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Physical Characterization and Electrochemical Properties of Molybdenum Oxide Thin film

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Abstract : There is a growing necessity of transition metal oxide thin film for many important technological applications such as smart windows gas sensors, solar cells, super capacitors etc. Among the other transition metal oxides, Molybdenum oxide is a potential material as it exhibits interesting structural, optical, chemical, electrical properties. In this investigation Molybdenum oxide thin films have been synthesized using spin coating technique. Here Molybdenum oxide thin films have been deposited on stainless steel substrate by sol-gel spin coating method. Thin film properties of deposited samples were studied by XRD ,SEM, FTIR,EDAX. Thin films were used as electrodes for supercapacitor with 0.1 M KOH electrolyte. It showed maximum capacitance of 1010 F/g for scan rate of 10 mv/sec. Also stability of the electrode was calculated. Power density and energy density were determined from galvanostatic charge-discharge analysis.
Keywords: Supercapacitor, Molybdenum oxide, Sol-gel Spin-coating, CV, Galvanostatic charge-Discharge.

I. Introduction

Supercapacitors are the best candidates to provide the high power and long durability needed for the new energy devices [1]. The high capacity of supercapacitors mainly comes from the faradaic reaction within electroactive materials [2] The performance of Supercapacitor is attributed to the high electrochemical reversibility of redox transitions within electrode materials.[3]. Supercapacitor can store and deliver charge on a time scale of the order of several tens of seconds. Thus , they are becoming attractive energy storage devices particularly for high power requirements. Metallic oxides, conducting polymers have been generally used as electrode materials for supercapacitors.[4-7] Among these materials, Molybdenum oxide has been recognized as one of the most promising candidates for its good electrochemical capacitance performance and high specific capacitance.[8]In the present manuscript, we report the synthesis of Molybdenum oxide thin films using sol-gel spin coating method on stainless substrate. The structural ,morphological , vibrational properties were presented for as deposited films. The cyclic voltammetry study and chronopotentiometry was carried out with 0.1M KOH electrolyte to study the supercapacitor properties.

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II. Experimental

The molybdenum oxide thin films had been synthesized by a sol-gel spin coating technique using ammonium molybdate tetra hydrate as a source of Molybdenum oxide. In a typical experiment, 0.01 M solution of ammonium molybdate tetra hydrate was prepared. To obtain homogeneous solution a magnetic stirrer was used. After aging for 24 hours a gel was formed and then deposited on steel substrate by Spin coating unit. The sample was then rotated about 3000 rpm and films were annealed at a temperature of 600^0C so as to get the better results needed for supercapacitor application. The films were deposited on glass substrate by using 0.01 M Ammonium Molybdate tetrahydrate and annealed at a temperature of 600°C

$$[NH_4]_6Mo_7O_{24}4H_2O \xrightarrow{\Delta} 7MoO_3 + 6NH_3 + 7H_2O$$

600°C

NH_3 and H_2O were diffused out and MoO_3 was left as final product.

III. Results and Discussion

III. A. Physical Characterization

1. Structural Analysis

The structural changes and identification of phases were studied. Fig 1 shows X-ray diffraction pattern for MoO_3 thin films deposited on glass substrate annealed at a temperature 600^0C by spin-coating technique. Table 1.gives the details of calculated and standard 'd' values and planes of MoO_3 deposited thin films.

The reported pattern exhibits [111] phase (d=3.338), [121] phase (d=2.255), [232] phase (d=1.370) XRD peaks corresponding to MoO_3 monoclinic phase. These peaks were indexed by comparing the experimental data with JCPDS card No. 89-1514.[10]

The obtained values of lattice parameters were a= 6.881A°, b= 5.297 A°, c= 5.56 A° which are in good agreement with the values as compared with JCPDS card No.89-1514, which verifies the structure of as deposited thin films as monoclinic.[21]

