

Mn doped Ruthenium Oxide Permeable Structures and Their Electrochemical properties

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ABSTRACT

Mn-doped and Undoped Ruthenium Oxide composite nanostructures in thin film form were prepared on stainless steel substrates by sol-gel spin coating method. The at % of Mn was increased as 0.1, 0.2, 0.5, 1 and 2 %. The XRD pattern of undoped and Mn-doped Ruthenium oxide films showed crystalline nature with porous morphology. EDAX confirms the successful doping of Mn in RuO₂. The infrared spectrum illustrates stretching mode of Ru=O and O-Ru-O and absorption peaks attributed to the -OH bending vibrations along with Mn atoms was also seen. Electrochemical behaviour of the deposited films was attempted in 0.1 M KOH aqueous electrolyte using cyclic voltammetry, chronopotentiometry and electrochemical impedance spectroscopy (EIS) tests. For 1 at % Mn:RuO₂ thin films electrode showed maximum specific capacitance of 328 F/g. Chronopotentiometry study showed that for 1 at % Mn doping the specific energy and specific power are increased than undoped Ruthenium oxide and decrease in the charge transfer resistance .

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1. Introduction

The climate variation and insufficient availability of fossil fuels have greatly affected the world's economy as well as ecology. Accordingly the important matters related with energy crisis and global warming are the production, conversion, storage and utilization of energy. Electricity plays a vital role in our daily lives. It is a versatile form of energy and not easy to store in a hurry. So the prominence is on the proficient storage of energy for proficient consumption or utilization. So the energy storage devices such as batteries, fuel cells and supercapacitors are playing a larger part in our life. Electrochemical energy conversion has attracted a lot of attention as the efficiency of conversion is high and is reusable over a large number of cycles [1]. An electrical charge works as a clean, efficient and versatile oxidizing or reducing agent for several electrochemical reactions [2].

As per demand, it is necessary to store and release large amounts of electricity very quickly. Hence, the energy storage devices such as electrochemical capacitors which are having high power density, long cycle life, cost effective and small size are useful. Because of their tremendously high capacitance density, electrochemical capacitors are also known as Supercapacitors. Most have reported that in both crystalline and amorphous forms RuO₂ has been considered as the most promising candidate for electrode materials owing to its reversible charge-discharge process and large capacitance, high chemical and thermal stability, electrochemical redox properties [3-6].

Even though RuO₂ has a great advantage in terms of wide potential range of highly reversible redox reactions with high specific capacitance, it is somewhat expensive for commercial electrodes in bulk type electrochemical capacitors.

Development of high energy and power density electrochemical energy source is now a day's interest, so main goal is to increase the power density of an electrochemical device and also to develop high surface area, low cost electrode materials. Hence reducing the amount of RuO₂ to meet energy density and power demands by increasing its utilization efficiency and its specific capacitance is always a key issue for making the devices more cost effective [7]. So in order to get electrode material with high capacitance and moderate price one way is to use doped metal oxide. One such cheaper metal oxide can be doped with expensive metal oxide. So another suitable metal oxide can be manganese oxide. Manganese dioxide is one of the potential candidates as electrode materials in supercapacitors because of its low cost, natural abundance, excellent capacitive behavior and environmental capability, high energy density [8].

In the present investigation, thin films of undoped ruthenium oxide and Mn doped Ruthenium oxide thin films were synthesized by sol-gel spin coating technique. The impurity concentration of Mn was increased as 0.1, 0.2, 0.5, 1 and 2 at %. The effect of increase in Mn doping on structural, morphological and supercapacitive properties was investigated in detail.

2. Experimental

2.1 Synthesis of Mn: RuO₂ thin films

Synthesis of Mn doped Ruthenium oxide thin films was done by Sol-gel spin coating technique taking into account the high cost of ruthenium oxide. Doping of Mn will minimize the quantity of ruthenium material with better results. 0.01 M Ruthenium trichloride and Manganese trichloride solutions were used as precursors. Continuous stirring for 3 hours and 24 hours setting resulted in gel formation.

