# Electrochemical synthesis and investigation of nano $MnO_2$ electrode material for supercapacitor application

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## Abstract

$MnO_2$ metal oxide electrode material is synthesized by simple electrodeposition method on stainless steel substrate. The crystal structure and surface morphological characterizations of the obtained electrode are carried out by using X-ray diffraction (XRD) technique and Field Emission-Scanning Electron Microscopy (FE-SEM) respectively. The FE-SEM micrographs show highly porous well developed interconnected uniform nanosphere like morphology. The electrochemical properties of $MnO_2$ electrode like Cyclic Voltammetry (CV), Galvanostatic Charge-Discharge (GCD) and Electrochemical Impedance Spectroscopy (EIS) etc are studied in a 0.5 M $Na_2SO_4$ solution as electrolyte. The maximum specific capacitance is 543 F/g at scan rate 5 $mVs^{-1}$ obtained from cyclic voltammetry (CV). The electrochemical stability of $MnO_2$ electrode is investigated using cyclic voltammetry for 1000 cycles. The $MnO_2$ electrode exhibits good cycling stability for 1000 cycles at scan rate100 $mVs^{-1}$. The values of energy density and power density of $MnO_2$ electrode material obtained from Galvanostatic charge-discharge studies. From all the electrochemical properties of $MnO_2$ electrode, it indicates that it will be promising electrode material for supercapacitor application. 

**Keywords:** $MnO_2$, electrodeposition, cyclic voltammetry, galvonostatic charge–discharge studies, Electrochemical Impedance Spectroscopy (EIS).

## Introduction

Electrochemical energy storage and conversion devices are found to be more interesting topics for the current and future energy needs, as the need of energy is growing day to day and there is a continuous depletion of fossil fuels [**1**]. The major types of electrochemical energy storage systems are batteries, capacitors, fuel cells and supercapacitors. As compared to conventional energy storage systems supercapacitor have remarkable properties such as fast charging time (1-10 s), long cycle life (1 million or 30,000 hrs) and wide range of operating temperature (-40º to 70ºC) [**2**]. Depending on the storage mechanism supercapacitors are classified into two major types 1) Electric Double Layer Capacitors (EDLC) in which energy is stored through physical ion adsorption. The charge transfer is non-faradic i.e. without redox reaction taking place within or across the electrode-electrolyte interface. EDLC materials exhibit rapid cycling, longer cycle life and higher columbic efficiency than batteries. However, carbonaceous compound suffers from major drawback of higher resistivity due to contact resistance between carbon particles give rise to high internal resistance [**3**]. 2) Pseudocapacitors in which energy is stored through the fast reaction at the interface between electrolyte and electroactive materials. Charge transfer is faradic in nature. Pseudocapacitors have higher energy density than EDLC but they suffer lower cycleability. Pseudocapacitive material includes transition metal oxides such as $RuO_2$, MnOx, CoOx, NiO, $Fe_2O_3$ and polymers such as Polyaniline, Polypyrol etc. Among many transition metal oxides there is increasing interest in $MnO_2$ based electrode material for energy storage applications because of its cost effectiveness, environment friendly, abundant in nature and pseudocapacitive characteristics [**4**]. Recent years, $MnO_x$ in various forms has been widely studied as electrode material in various energy storage systems, such as alkaline batteries and supercapacitors. In all cases; $MnO_x$ has been proven to be a reliable electrode material with high performance. Various researchers have reported specific capacitance of

$MnO_2$ electrode and it's composite with other electrode material synthesized by various deposition techniques. Jadhav et.al reported maximum specific capacitance of $MnO_2$ electrode 393 F/g which is synthesized by electrodeposition technique [**5**]. Zhu et.al reported maximum specific capacitance of $MnO_2$ electrode material 244 F/g synthesized by hydrothermal method [**6**]. Wang et.al reported maximum specific capacitance of $MnO_2$/carbon composite electrode 412 F/g [**7**]. Among various deposition techniques electrodeposition is found to be most advantageous technique to synthesize $MnO_2$ electrode, in this technique the final product will result in a homogeneous, porous thin film on a conducting substrates i.e. stainless steel, titanium foil etc without using any type of binder [**8**].