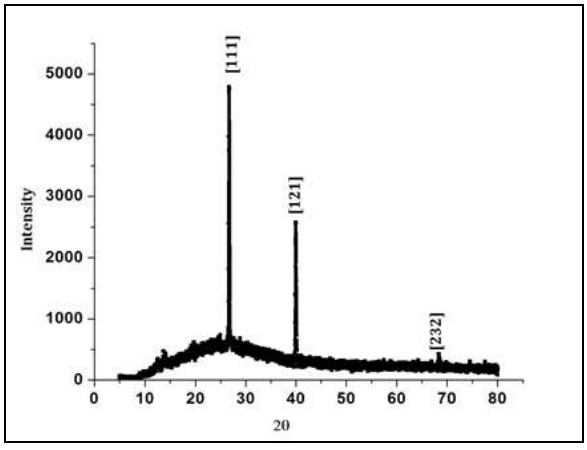

Figure 1. XRD Pattern for Molybdenum Oxide Spin Coated Thin Films

2. Surface Morphological Analysis

The surface morphological study of the MoO_3 thin film has been carried out from SEM image. Figure 2.(a),(b) shows scanning electron microscopic (SEM) photographs of molybdenum oxide thin films at 5000 and 40000 magnifications. It showed that the substrate is well covered with MoO_3 material. The SEM image shows non-uniformly distributed aggregates giving rise to a high surface roughness. The porous and crystalline morphologies clearly found on these annealed MoO_3 films which is favourable for penetration of electrolyte. In

the inset, one can see the particles are well connected yet provide porous structure, which is much required for supercapacitors. The rough texture represents the grain boundary surfaces. The size of grains laid in the range 282.2 - 964.5 nm. In electrochemical supercapacitors, an increased amount of charge can be stored on the highly extended surface area created by large number of pores within a high surface area electrode material. Nano crystalline and porous materials as electrode material exhibit good electrochemical performance because these materials possess both a high surface area and pores which are adapted to the size of ions. [12-14] [21]

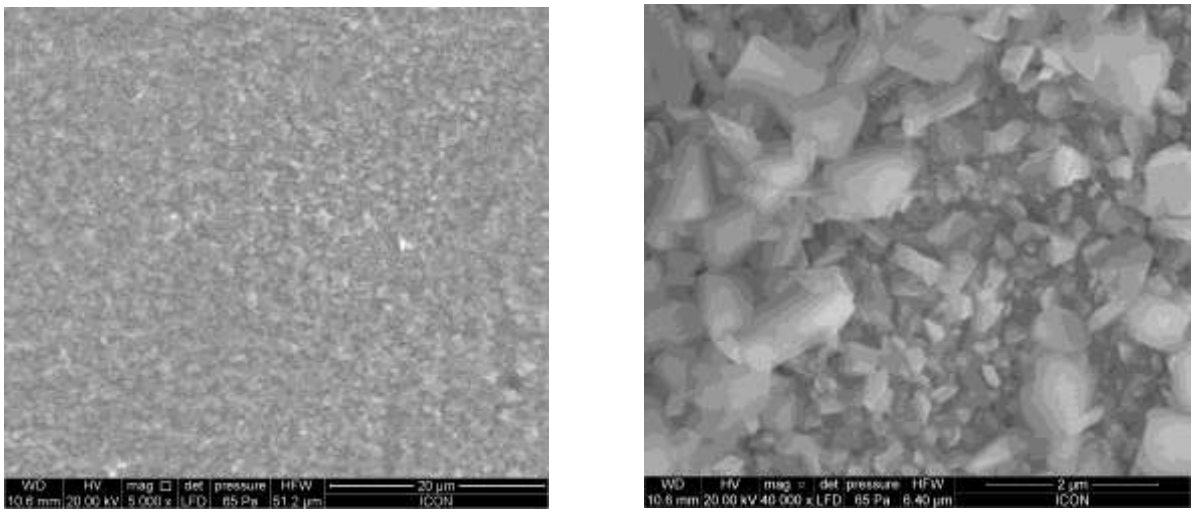

Figure 2.a) SEM images at X5000 magnification Figure 2.b)SEM images at X40000 magnification