Then the gel was spread uniformly on clean stainless steel substrates in spin coater unit by spinning at 300 rpm. Then doping percentage of Mn was increased as at 0.1 %, 0.2%, 0.5%, 1% and 2%. After stirring and setting for 24 hours gel was formed. Then the gel was deposited on properly cleaned SS substrates in spin coater unit. After annealing, uniform and thin films were obtained and were used for further characterization.

2.2 Characterization and Electrochemical Techniques

The weight of the film was measured by a micro-analytical balance (Contech) having 0.1 mg. sensitivity using weight difference method. The structures of thin films were analysed by X-ray diffraction with a diffractometer Rigaku Ultima IV, Japan using $\text{CuK}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) by varying diffraction angle 2θ from 10° to 80° . The surface morphology was analyzed by scanning electron microscopy (SEM JEOLJSM 6360). The compositional analysis of the as deposited thin films was carried out using EDAX technique by Quanta 200 ESEM instrument. The spectral analysis was carried out in the range 500 to 4000 cm^{-1} at room temperature using infrared spectrophotometer (Nicolet IR-10 Thermofischer Scientific, USA).

The area of 1 cm^2 at an end of the strip was dipped in the electrolyte and used for characterization and the remaining was polished which works as current collector. Cyclic voltammetry measurements were performed using an electrochemical workstation CH Instruments CH1608E. 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 as counter electrode and a saturated Calomel electrode as reference electrode.

3. Results and Discussions:

3.1 Structural, Morphological and Optical Studies

The X-ray diffraction pattern of undoped RuO_2 and Mn : RuO_2 thin films are shown in Fig.1.

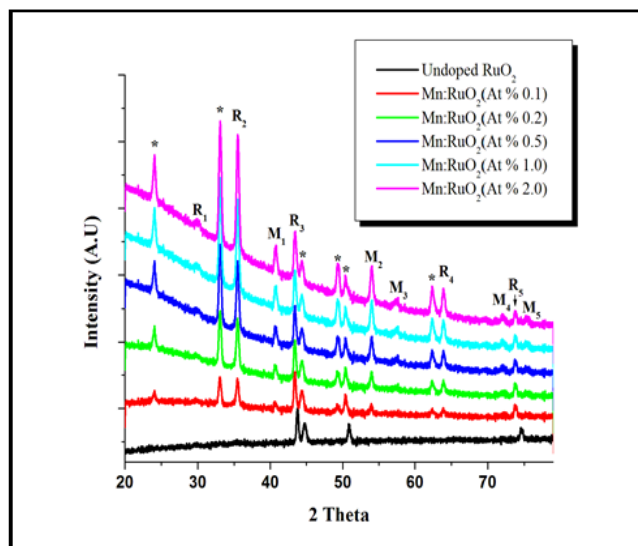


Figure 1. XRD of pristine and Mn doped RuO_2 thin films.

Existence of many intense peaks shows high crystallinity for both undoped and Mn: RuO_2 thin films. The experimental data showed the crystalline nature of RuO_2 with tetragonal structure and orthorhombic structure of MnO_2 . The observed (d) values matches well with the standard (d) values from JCPDS cards [JCPDS Card No.-88-0322 and JCPDS Card No.-82-2169 respectively]. The peaks which are labelled as “*” correspond to stainless steel. The SEM image, figure 2. showed network like porous structure giving rise to surface

roughness. Such porous morphology is favourable for penetration of electrolyte.

