

Electro-Chemical Properties (Ru:Mo) Composite Thin Films Electrode for Supercapacitors

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Abstract: The present work examines the effect percentage of Ru on MoO₃(Ru:Mo oxidecomposite) thin films on steel substrate deposited by Sol-gel spin coat method. The annealing temperature was 800⁰C for composite thin films. The percentage concentration of Ru was varied from 10 to 50%Ru:Mo oxidecomposite thin films on SS electrodes thin films have been studied for the supercapacitor application with cyclic voltammetry, charge-discharge, and electrochemical impedance techniques for 0.1 M KOH electrolyte aqueous electrolyte. The CV Revealed that at lowest scan rate of 10 mV.s⁻¹, maximum specific capacitances are found to be 1010 F.g⁻¹ for (Ru:Mo) oxidecomposite electrodes, The charge–discharge behaviour of the (Ru:Mo) oxide composite electrodes]. The maximum energy density of 10.8948 Wh.kg⁻¹ at still high power density of 30.576 kW.kg⁻¹

Keywords: CV, CP, Sol-gel Spin Coating

1. Introduction

Ruthenium oxide is superior due to the unique combination of characteristics, such as metallic conductivity, high chemical and thermal stability, catalytic activities, electrochemical redox properties, highly reactive with reducing agents due to its oxidizing properties and field emitting behaviour etc. [1]. It has been widely used in supercapacitor because of its good catalytic properties [2]. But Ruthenium is costly and toxic. For the last several years, molybdenum oxide has attracted attentions because of their potential applications in gas sensing devices, optically switchable coatings and catalysis etc. It also exhibits electrochromism, photochromism after intercalating with an appropriate cation (such as Li⁺, Na⁺) making suitable for use in display devices, smart windows and electrochemical storage. Such a wide range applications is due to the non-stoichiometric nature of molybdenum oxide and to the occurrence of different phases of molybdenum oxide(Ru:Mo) oxide composite thin films have been prepared using various techniques, including organometallic chemical vapour deposition [3], sol gel [4], electro deposition [5]. Here, attempts are made to deposit (Ru:Mo)composite thin films using sol-gel spin coating deposition technique. Their electro chemical properties had been studied.

2. Effect of Scan Rate Variation (Ru:Mo) oxidecomposite thin film

The CV curves of (Ru:Mo) oxidecomposite electrode at different scan rates are shown in Fig. 1 (a), (b), (c), (d), (e), (f), (g), (h), (i) for different percentage of Ru with Mo. This mainly results in the increase of ionic resistivity leading to the drop in the capacitances of the electrode. Fig. 2 and Fig.3 shows the variation of specific and interfacial capacitances with scan rate of the (Ru:Mo) oxidecomposite thin films. The decreasing trend of the capacitance suggests that parts of the surface of the electrode material are inaccessible at high charging–discharging rates. Hence, the

specific capacitance obtained at the slow scan rates is believed to be closest to that of full utilization of the electrode material [6]. At lowest scan rate of 10 mV.s⁻¹, maximum specific capacitances are found to be 1010 F.g⁻¹ for (Ru:Mo) oxidecomposite electrodes, From the fig. 2 it is observed that the specific capacitance of (Ru:Mo) oxide is more (Ru_{0.15}:Mo_{0.85}) G6. Also shows the variation of specific capacitance of (Ru:Mo) oxidecomposite electrode with scan rate.