3. EDAX:-

The compositional analysis of the as deposited MoO_3 thin film was carried out using EDAX technique by Quanta 200 ESEM instrument. The typical EDAX pattern given in figure 3. shows the formation of MoO_3 on the substrate.[21] Table 2 shows percentage of elements in composition

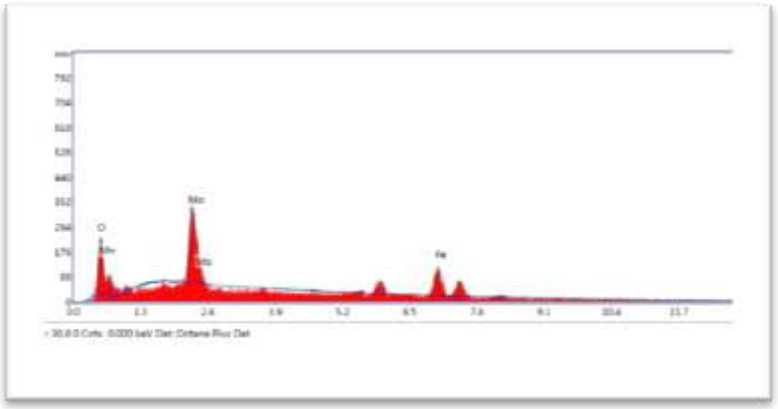

Figure 3. EDAX pattern of MoO_3 thin film.

4. FTIR Spectroscopy:

I.R. spectroscopy was used to obtain additional information on the phases as well as structure transformations of MoO_3 phases.Fig.4 describes the dependence of optical spectra in the range 500 to 4000 $cm^{-1}$for Molybdenum Oxide thin films.[21]The infrared spectrum of as deposited MoO_3 thin film depicts strong absorption bands at 899 and 764 cm^{-1} indicating the stretching mode of Mo=O. The dominant band at 899 $cm^{-1}$is associated with the vibration of Mo=O stretching [11-12] and band at 764 cm^{-1} indicates the weak O-Mo-O stretching. Bouzidi *et al* observed the similar results[13-21].