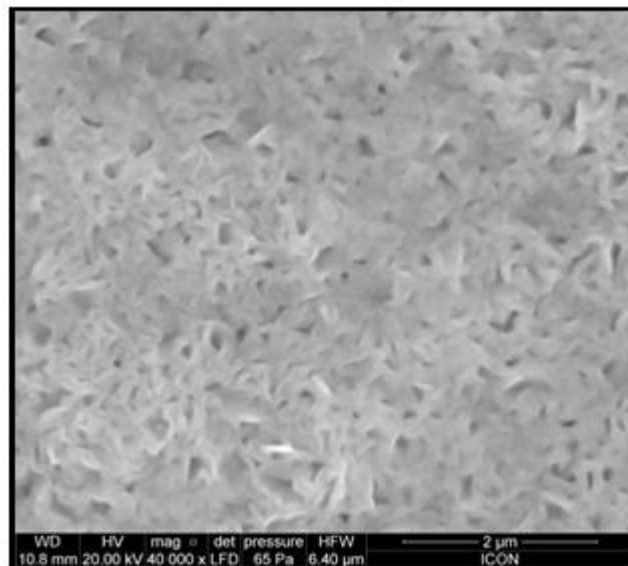


Figure 2. Surface Morphology of pristine RuO_2 thin film X40, 000 magnification.

The surface morphological images of Mn doped RuO_2 thin films with increasing doping concentration of Mn for higher magnification are depicted in figure 3.

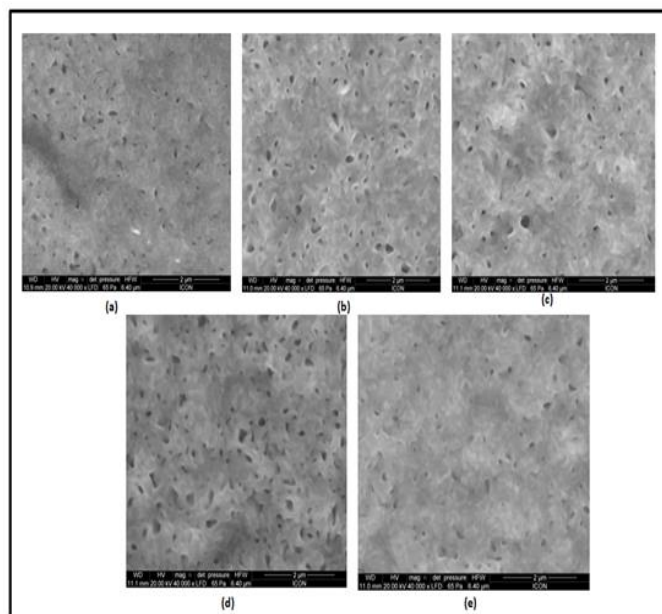


Fig 3. SEM images for Mn doped RuO_2 samples (a) 0.1 at % (b) 0.2 at% (c) 0.5 at% (d) 1 at% (e) 2 at%.

The morphology showed that the substrate is well covered with RuO_2 material. The porous structure creation due to the various randomly distributed interconnected structures were seen. The number and size of pores was increased with Mn doping. Admirable electrochemical performance as an electrode for a supercapacitor could be demonstrated due to the interconnected structure [9].

Sufficient void spaces in and between the pores, pore size distribution and such porous structure greatly assist the ion diffusion from the electrolyte into the electrode, which raises the specific capacitance. Admirable electrochemical performance as an electrode for a supercapacitor could be demonstrated due to the interconnected structure [10]. The pore size variation for undoped and doped ruthenium oxide film is as shown in figure 3.

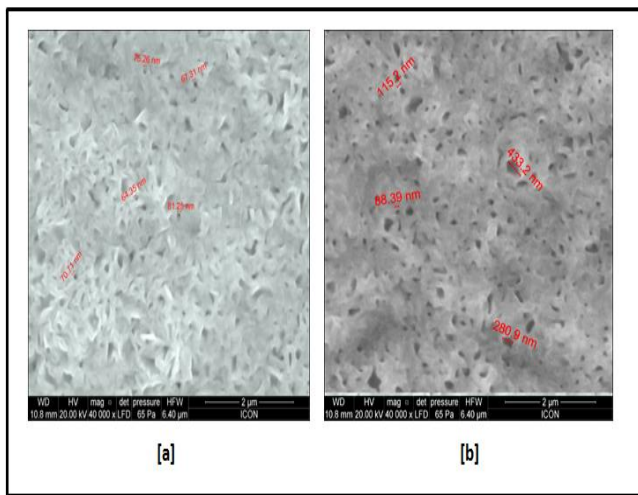


Figure 4. Pore size variation of [a] Undoped RuO_2 , [b] $\text{Mn}:\text{RuO}_2$ (1 at %) thin films.

