the electrode. The diameter of the semicircle represents ESR value. The value of power density increases with decrease in faradaic resistance⁸. The plot through 45° phase angle corresponds to the Warburg impedance and it points to a high ion diffusion resistance. A straight line sharply increasing at the low-frequency region represents the dominance of capacitive behaviour. The initiation point of the line corresponds to knee frequency f_k and its corresponding resistance R_k is given by Z'_k . The values of R_s , R_p , ESR, f_k , R_k are detailed in table 4.

Good agreement of simulated (indicated by green color in figure 7) and measured data (indicated by red color in figure 7) was found for the comparable circuit to the proposed one for individual as well as composite thin film electrodes.

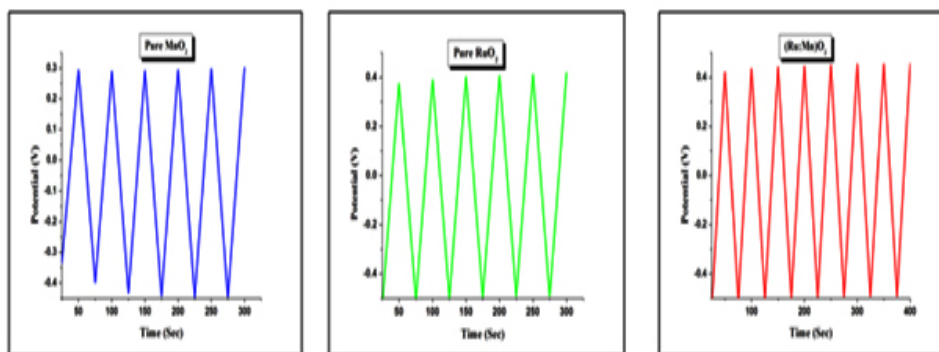


Fig. 6: Charging-discharging curves of (a) MnO_2 (b) RuO_2 (c) $(\text{Ru:Mn})\text{O}_2$ thin film electrodes

Table 3: Energy density, Power density and coulombic efficiency for MnO_2 , RuO_2 , $(\text{Ru:Mn})\text{O}_2$ thin film electrodes

Thin Film Electrode	Energy density (Wh/Kg)	Power density (KW/Kg)	Coulombic efficiency (%)
MnO_2	1.66	10.00	150
RuO_2	2.22	10.00	133
$(\text{Ru:Mn})\text{O}_2$	4.06	15.38	95

The proposed equivalent circuit is given in figure 7(d). Conway and Pell described the impedance of porous electrode using 5 element ($n=5$) circuit [9]. C elements represent double layer capacitance and pseudo capacitance whereas R elements represent electrolyte resistance in pores, Faradaic resistance and equivalent series resistance of the electrodes¹⁰. The Constant Phase Element (CPE) or Q-element describes a leaking capacitor with microscopic roughness of the surface and capacitive dispersion of interfacial origin. EIS data gives the low value of ESR for the composite film than individual oxide thin

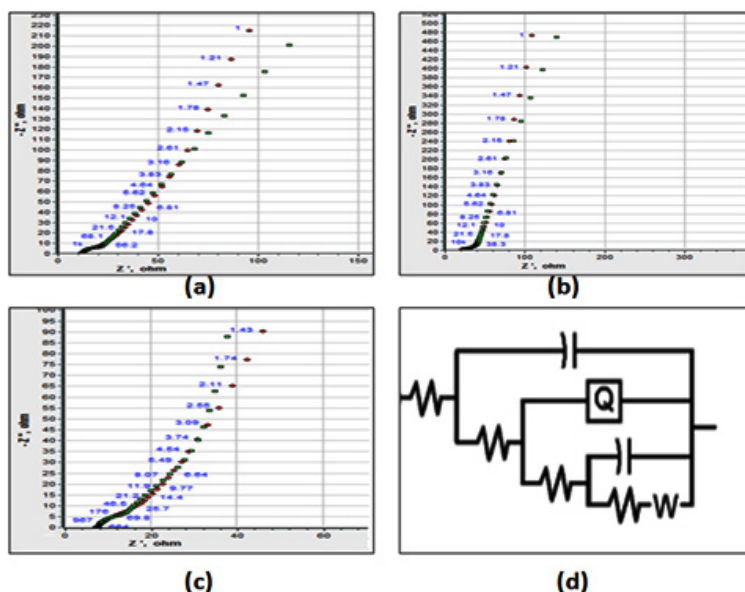


Fig. 7: Electrochemical Impedance Spectroscopy of (a) MnO_2 , (b) RuO_2 (c) $(\text{Ru:Mn})\text{O}_2$ thin film electrodes

Table 4: The values of R_s , R_p , ESR, f_k , R_k for MnO_2 , RuO_2 and $(\text{Ru:Mn})\text{O}_2$ composite thin film electrodes

R_s (Ω)	R_p (Ω)	ESR (Ω)	f_k (Hz)	R_k (Ω)	Thin film Electrodes
14	17	3	55	3.83	MnO_2
21.5	24	2.5	85	2.61	RuO_2
9.2	11.2	2	34	3.09	$(\text{Ru:Mn})\text{O}_2$

film. Moderately low resistance is advantageous for high power supercapacitors.

CONCLUSION

Crystalline and highly porous (Ru: Mn) O_2 composite thin films were prepared by sol-gel spin coating technique. The composite films showed admiring changes in structural and morphological properties for composite films as compared with single metal oxide thin film. Electrochemical analysis

showed the maximum capacitance of 515 F/g, high power density of 15.38KW/Kg, high energy density of 4 Wh/kg and for composite film. The measured EIS data is in good agreement with calculated EIS data.

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