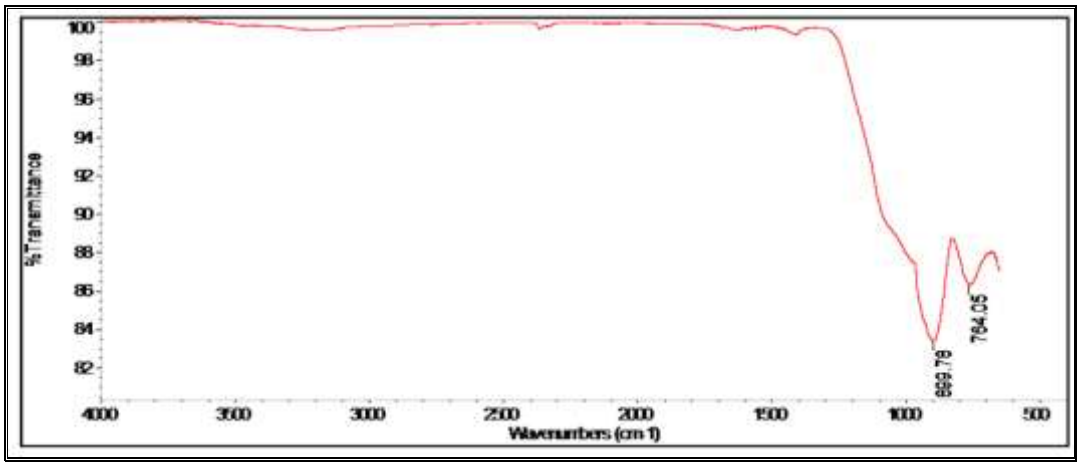

Fig. 4. FT-IR spectrum of MoO_3

III.B. Electrochemical Characterization

1. Cyclic Voltammetry Analysis

The electrochemical behaviour of MoO_3 thin films was analyzed by cyclic voltammetry technique in 0.1 M KOH electrolyte. Figure5(a) shows the C-V of molybdenum oxide thin film electrodes annealed at 600^0C temperature. The capacitive behaviour of the oxide is enhanced by rectangular shape of the plot. [19] The electrode potential scanned between -1.30 mV to 0.65mV in both anodic and cathodic directions for a thin film electrode annealed at 600°C showed the typical pseudocapacitive behaviour The specific capacitance decreased with increase in current density. The decrease in specific capacitance with increase in current density is attributed to decrease in the efficiency of material utilization of the active material at high current densities. Similar inclination were reported in the literature[20].When the scan rate is low, interaction of the active material with the inner surface increases and when the scan rate is high, surface of electrode material that is accessible is less. That shows the increase in CV plot area and decrease in specific capacitance. Full utilization of electrode material is believed to be at lower scan rates. It showed maximum specific capacitance of 581 F/g at a scan rate of 5 mV/Sec.[21] Fig. 5 (b) and (c) shows specific capacitance , interfacial capacitance graph.

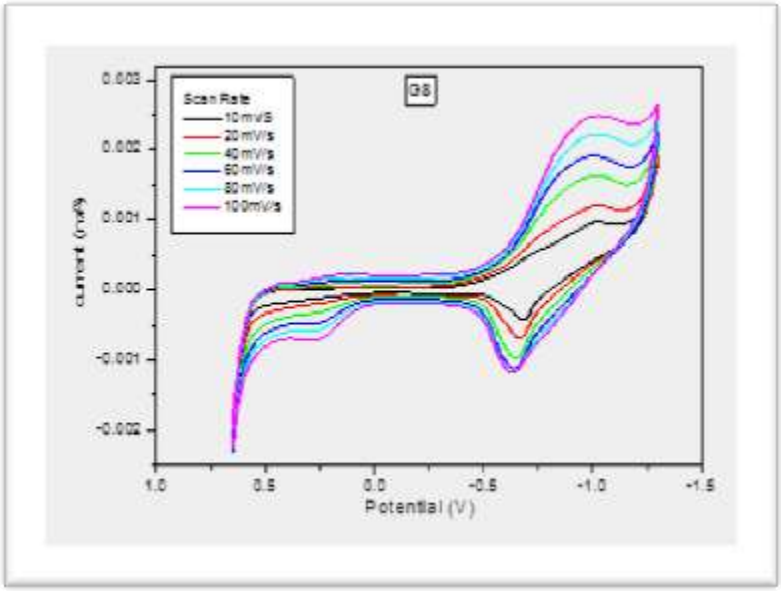

Figure 5. a) Cyclic voltammogram of molybdenum oxide thin films annealed at 600^0C