From figure 4, it is seen that for both the thin films, the surface consists of randomly distributed pores. But average pore size for undoped ruthenium oxide lies in the range of 75-80nm and due to doping, pore size is increased upto 200-300 nm on an average. This type of highly porous structure is expected to produce high capacitance values. The morphology shows that 1 at %, the addition of Mn modifies the surface of RuO_2 film. The variation of RuO_2 to $\text{Mn}:\text{RuO}_2$ leads to increase in surface area. The infrared spectrum of as deposited undoped RuO_2 thin film as shown in figure 5 depicts strong absorption bands at $880.41(\text{II})\text{ cm}^{-1}$, $749.52(\text{I})\text{ cm}^{-1}$ and at $3410\text{ cm}^{-1}(\text{III})$ indicate the stretching mode of $\text{Ru}=\text{O}$ and $\text{O}-\text{Ru}-\text{O}$ and stretching vibrations of OH^- respectively [11]. This result indicated that, as deposited film contained hydroxide and other bonds, which indicates that formation of hydrous ruthenium oxide that may play important role in capacitive behavior [12]. The absorption peaks around 1650 cm^{-1} may be attributed to the $-\text{OH}$ bending vibrations along with Mn atoms [13].

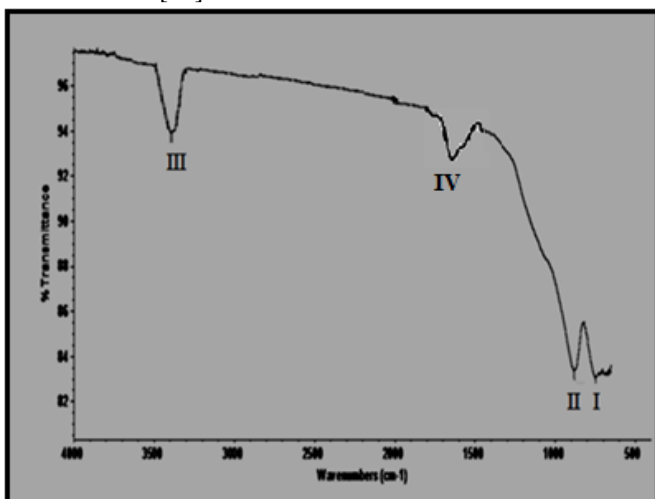


Figure 5. FTIR Spectrum of $\text{Mn}:\text{RuO}_2$ Thin Film.

3.2 Electrochemical Studies

Cyclic Voltammetry was used to determine the electrochemical properties of the spin coated $\text{Mn}:\text{RuO}_2$ thin films. The electrode potential was scanned between -0.8V to 0.8V in both anodic and cathodic directions and current response was measured indicating the typical pseudocapacitive behavior. Figure 6. A and 6.B shows the C-V of undoped and $\text{Mn}:\text{RuO}_2$ electrode of different doping percentage of Mn.

Due to doping of Mn, the potential window has been increased. The rectangular shapes and mirror-image characteristics of CV curves show the ideal supercapacitive behaviour for all the electrodes. This indicates Mn: RuO_2 thin films can be used as promising electrodes in supercapacitors. The values of specific capacitance as calculated from CV are 182, 232, 278, 308, 328 and 297 F/g for undoped, and 0.1, 0.2, 0.5, 1 and 2 at % Mn respectively at 100 mV/Sec.