In this work, nano $MnO_2$ film grown on stainless steel (SS) substrate by cathodic electrodeposition method. The electrodeposition was carried out using CH Instruments electrochemical workstation (66 $^0$C). High specific area, high electrochemical stability and good electrolyte accessibility to intra-pore regions are usually the qualities of high performance supercapacitor electrode. In this work values of specific capacitance are comparable or more than reported value for other nanostructure of $MnO_2$ electrode. The obtained nano $MnO_2$ shows excellent capacitive performance in terms of specific capacitance, good cycleability, energy density and power density which is promising for supercapacitor application.

## Experimental

### *Materials*

The nano $MnO_2$ electrode were synthesized by potentiostatic electrodeposition method on SS substrate. For that purpose, 0.2 M Manganese chloride ($MnCl_2.4H_2O$) of purity 99.9% is used as precursor. Stainless steel (SS) substrate of 304 grade is used as conducting substrate for deposition of active material.

### *Synthesis of manganese oxide ($MnO_2$)*

Manganese chloride ($MnCl_2.4H_2O$) 0.2 M of purity 99.9% is used as precursor in 100 ml double distilled water.Before deposition ss substrates were polished with emery paper, washed with detergent, kept in ultrasonic bath for 30 minutes after that rinsed in double distilled water and dried in air. Electrodeposition were carried out using CHI electrochemical workstation (CHI 660 C)

### *Material synthesis*

Potentiostatic electrodeposition of nano $MnO_2$ was carried out using CH Instruments electrochemical workstation (660C) in three electrode electrochemical cell. The cell consists of three electrodes such as SS (304 grade) as working electrode, graphite as counter electrode and standard calomel electrode (SCE) as reference electrode. The electrodeposited manganese hydroxide [$Mn(OH)_2$] film was annealed at 350$^o$ C for 3 hrs. After annealing well deposited reddish brown colored manganese oxide films were obtained which were used for structural, morphological and supercapacitive characterization.

### *Characterization*

To determine the structural properties of electrodeposited nano $MnO_2$ electrode X-ray diffraction was carried out at room temperature using RIGAKU MINIFLEX (CuKα radiation) between 20°-80°.Field Emission - Scanning Electron Microscopy (FE-SEM JEOL-JSM 6360) was used to study the surface morphology of nano $MnO_2$ electrode. The supercapacititve properties of nano $MnO_2$ electrode such as Cyclic Voltammetry (CV), stability and Galvanostatic charge –discharge (GCD) studies were performed using CH Instruments Electrochemical workstation (660C) in aqueous solution of 0.5M $Na_2SO_4$ as electrolyte. Electrochemical Impedance spectroscopy of the $MnO_2$ electrode is studied using CHI electrochemical workstation at open circuit potential.

## Results and discussion

### *Structural and morphological analysis*

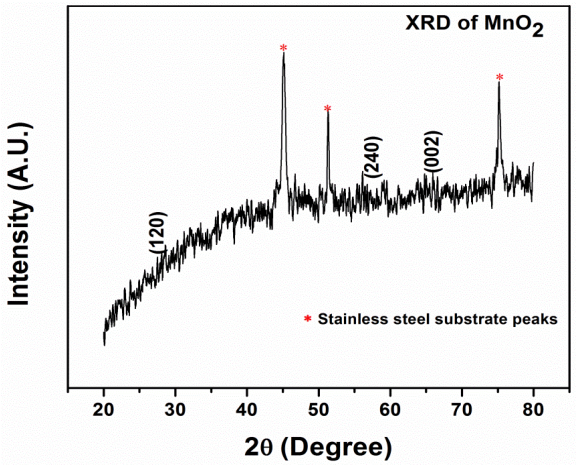


**Fig. 1.** X-ray diffraction pattern of $MnO_2$ thin film.

**Fig. 1** shows XRD pattern of electrodeposited $MnO_2$ thin film. The sample is poorly crystallized. All diffraction peaks would be indexed as orthorhombic phase of $MnO_2$ with its characteristic peaks are at 27.50˚ (120), 56.76˚ (240), 65.08˚ (002) matches with ICSD no.024034.The peaks indicated with star are the standard SS substrate peaks. FE-SEM micrograph in the **Fig. 2** shows the well - developed interconnected porous nano sphere like morphology.

