Supercapacitive Behaviour of [Co:Mn:Ru] Oxide Composite Thin Film Electrode

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Abstract :

The research in material science shows that it is difficult to satisfy the requirements of different applications by a single material. Nanocomposite films can achieve more than a single or doped thin film. This paper includes the synthesis and supercapacitive behaviour of [Co:Mn:Ru] Oxide nanocomposite thin films . The homogenous films were deposited on glass plate by sol-gel spin coating technique .As deposited thin film electrodes showed the highest specific capacitance of 440 F/g at a scan rate of 10 mV/Sec and good cycling stability with about 75% retention after 1000 cycles. It also showed the specific energy and specific power of 158.76Wh/kg and 83.04 KW/kg respectively demonstrating the good electrochemical performance for supercapacitor application.

Keywords: Nanocomposite, Sol-gel, Electrochemical Behaviour

1. Introduction

Recently, various nanocomposite films consisting of either metal-metal oxide, mixed metal oxides, polymers mixed with metals or metal oxides, or carbon nanotubes mixed with polymers, metals or metal oxides have been synthesized and investigated for their application as active materials for supercapacitors. Design of the nanocomposite films for such applications needs the considerations of many factors, for example, the surface area, interfacial characteristics, electrical conductivity, nanocrystallite size, surface and interfacial energy, etc., all of which depend significantly on the material selection, deposition methods and deposition process parameters. Materials can be deposited in the form of thin film on a substrate by a variety of methods such as physical vapour deposition, chemical vapour deposition, wet-chemical processes such as sol-gel and electrochemical deposition and spray pyrolysis etc. [1]. It is believed that transition metal oxides are good candidates as electrode materials, because they have variation in oxide states which is suitable for effective redox charge transfer [2,3]. Non-noble oxides such as NiO, Co_3O_4, RuO_2, MnO_2 are very promising candidates for electrode materials in supercapacitors [4-5]. However, the relatively low specific capacitance needs to be improved for supercapacitor application. Recent research is focused on increasing the specific capacitance of the oxides by introducing other oxides technology [6-7]. In this study, [CO:Ru:Mn] oxide composite thin films as electrode materials were prepared by Sol-gel spin coat method.

2. EXPERIMENTAL

The composite thin films were deposited on stainless steel substrates by sol-gel spin coating technique. The substrates were polished using polish paper, washed with detergent and double distilled water, then dried and kept in desiccator. The schematic presentation of the deposition procedure as shown.

The as deposited films were uniform and well adherent to the substrate.

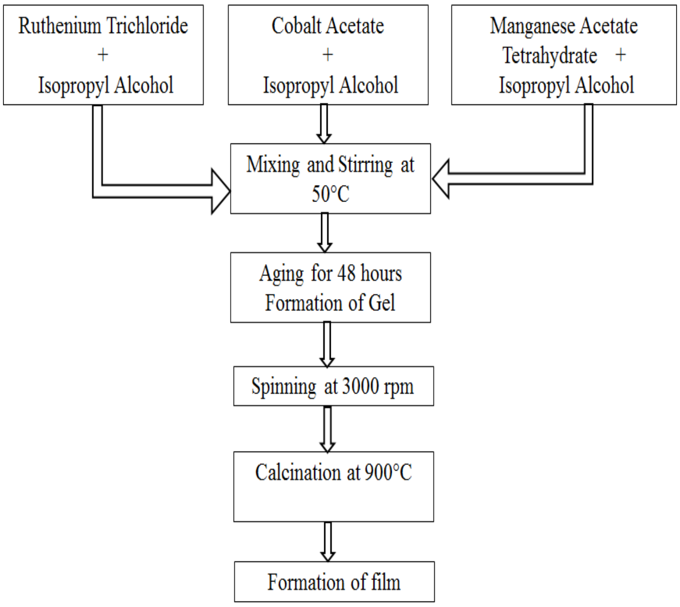


Fig. 1. Flow chart for deposition of [Co:Mn:Ru] Oxide Composite Thin Film

The films were structurally characterized by X-ray diffraction in the range of scanning angle 10°–90° using diffractometer D2 PHASER using CuKα radiation (λ= 1.54 A°).The surface morphology of the film was studied by scanning electron microscopy (SEM) (Model: JEOL JSM-6360). EDAX analysis is carried out using Quanta 200 ESEM instrument.Electrochemical characterization of electrodes was performed in 1 M KOH electrolyte solution in a three – electrode cell employing Pt auxiliary electrode and a SCE reference electrode. Potential values are reported against SCE.