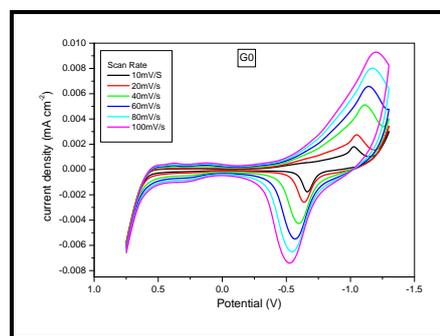


Figure 1 (a): (Ru_{0.10}:Mo_{0.0}) oxide G0

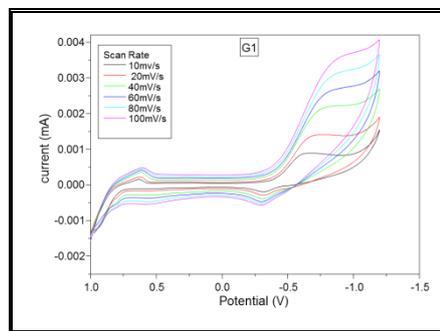


Figure 1 (b): (Ru_{0.5}:Mo_{0.5}) oxide G1

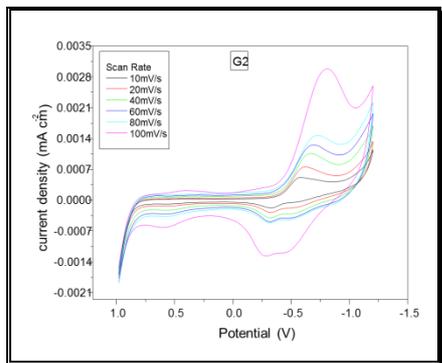


Figure 1 (c): (Ru_{0.4}:Mo_{0.6}) oxide G2

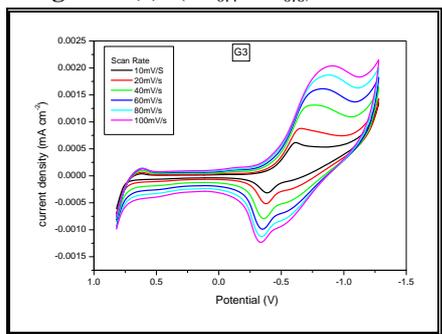


Figure 1 (d): (Ru_{0.3}:Mo_{0.7}) oxide G3

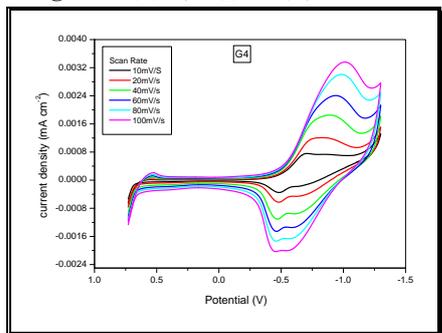


Figure 1 (e): (Ru_{0.25}:Mo_{0.75}) oxide G4

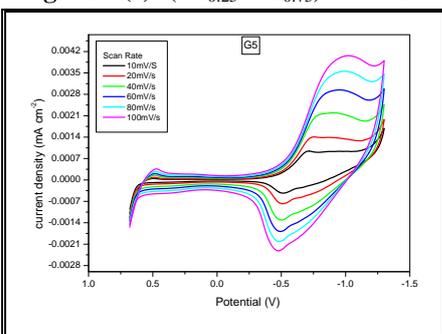


Figure 1 (f): (Ru_{0.2}:Mo_{0.8}) oxide G5

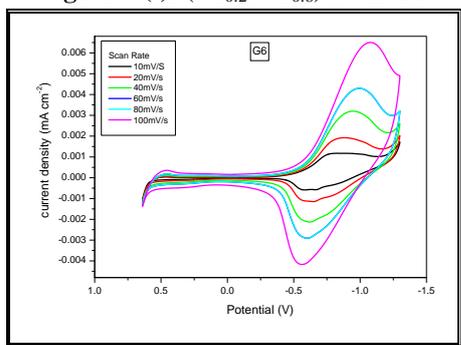


Figure 1 (g): (Ru_{0.15}:Mo_{0.85}) oxide G6

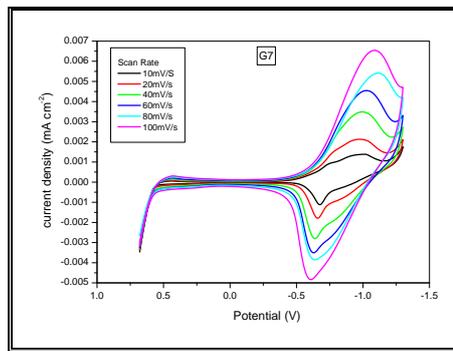


Figure 1 (h): (Ru_{0.1}:Mo_{0.9}) oxide G7

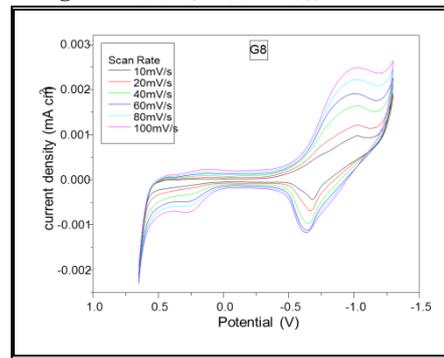


Figure 1 (i): (Ru_{0.0}:Mo_{1.0}) oxide G8

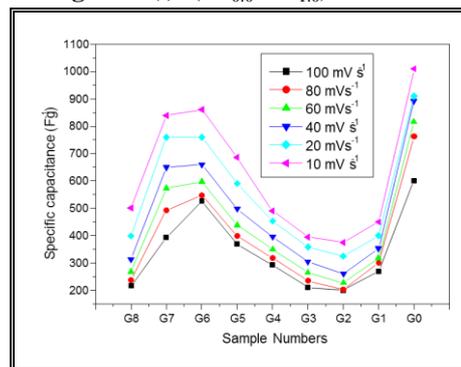


Figure 2: Variation of Specific capacitance of (Ru:Mo) oxide at different scan rate

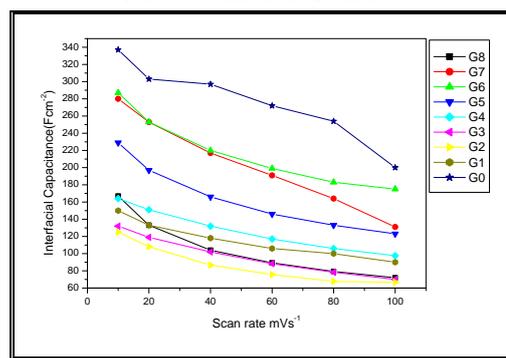


Figure 3: Interfacial Capacitance with different scan rate (different samples)

The fig. 2 shows the CV curves of (Ru:Mo) oxide electrode. Sample G0 is pure RuO₂ and G8 for pure MoO₃, while sample G1 to G7 are (Ru:Mo) oxide at different percentage. Scan Rate is varied from 10 mV s⁻¹ to 100 mV s⁻¹. Higher scan rate potential window increases the current. So voltametric current is directly proportional to the scan rate of CV [7]. This is the supercapacitive behaviour. Along with this in each CV curves reduction and oxidation peaks are visible, hence electrochemical capacitance of electrodes

results pseudocapacitance. The entire electrode exhibited that, as scan rate increases specific capacitance decreases. At low scan rate optimum specific capacitance [8], this is because of ions takes longer time to penetrate and reside in the electrode pores and from electric double layers, which is needed to generate higher capacitance[9].

From the fig. 2 as percentage of Ru goes on increasing from 0% to 15% SC goes on increasing, then Ru increases from 20% to 40% SC goes on decreasing for all scan rates. Initially Ru incorporation SC value increases rapidly, at !5% of Ru and 85% of Mo SC is maximum for all scan rates. Further % of Ru and Mo SC goes on decreasing. Initial increasing in percentage of Ru indicates that ion concentration which increases the electrical conductivity of films. G6 sample electrode shows better SC for all scan rates. This electrode shows large area under curve and high value of current. It may be due to capacitive favourable phase of Ru:Mo formed at that incorporation leading to optimum Ru incorporation an formation of good porous nature of sample as evidence from SEM. The interconnected crystallites of both RuO_2 and MoO_3 may create many micro pores, which help in electrolyte transport and provide large surface area for charge transport reaction for easy ionic intercalation between species leading to the increase in SC value of G6 electrode [10].