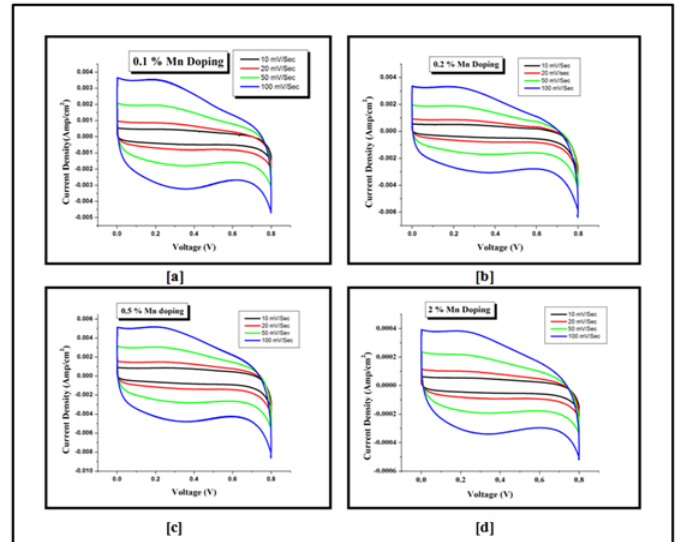


Figure 6. A. Cyclic voltammogram of $\text{Mn}:\text{RuO}_2$ at different doping percentage of Mn.

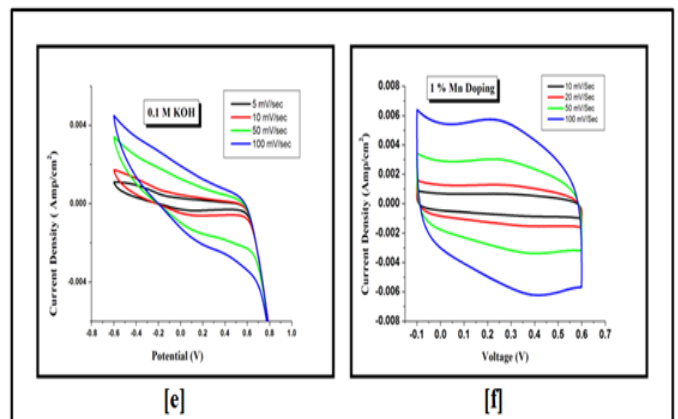


Figure 6. B. Cyclic voltammogram of undoped RuO_2 and $\text{Mn}:\text{RuO}_2$ at % 1 Mn Doping.

The specific capacitance decreased with increase in scan rate for all the samples but this variation for undoped and $\text{Mn}:\text{RuO}_2$ (at % 1) is shown in figure 7.

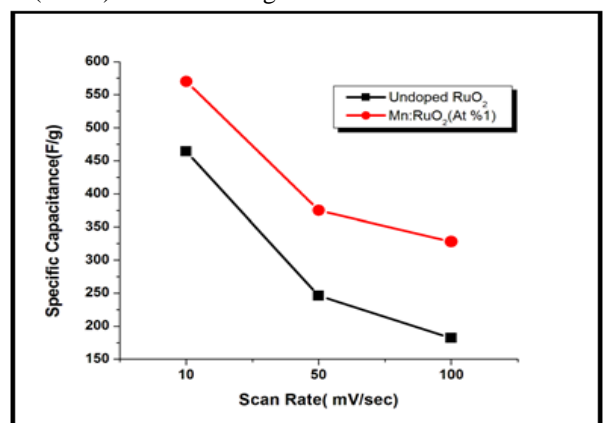


Figure 7. Effect of Scan Rate on specific Capacitance for RuO_2 and $\text{Mn}:\text{RuO}_2$ thin film electrodes.

When the scan rate is low, the K^+ ions slowly diffuse into the pores of Mn: RuO_2 . Thus all surface area can be utilized for charge storage. But at higher scan rate, the movement of K^+ ions is limited by diffusion and only outer surface is utilized for charge storage.