3. RESULTS AND DISCUSSION

3.1 Structural Properties

The fig. 2. shows the XRD pattern for [Co:Mn:Ru] oxide composite thin films. XRD pattern exhibited crystalline nature with orthorhombic [8] and cubic phase [9] for MnO_2,, Co_3O_4 films respectively and tetragonal for RuO_2 The XRD pattern of [Co:Mn:Ru] oxide composite thin films showed dominating peaks of Three oxides and two new peaks of MnO_2.

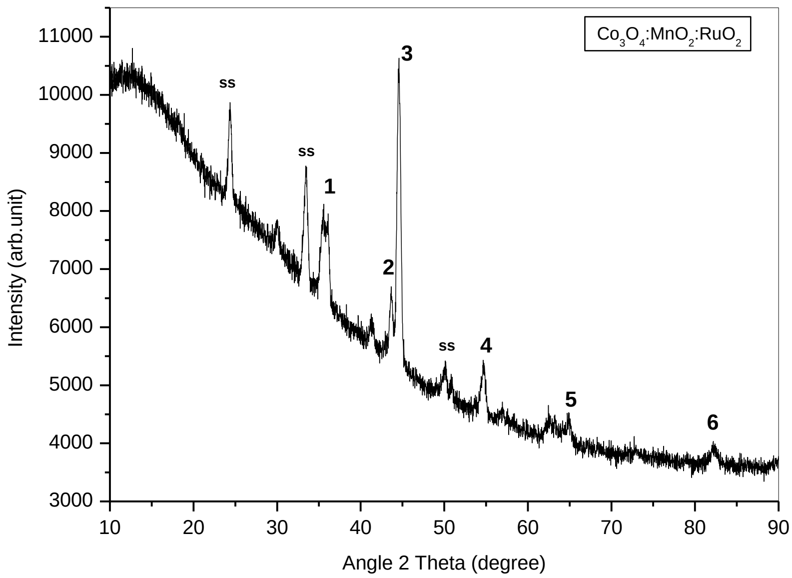
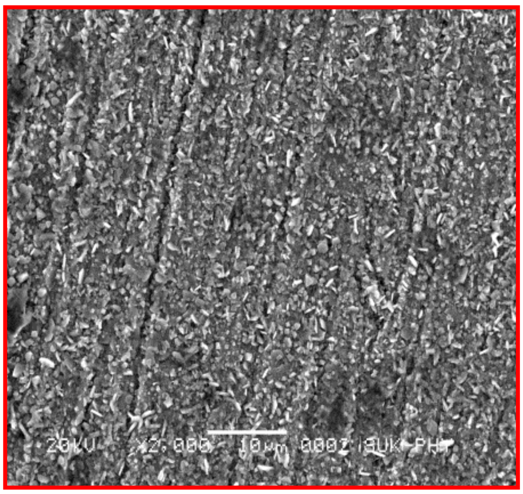


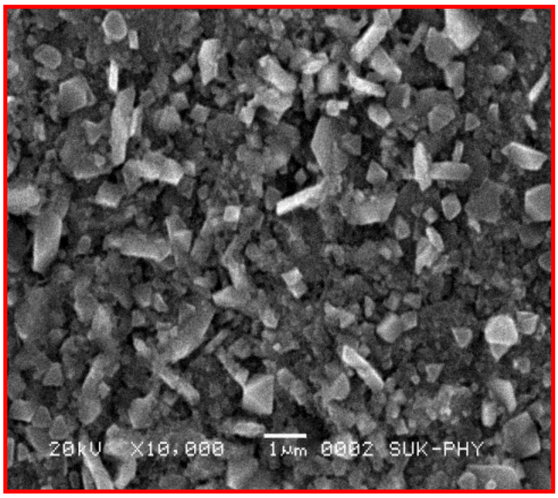
Fig. 2. XRD patterns of [Co:Mn:Ru] oxide thin film

3.2 Morphological Properties

From the SEM analysis it has been observed that the grain structure of MnO_2 ,RuO_2 and Co_3O_4 films is well adherent and porous surface



[a]



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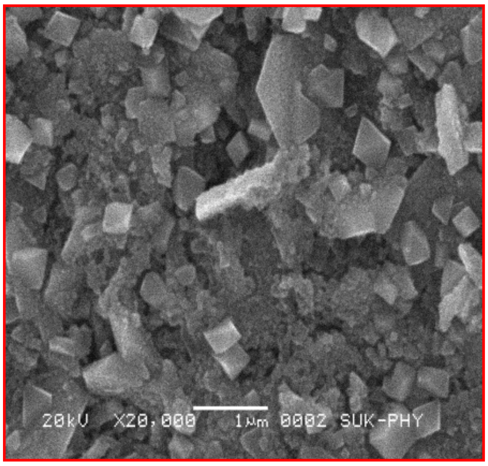

[c]

Fig. 3. SEM micrographs of [Co:Mn:Ru] oxide thin film.