 

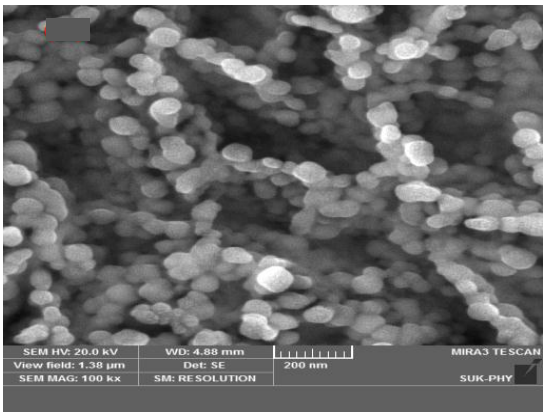


**Fig. 2.** SEM micrograph of $MnO_2$ thin film.

The porous morphology of nano MnO2 will provide more active sites for faradic redox reaction, effective contact on the surface of the electrode, accelerate ion and electron transfer in the interface between the electrolyte and nano MnO2 electrode resulting in the excellent supercapacitive performance. This porous morphology will enhance the supercapacitive performance of MnO2 electrode.

***Supercapacitive properties of $MnO_2$***

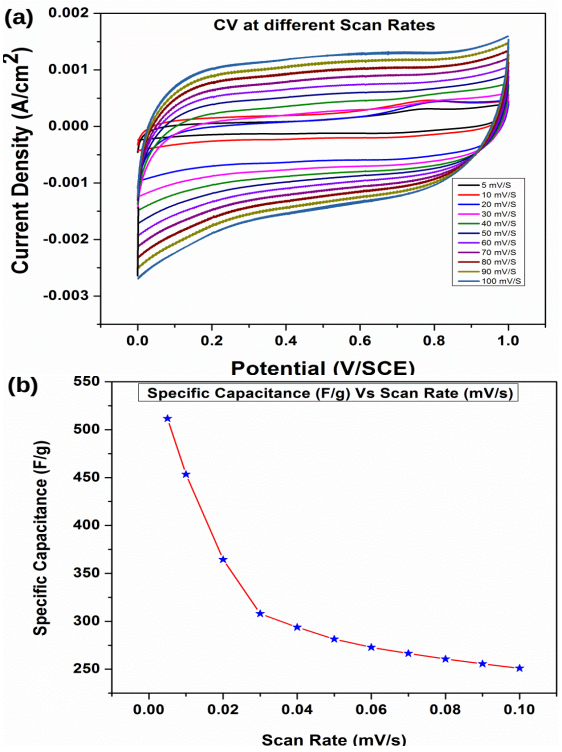


**Fig. 3.** (a) Cyclic Voltammetry curve of $MnO_2$ thin film at different scan rates. (b) Specific Capacitance (F/g) Vs Scan Rate (mV/s-1) for MnO2 thin film.

**Fig. 3(a)** Shows Cyclic Voltammetry studies at different scan rates ranging from 5mVs$^{-1}$ to 100 mVs$^{-1}$ of $MnO_2$ electrode material. CV was carried out in 0.5 M $Na_2SO_4$ as electrolyte within the potential range 0 to 1 V/SCE. CV curve shows rectangular shape indicating the ideal pseudocapacitive behavior. Pseudocapacitive nature arises due to redox reactions between nano $MnO_2$ electrode and electrolyte interface, i.e. the possible reaction mechanism of the insertion and de-insertion of $Na^+$ from the electrolyte into the $MnO_2$ matrix as shown below [**8**].