3. Charge-Discharge Study of (Ru:Mo) oxide composite thin film

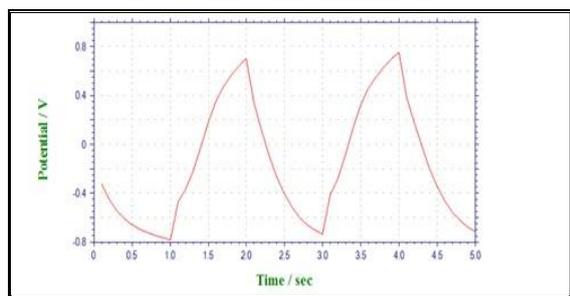


Figure 4 (a): $(\text{Ru}_{1.0}:\text{Mo}_{0.5})$ oxide G0

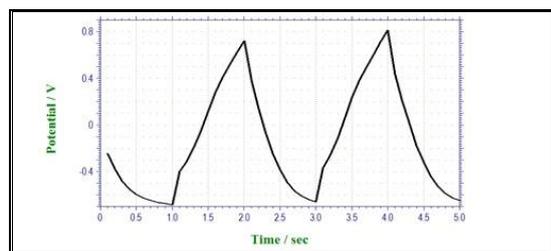


Figure 4 (b): $(\text{Ru}_{0.5}:\text{Mo}_{0.5})$ oxide G1

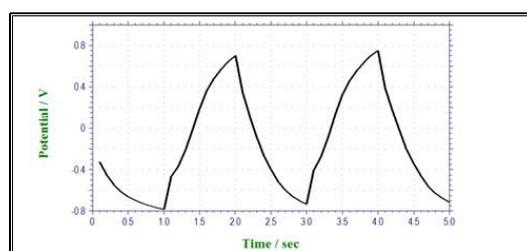


Figure 4 (c): (i) $(\text{Ru}_{0.4}:\text{Mo}_{0.6})$ oxide G2

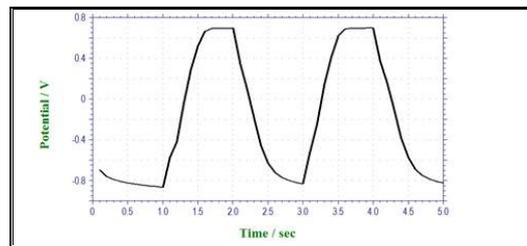


Figure 4 (d): $(\text{Ru}_{0.3}:\text{Mo}_{0.7})$ oxide G3

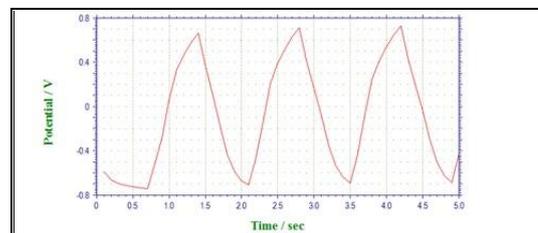


Figure 4 (e): $(\text{Ru}_{0.25}:\text{Mo}_{0.75})$ oxide G4

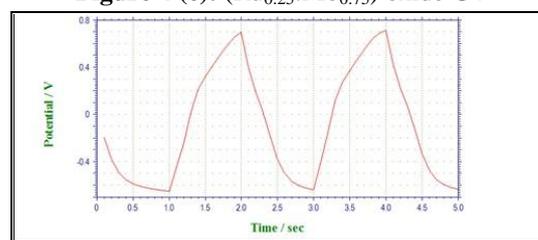


Figure 4 (f): $(\text{Ru}_{0.2}:\text{Mo}_{0.8})$ oxide G5



Figure 4 (g): $(\text{Ru}_{0.15}:\text{Mo}_{0.85})$ oxide G6

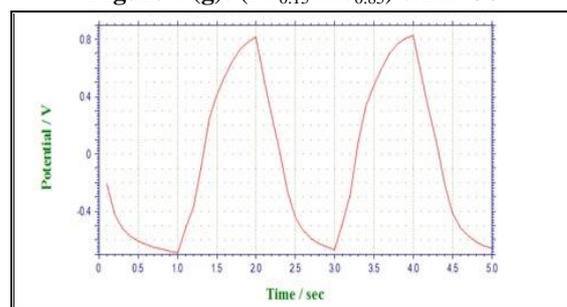


Figure 4 (h): $(\text{Ru}_{0.1}:\text{Mo}_{0.9})$ oxide G7

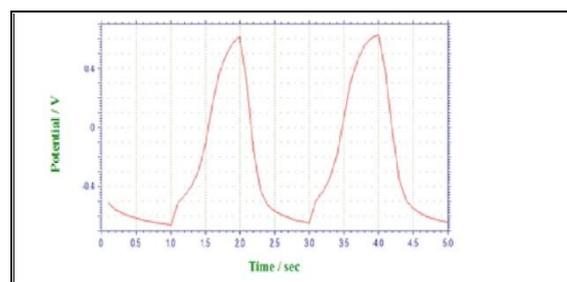


Figure 4 (i): $(\text{Ru}_{0.0}:\text{Mo}_{1.0})$ oxide G8

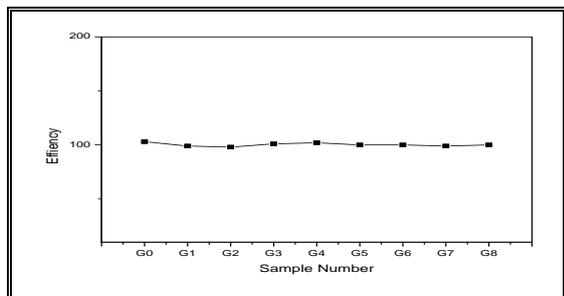


Figure 5: Variation of efficiency in (Ru:Mo) oxide

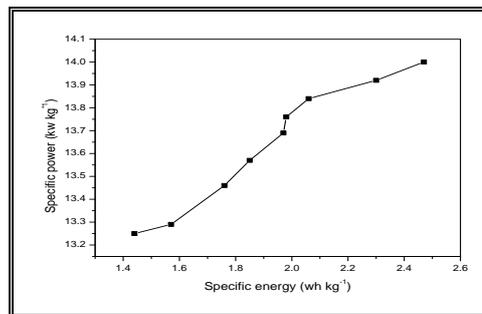


Figure 7: The Ragone plot for (Ru:Mo) oxide composite electrode for samples

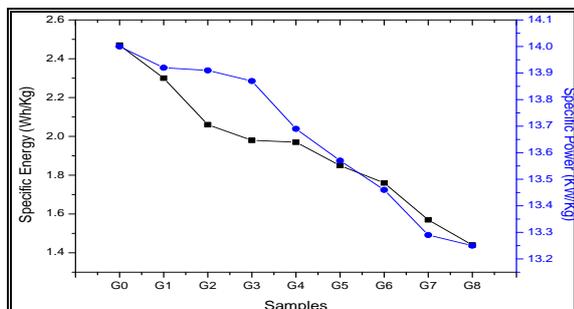
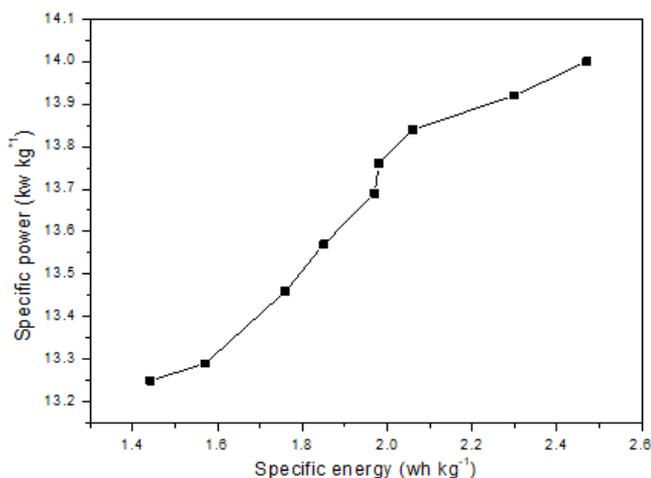


Figure 6: Variation of specific energy and specific power Ru added with Mo

The charge–discharge behaviour of the (Ru:Mo) oxide composite electrodes (G0 to G8) is examined by chronopotentiometry from -0.8V to 0.8V vs. SCE at the current density of $2\text{ mA}\cdot\text{cm}^{-2}$ in 0.1 M KOH electrolyte is shown in fig. 4.17. A nonlinear variation of potential versus time is displayed, which may be due to pseudocapacitance performance arisen from the electrochemical adsorption–desorption or redox reaction at an interface between the electrode and the electrolyte [12]. Fig. 7 shows Ragone plot relating power density to achievable energy density. From the plot, it is observed that the observed values of energy density and power density of composite electrodes are according to Ragone plot typically calculated for supercapacitors [11]. From the plot, it is observed that composite G6 has maximum energy density of $10.8948\text{ Wh}\cdot\text{kg}^{-1}$ at still high power density of $30.576\text{ kW}\cdot\text{kg}^{-1}$. As the energy density is dependent on the value of discharging time, the high energy density observed is due to the large discharging time of the (Ru:Mo) oxide composite electrode [13].