The variation of specific capacitance with increase in Mn doping (at 100 mV/Sec scan rate) is shown in figure 8. It is clear from figure that the specific capacitance of RuO_2 electrode increases with increase in Mn doping percentage upto 1%. But after that further increase in doping percentage decreases the specific capacitance. The reason behind this may be the decrease in porosity which leads to decrease in surface area of the electrode. This is observed in SEM images (figure 5). Even though all the CV are rectangular in shape, 1 at % Mn doped RuO_2 electrode has largest enclosed area which shows better charge storage performance. The larger enclosed area means higher energy density of the oxide could be attained. Thus surface morphology is most important characterization that governs the capacitance of Mn: Ruthenium oxide. Overall capacitance of the electrode is affected by the amount of Mn oxide added considerably.

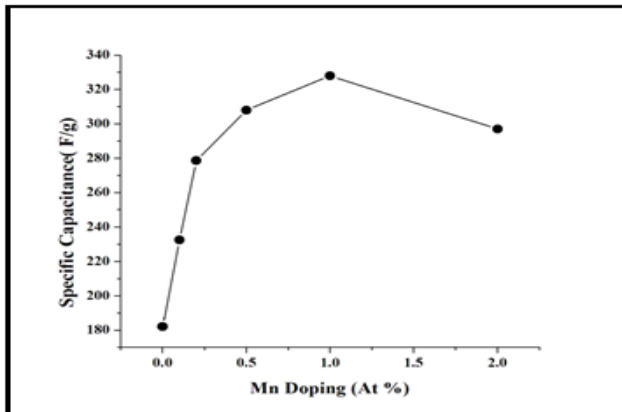


Figure 8 . Variation in specific capacitance with increase in doping % of Mn.

The electrochemical stability of Mn: RuO_2 electrodes was evaluated by repeating CV test for 2000 cycles at 500 mV/Sec scan rate. Specific capacitance decreased with increasing cycle number. Figure 9 gives the variation of specific capacitance with increase in cycle numbers for increase in doping percentage of Mn. The specific capacitance decreased with cycle numbers for all the samples. This is because the active material is lost, may be due to dissolution or fast charging/discharging cycles in the electrolyte. That affects on the specific capacitance due to loss of the electrode. There is a negligible loss in the current.

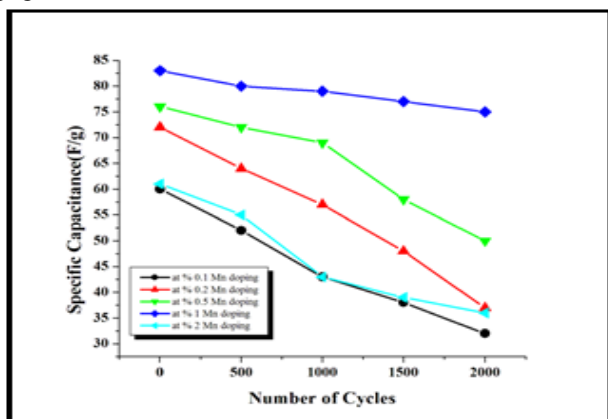


Figure 9 . Stability of Mn:RuO₂ electrode at 1% Mn doping.

Figure 10 shows the stability graph of 1 at % Mn: RuO_2 electrode and a graphical representation of specific capacitance for 2000th cycle at 500 mV/Sec and % retention in capacitance after 2000th cycle for each sample. The 1 at % Mn: RuO_2 sample showed maximum retention. The current under curve for the same has been decreased by only 11% up to 2000 cycles. From the stability study, Mn: RuO_2 thin film electrode is observed to be useful in energy storage applications.