$$MnO_2 + Na^+ + e^- \longleftrightarrow MnOONa^+$$

The specific capacitance was calculated by using eq$^n$. (1) as given below which 543 F/g at scan rate 5mVs-$^1$ [**9**].

$$\text{Specific Capacitance} = \frac{C}{W} \quad (1)$$

where, C-capacitance (Farad), W-mass of active material (gram). **Fig. 3(b)** shows effect of scan rate on the specific capacitance of $MnO_2$ electrode. At lower scan rates, diffusion of $Na^+$ from the electrolyte can gain access to the almost all interior nanosphere matrix, leading to complete insertion reaction. At higher scan rates, $Na^+$ ions only reached the outer surface layer of the electrode and cannot utilize the interior pores of nanosphere. So that, the effective interaction between ions and the electrode is significantly reduced this reduces the specific capacitance of active material [**5**].

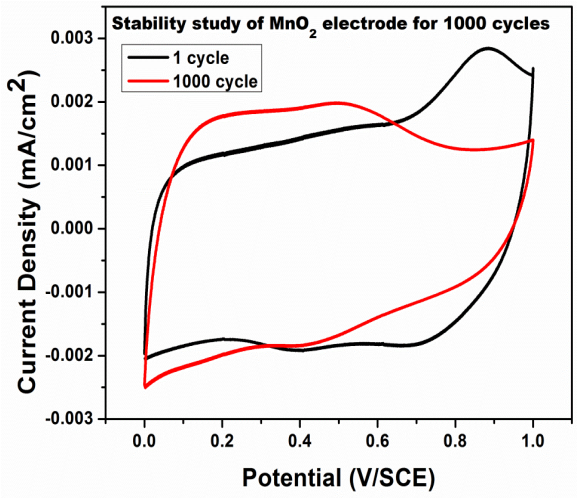


**Fig. 4.** Stability of $MnO_2$ thin film over 1000 cycles at scan rate 100 mVs$^{-1}$.

**Fig. 4** shows the stability of nano $MnO_2$ electrode material over 1000 cycles at scan rate 100 mVs$^{-1}$. Stability of nano $MnO_2$ electrode was tested using cyclic voltammetry technique and specific capacitance over 1000 cycles was calculated. The specific capacitance goes on decreasing and remains constant after 1000 cycles. Only 20% loss of active material were observed after 1000 cycles, this capacitive loss may be due to the dissolution and/or detachment of active material during early charging/discharging cycles in the electrolyte. The stability study shows 80% retentitvity over 1000

 

cycles. The stability studies of nano $MnO_2$ electrode demonstrate that the nano $MnO_2$ electrode was a good candidate for supercapacitor application.

**Fig. 5** shows Galvanoststic charge-discharge (GCD) curve of nano MnO2 electrode performed using chronopotentiometry technique at different current densities from 0.5 mA/g to 0. 5 A/g in 0.5 M Na2SO4 electrolyte. Discharge curve show two regions 1) Straight line shows IR drop arises due internal resistance of solution 2) non-linear variation of potential with time shows the pseudocapacitive nature arises due to redox reaction between nano MnO2 electrode and electrolyte interface **[10]**. The small IR drop indicates low internal resistance which important feature of the nano MnO2 electrode material.

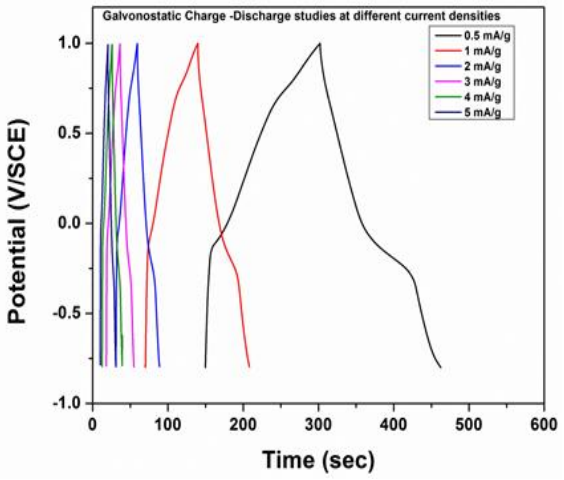


**Fig. 5.** Galvanostatic Charge-Discharge Studies at different current densities.

The values of Specific Capacitance (SC), Specific Energy(SE) and Specific power(SP) at current density 0.5mA/g were calculated from following formulae (2,3,4) respectively.