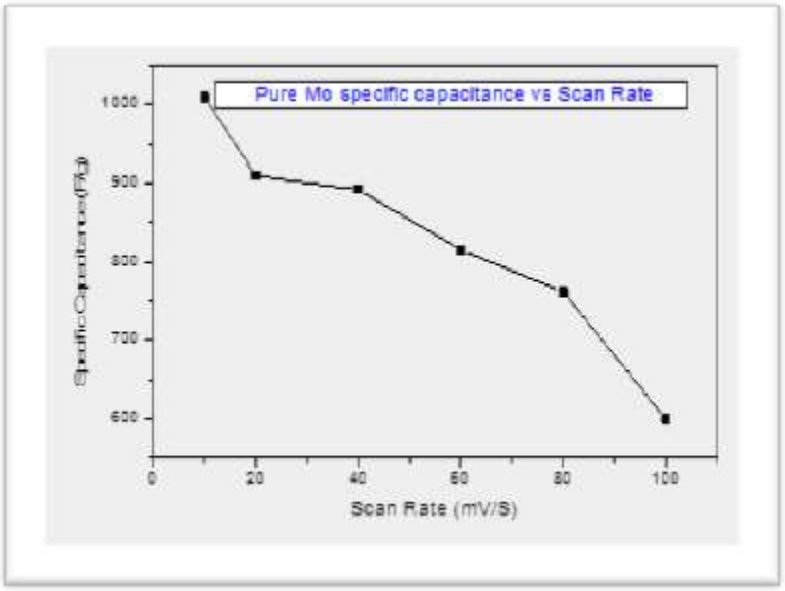

Figure 5. b) graph of specific capacitance vs scan rate

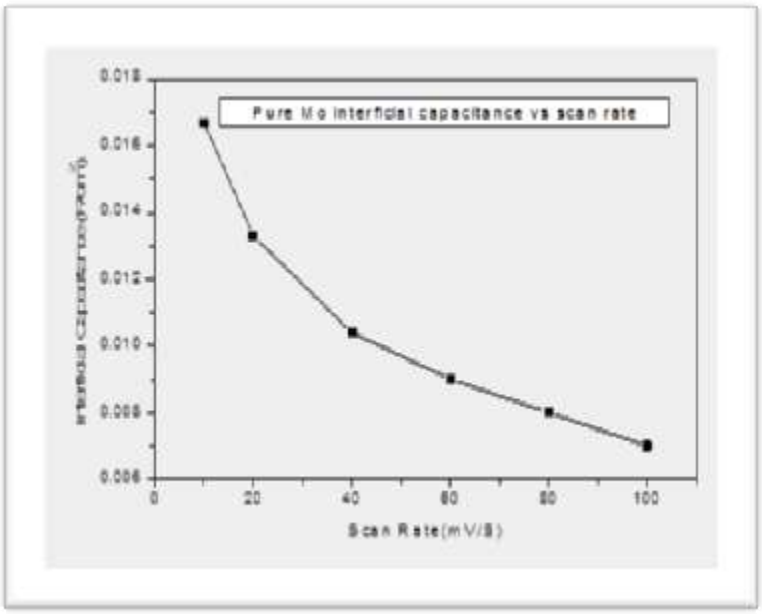

Figure 5. c) Graph of interfacial capactance vs scan rate

2. Galvanostatic Charge –Discharge Analysis

The galvanostatic charge–discharge curves of the MoO_3 thin films were measured by chronopotentiometry technique between -1 V to +1 V in 0.1M KOH electrolyte. The galvanostatic charge/ discharge curves of molybdenum oxide thin film electrode at was studied for the current densities 2 mA/cm^2 are shown in figure 8. A typical capacitive behaviour was indicated by the linear relationship between voltage and time. The interfacial capacitances of the MoO_3 thin film electrode was calculated based on the CV curve. The areal capacitance of the MoO_3 electrode can reach about 16 mF/cm^2 at a current density of 2 mA/cm^2 . Which indicates better rate performance. MoO_3 thin film electrode showed the energy density of 8.0301KWh/kg. and power density of 29.112KW/kg[21]The cyclic stability of MoO_3 electrode in 0.1M. KOH was investigated by continuous sweeping the potential for 1000^{th} cycles between -0.799 to 0.799V at a scan rate of 100 mV/sas shown in figure 10. The current under curve is decreased by 17% up to 1000 cycles. The specific and interfacial capacitance values are decreased in small amount with the number of cycles due to the loss of active material.

The capacitance decreased from 48 F/g to 28.8 F/g for 1000 th cycle as shown in figure 9. The initial high value of the capacitance may be due to the electrode activation process, involving the penetration of the electrolyte into the electrode , resulting in an increase of the electrode–electrolyte interface. The decrease of the capacitance for the following cycles is probably due to the dissolution or loss of the active material into the electrolyte during the long time cycling. No capacitance loss was achieved by the film after 1000 cycles, signifying better cycling stability of the molybdenum oxide thin film electrode.