As seen in fig.3. MnO_2 ,RuO_2 and Co_3O_4 thin films possess large grains uniformly distributed throughout the film surface, the average grain size calculated from the SEM images are around 500 nm and 600 nm respectively. From fig [c] it is observed that, the grains are more equated with continuous grain boundary with decreased grain size in the range 250 nm, this indicates [CO:Ru:Mn] oxide thin film exhibit enhanced pore density and grain density which is major requirement in supercarpacitor.

3.3 EDAX Analysis

The EDAX spectrum of [CO:Mn:Ru] oxide thin film composite thin film is shown in figure 4. Manganese, Ruthenium, Cobalt and Oxygen elements existed in the sample.

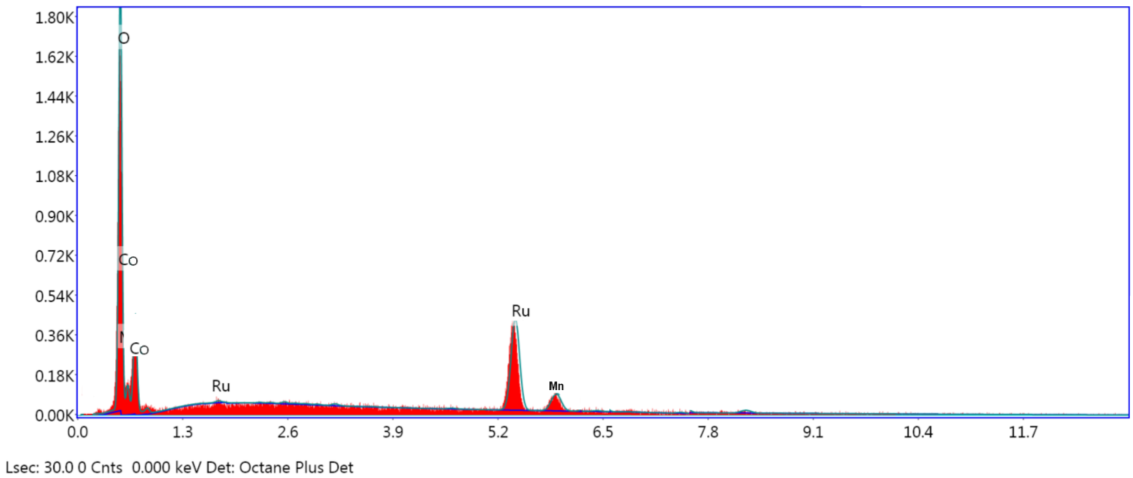

Fig. 4. EDAX patterns of [Co:Mn:Ru] oxide thin film

3.4 Electrochemical Properties

3.4.1 Cyclic Voltammetry Analysis

The CV measurements were performed with composite [Co:Mn:Ru] oxide thin films as working electrodes and platinum wire as counter electrode and SCE as a reference electrode in 1 M KOH electrolyte. Fig. 5. shows the cyclic voltammograms, with varying potential windows such as 0.65V to -1.3V at various scan rates 10, 20, 40, 60, 80 and 100mV/sec. From CV analysis, composite [Co:Mn:Ru] oxide films showed maximum specific capacitance of 440 F/g, at 10mV/s scan rate.[10]