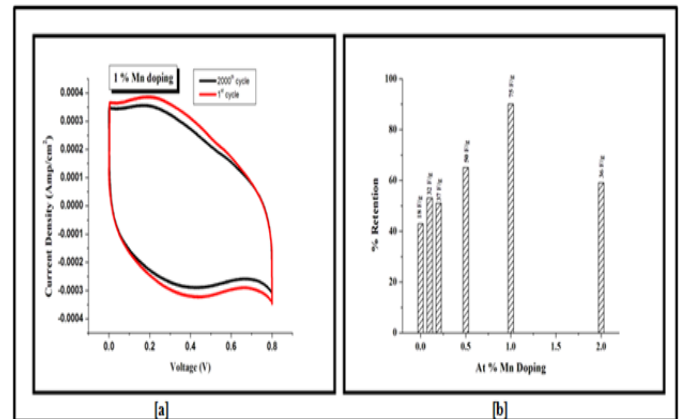


Figure 10..[a] Stability curve of Mn: RuO_2 electrode at 500 mV/Sec and [b] Variation of specific capacitance and % retention as a function of % Mn doping .

Now, only RuO_2 and Mn: RuO_2 (1 at %) films are used for further characterizations.

The chronopotentiometry profile of Mn: RuO_2 electrode in 0.1 M KOH electrolyte is presented in figure 11. The anodic and cathodic current rate is 2mA/cm² and the operational potential range is between -1 to 1 V/SCE. It is seen that the charge profile is slightly curved which suggests a pseudocapacitive characteristics. Because of electrode polarization, there can be a potential drop where the current is reversing. During charging and discharging processes, there is a linear variation of potential which is another criterion for capacitance behavior of a material besides exhibiting rectangular voltammograms. Figure 11 shows that the time periods of charge and discharge are almost the same, which implies high reversibility and high Coulomb efficiency.

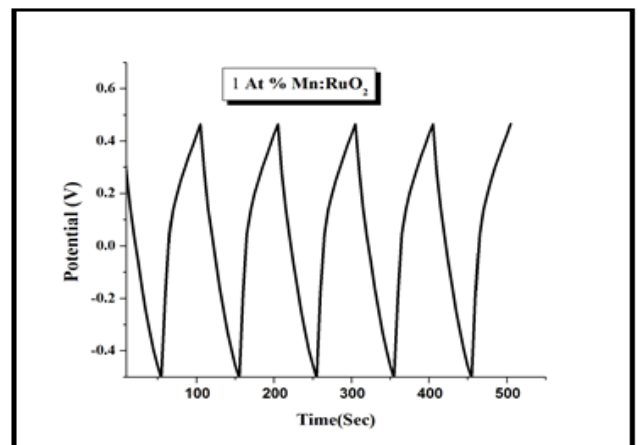


Figure 11. Chronopotentiometry curve of 1at % Mn: RuO_2 electrode in 0.1 M KOH electrolyte.

For undoped RuO_2 thin film, the calculated specific energy and specific power were 3.96 Wh/Kg and 36 W/Kg. For 1 at % Mn doping the specific energy slightly increased to 4.06 Wh/Kg and specific power to 50 W/kg with efficiency 95%. These changes in the values may be due to increased time for charging and discharging of a capacitor.

Electrochemical Impedance spectrum in the form of Nyquist plot for Mn: RuO₂ electrode is shown in figure 12. EIS measurement was carried out at a dc bias of 0.083 V with a sinusoidal signal of 5 mV over the frequency range of 1 Hz to 10⁵ Hz. Real and imaginary parts of the impedance are shown by Z' and Z'' respectively. Faradaic reactions are related to the semi-circle in high frequency region. Diffusion controlled process is attributed to the linear curve at the low frequency region. The non-zero intercept at Z' at the beginning of the semicircle is due to the electrolyte resistance and that nature is same for undoped as well as Mn: RuO₂ thin films. The resistance proposed by semicircle is due to the active electrode material. Its value is 2.3 Ω for undoped RuO₂ film and for 1 at % Mn: RuO₂ film it is 1.5 Ω . This indicates that addition of Mn in RuO₂ decreases the charge transfer resistance and increases the conductivity. Good agreement of simulated and measured data was found for the equivalent circuit. Hence Mn:RuO₂ can be concluded as the most promising electrode material in supercapacitor applications.