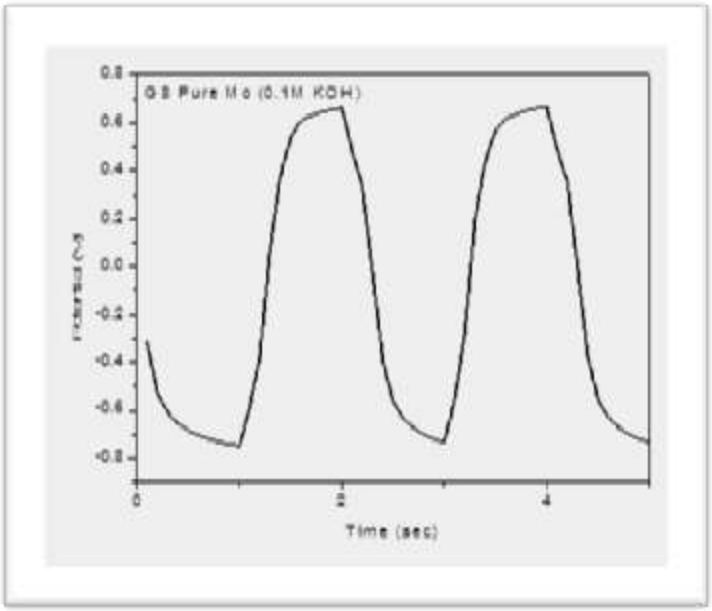

Figure 6. Charge/discharge curves for molybdenum oxide thin films at 2 mA/cm^2 current

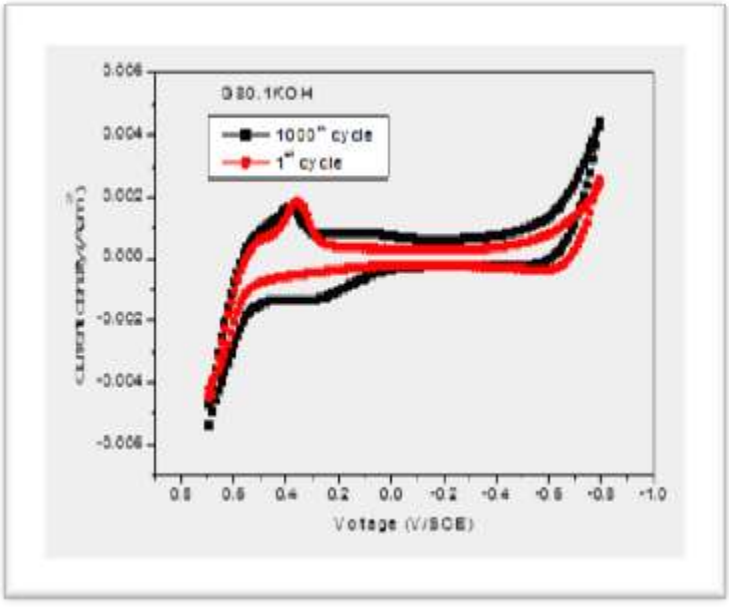

Fig.7.C-V for stability

IV. Conclusions

In conclusion, MoO_3 thin films were deposited on stainless steel substrate by sol-gel spin coating method. The suitable annealing temperature was 600°C.The structural study showed the rutile structure of molybdenum oxide. The SEM images showed the crystal structural morphologies with random and rough surfaces. IR spectroscopy showed the structure transformations of MoO_3 phases. C-V plot showed the

rectangular shape and maximum specific capacitance 1010 F/g at a scan rate of 10 mV/Sec. The interfacial capacitances of the MoO_3 thin film electrode were calculated based on the charge/discharge curves. A typical capacitive behaviour was indicated by the linear relationship between voltage and time The highest areal capacitance of the MoO_3 electrode can reach about16 mF/cm^2 at a current density of 2 mA/cm^2 . The specific and interfacial capacitance values are decreased as scan rate increases and stability is 65.75%

Table 1: Comparison of observed 'd' values, obtained from XRD data with the standard 'd' values, from JCPDS card No-89-1514.

	MoO_3 (films from this work)		**MoO_3 (Card No. 89-1514)**	
Peak No.	**2θ**	**D**	**d**	**[hkl]**
1	26.68	3.33856	3.3605	[111]
2	39.94	2.25540	2.2778	[121]
3	68.40	1.37040	1.39	[232]

Table 2: Elemental composition

Element	**Atomic %**
O	**76.43**
Ru	**0.00**
Mo	**23.57**

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