4. Conclusion

Ru:Mo oxide composite thin films on steel substrate deposited by Sol-gel spin coat method. The annealing temperature was 800°C for composite thin films. The CV Revealed that at lowest scan rate of $10\text{ mV}\cdot\text{s}^{-1}$, maximum specific capacitances are found to be $1010\text{ F}\cdot\text{g}^{-1}$ for (Ru:Mo) oxide composite electrodes, The charge–discharge behaviour of the (Ru:Mo) oxide composite electrodes. the maximum energy density of $10.8948\text{ Wh}\cdot\text{kg}^{-1}$ at still high power density of $30.576\text{ kW}\cdot\text{kg}^{-1}$

References

- [1] Gujar T.P., Kim W.Y., Puspitasari I., Jung K.D., Joo O.S., Electrochemically Deposited Nanograin Ruthenium Oxide as a Pseudocapacitive Electrode, *Int. J. Electrochem. Sci.*, 2007, 2, 666.
- [2] Zheng J.P., Cygan P.J., Jow T.R., Hydrous Ruthenium Oxide as an Electrode Material for Electrochemical Capacitors, *J. Electrochem. Soc.* 1995, 142, 2699.
- [3] Huang Y.S. and Liao P.C., *Solar Energy Mater. Sol. Cells*, 1998, 55, 179.
- [4] Zheng J.P., Cygan P.J., Jow T.R., Hydrous Ruthenium Oxide as an Electrode Material for Electrochemical Capacitors, *J. Electrochem. Soc.* 1995, 142, 2699.
- [5] Park B.O., Lokhande C.D., Park H.S., Jung K.D., Joo, O.S., Electrodeposited ruthenium oxide (RuO_2) films for electrochemical supercapacitors, *Journal of materials science*, 2004, 39, 4313.
- [6] P. R. Deshmukh, S. V. Patil, R. N. Bulakhe, S. N. Puswale, Jae-Jin Shim, and C. D. Lokhande, *Chemical Engineering Journal*, 45 (2014) 454
- [7] A. D. Jagadale, V. S. Jamadade, S. N. Puswale and C. D. Lokhande *Electrochimica Acta*, 9 (2012) 249
- [8] www.ce.sysu.edu.cn
- [9] www.arcjournals.org
- [10] R. C. Ambare, S. R. Bharadwaj, and B. J. Lokhande, *Current Applied Physics*, 6 (2014) 98
- [11] S. N. Puswale, P. R. Deshmukh, J. L. Gunjekar and C. D. Lokhande, *Materials Chemistry and physics*, 09 (2013) 45
- [12] Li. Yanhua, *Journal of Solid State Electrochemistry* 9 (2009) 46
- [13] L. Zhao, Li. Hongji, Xu. sheng, Li. Cuiping, Qu. Changqing, Lijun Zhang, and Baohe Yang, *Applied Energy* 8 (2016) 54
- [14] Xia, Hui, BoLi, and LiLu *RSC Advances*, (2014)

- [15] P. S. Joshi, S. M. Jogade, S. D. Gothe, D. S. Sutrave.
Asian Journal of Chemistry, 13 (2017)1991
- [16] A. D. Jagadale, V. S. Kumbhar, and C. D. Lokhande,
Journal of Colloid and Interface Science. 48 (2013) 627
- [17] V. Nabais, J. M. Bioresource Technology, 04 (2011) 92
- [18] A. Sezai, Sarae. Murut and Bilge. Kilic, Int. J.
ElectrochemSci, 3, (2008) 777
- [19] V. Ganesh. Journal of Power Sources, 34 (2006) 0825
- [20] R. Farma, M. Deraman, Awitdrus, I. A. Talib, R. Omar,
J.G. Manjunatha, M. M. Ishak, Int. J. Electrochem. Sci.,
8 (2013) 257