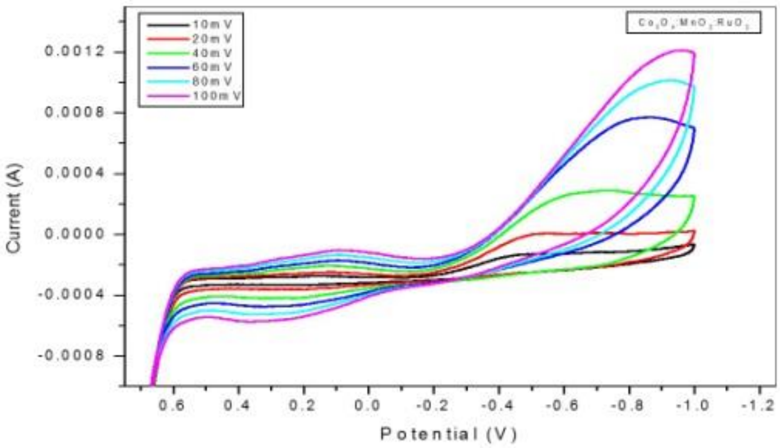

Fig. 5. Cyclic Voltammograms of ternary composite [Co:Mn:Ru] oxide thin film electrode

3.4.2 Chronopotentiometry

Typical charging and discharging curves for composite [CO:Mn:Ru] oxide thin film electrodes were measured between the voltage range of -0.6 to +0.6 V at a current density of 1mA/ cm^2 in 0.1 M KOH electrolyte as shown in fig. 6. It is observed that charging-discharging time are almost same. The supercapacitive parameters such as specific energy, specific power and coulombic efficiency were calculated from chronopotentiometry. [CO:Mn:Ru] oxide thin film exhibited specific energy 158.76 Wh/kg, and specific power 83.04 kW/kg. The columbic efficiency of the electrodes was fond to be 100%.

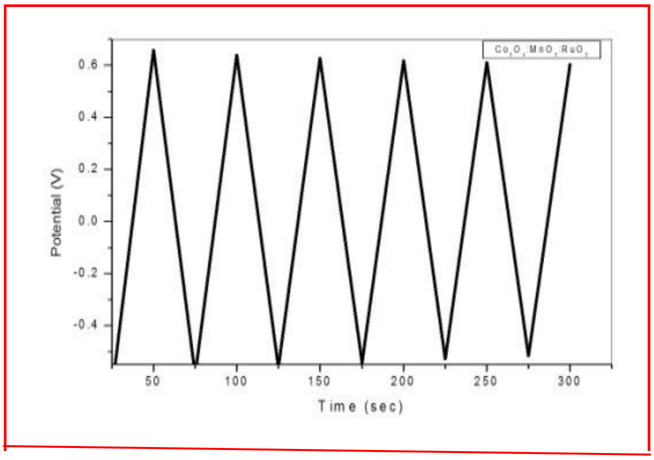

Fig.6. Charge-discharge curves of composite [Co:Mn:Ru] oxide thin film electrode

3.4.3 Cyclic Stability

Since the composite [CO:Mn:Ru] oxide thin film electrodes showed the highest capacitance, we investigated the stability of the film for longer votammograms upto 1000 cycles at the scan rate of $500mVs^{-1}$ in 0.1M KOH electrolyte lasting about 3hour, is shown in fig. 7 .The 75% stability is retained after 1000^{th} cycle, the value of specific capacitance is decreased by a comparably small amount which may be due to detatchment during early charging/discharging cycles in the electrolyte. [11]

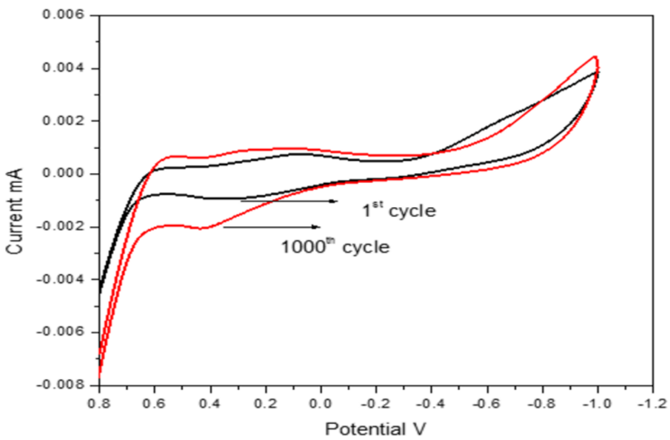

Fig. 7. Cyclic stability composite [CO:Mn:Ru] oxide thin film electrode

3.4.4 EIS Analysis

Figure 8. shows the Nyquist plot for composite [CO:Mn:Ru] thin film electrodes. EIS measurement was carried out at a dc bias of 0.066V with a sinusoidal signal of 5 mV over the frequency range of 1 Hz to 10^5 Hz. A sharp increase in the imaginary part of EIS at lower frequency is due to capacitive behavior of the electrode. A semicircle at higher

frequencies is due to the charge –transfer resistance. In the intermediate frequency region, the 45° line to Z‘ axis is the indication of ion diffusion into electrode materials. The semicircle representing the charge transfer resistance at the electrode/ electrolyte interface is observed.