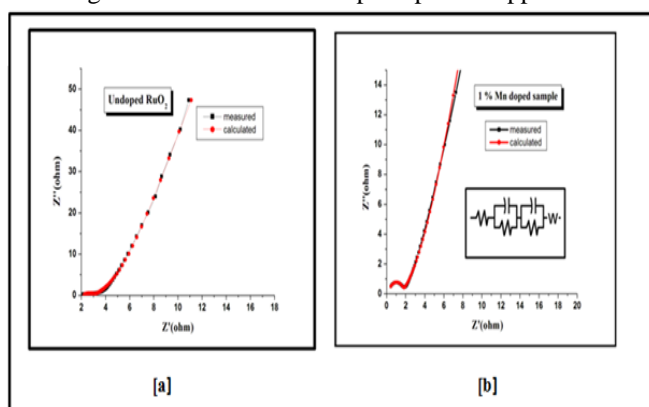


Figure 12 Nyquist Plot for [a] Undoped RuO₂ [b] Mn: RuO₂ (1 at %) thin film electrode.

4. Conclusions

Sol-gel spin coating is a simple route for synthesis of Mn:RuO₂ thin films. Increase in manganese doping increased the pore size. Supercapacitive performance is increased with ---% Mn:RuO₂ than undoped sample. The maximum value of specific capacitance at 100 mV/Sec Energy density and power density are 297 F/g, 4.06Wh/Kg and 50 W/Kg respectively. Mn: RuO₂ thin film electrode is observed to be useful in energy storage applications.

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References

- [1] M. Winter and R.J Broad, What are batteries, fuel cells and supercapacitors, *Chem. Rev.*,104(2004);pp4245-4269
- [2] F.C Walsh, *Pure Appl. Chem*, 73(2001);p1819.
- [3] C.C. Hu, K.H. Chang, *Electrochimica Acta*,45, (2000);p268
- [4] B.J Lee, "Carbon nanofibre/hydrous RuO₂ nanocomposite electrodes for supercapacitors", *Journal of Power Sources*,168(2007);pp546-552.
- [5] I.H Kim, K.B Kim, "Electrochemical characterization of Hydrous Ruthenium Oxide Thin Film Electrodes for Electrochemical Capacitor Applications", *Journal of The electrochemical Society*,153,(2006);pp383-389.
- [6] C.C Hu, M.J. Liu,K, "Anodic deposition of hydrous ruthenium oxide for supercapacitors" *Journal of power Source*, 163(2007);pp1126-1131.
- [7] S.L. Kuo, N.L. Wu, *Electrochemical and Solid State Letters*, 6(5), (2003); pp A85-A87
- [8] W. Wei, X. Cui, W. Chen and D.G Ivey, Manganese oxide-based materials as electrochemical supercapacitor electrodes, *Chem. Soc. Rev* 40(3), (2011); pp1697-1721.]
- [9] Y. Liu et.al, Manganese Dioxide nanosheet arrays grown on grapheme oxide as an advanced electrode material for supercapacitors, *Electrochim. Acta* 111,707-712(2013).
- [10] Liu, Y. et.al Manganese Dioxide nanosheet arrays grown on grapheme oxide as an advanced electrode material for supercapacitors. *Electrochim. Acta* 111,707-712 (2013)
- [11] P.S Joshi, D.S Sutrave, *International Journal for Research in Applied Science and Engineering Technology*, Ruthenium Oxide: Thin film and Electrochemical Properties, 4-V-III, (2016),765-772.
- [12] W. Sugimoto, H. Iwata, Y. Murakami, Y. Takasu, *J. Electrochem. Soc.*,151 (2004) A1181.
- [13] M. Ocana, Uniform particles of manganese compounds obtained by forced hydrolysis of manganese(II) acetate, *Colloid Polym. Sci.*,278 (2000) 443-449.