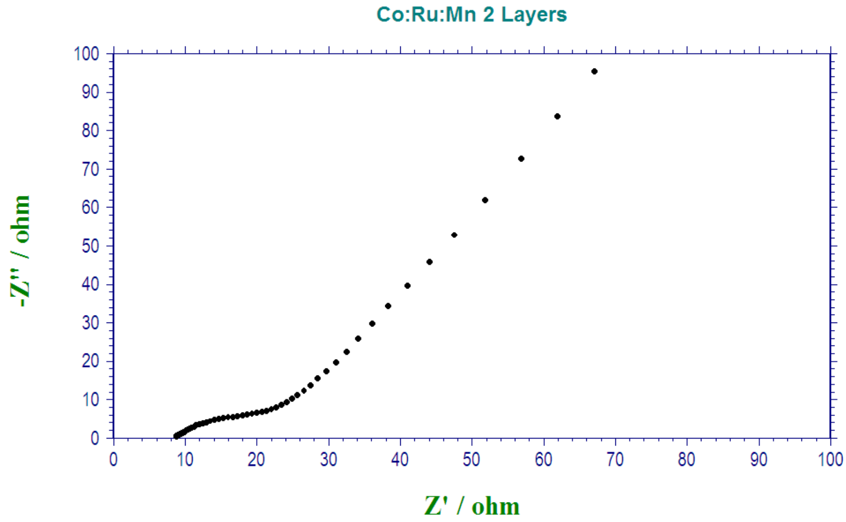

Fig. 8. Impedance Spectroscopy (Nyquist Plot) composite [CO:Mn:Ru] oxide thin films electrodes

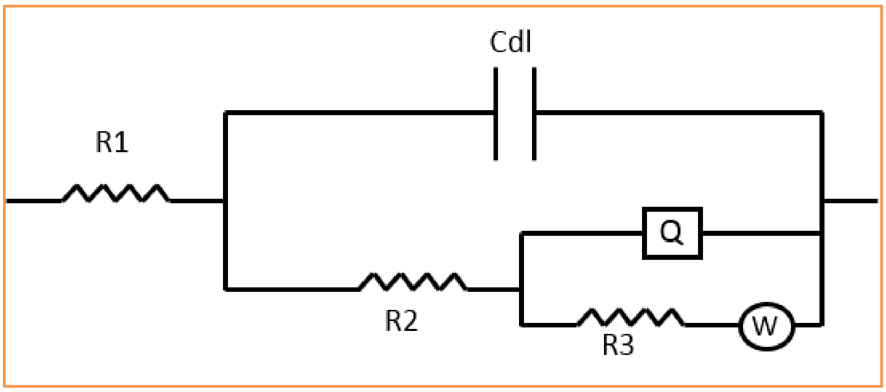

Fig. 9. A equivalent circuit for [Co:Mn:Ru] Oxide composite thin films electrodes

A simplified equivalent circuit is shown in figure. 9. Here C element represent double layer capacitance, R elements represent electrolyte resistance in pores, equivalent series resistance and Faradaic resistance and w is the Warburg diffusion resistance. The value of ESR estimated was 9.5 Ω. The lower ESR in the present case is attributed to the lower resistance of film which improves the redox activity during charging-discharging. Relatively low resistance is beneficial for high power.

Conclusions

The thin film of composite [Co:Mn:Ru] oxide deposited by solgel technique. The XRD pattern of composite film include peaks of all three oxides.The SEM images clearly indicated the enhanced porous nature of composite [Co:Mn:Ru] oxide as compared to pure thin films.The composite [Co:Mn:Ru] oxide films showed maximum specific capacitance of 440 F/g, at 10mV/s scan rate with 1M KOH electrolyte. The composite[Co:Mn:Ru] oxide films showed maximum specific capacitance of 440 F/g, at 10mV/s scan rate with 0.1 M KOH electrolyte. The composite [Co:Mn:Ru] oxide films exhibited specific energy 158.76 Wh/kg, and specific power 83.04 kW/kg. The 75% stability is retained after 1000th cycle.The columbic efficiency of the electrodes was found to be 100%. ESR estimated was 9.5 Ω. It has been also observed that value of specific capacitance is more for composite electrode as compared to pure electrodes.

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