$$\mathbf{SC} = \frac{\boldsymbol{Id \times Td}}{\boldsymbol{\Delta V \times W}} \quad (2)$$

$$\mathbf{SE} = \frac{\boldsymbol{SC \times \Delta V^2}}{\mathbf{2}} \quad (3)$$

$$\mathbf{SP} = \frac{\boldsymbol{SE}}{\boldsymbol{Td}} \quad (4)$$

where, $I_d$- Discharge current, $T_d$- Discharge time, ΔV- Potential window, $W$ -mass of active material. The nano $MnO_2$ electrode material shows maximum specific capacitance =411 F/g, specific Energy =200 Wh/kg and specific power=4.49 kW/kg at current density 0.5mA/g.

The values of high specific capacitance, specific energy and power arrive due to porous nature of $MnO_2$ electrode EIS measurement is an important tool to examine the fundamental behavior of the electrode material for supercapacitor application. **Fig. 6** shows original and simulated Nyquist plot of nano $MnO_2$ electrode.EIS measurement was carried out in 0.5 M $Na_2SO_4$ as electrolyte within the frequency range 10 Hz-1MHz at open circuit potential of $MnO_2$ electrode.

The graph shows depressed arc at high frequencies indicating the process taking place at the electrode /electrolyte interface The electron transfer taking place in this region during the charge discharge process is represented by an interfacial charge transfer resistance (Rct). The observed values of series resistance R0=1.53 Ω and charge transfer resistance Rct= 2.5 Ω. The simulated values of series resistance (R0) and charge transfer resistance (Rct) are well matches with observed values. After the semicircle, the nyquist spectrum shows a straight line in low frequency region related to Warburg resistance or diffusion coefficient. Nano MnO2 electrode exhibit high specific capacitance, it may be due to the fact that the thinner film shows considerable lower contact resistance between film matrix and current collector.

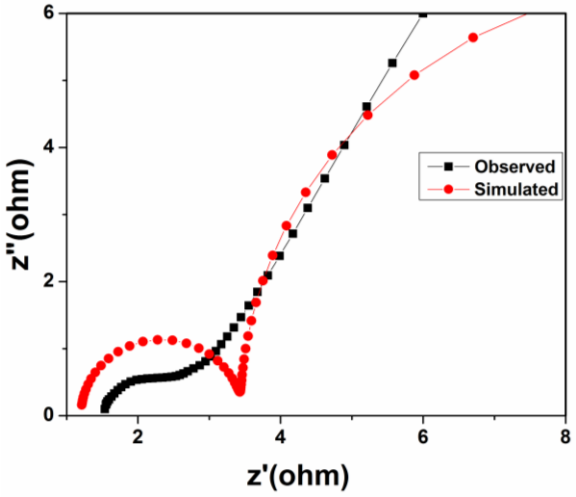


**Fig. 6.** Nyquist Plot of $MnO_2$ thin film at Open Circuit Potential.

## Conclusion

In conclusion nano $MnO_2$ electrode was successfully synthesized by cathodic electrodeposition method. XRD spectra show poorly crystalline nature of nano $MnO_2$ electrode material. FE-SEM micrograph show well developed interconnected porous nanosphere like structure. Cyclic voltammetric studies show maximum specific capacitance which is 543 F/g at scan rate 5 $mVs^{-1}$. The values of specific capacitance, specific energy and specific power from galvanoststic charge discharge studies are SC=411 F/g, SE=200.402 Wh/kg and SP=4.49 kW/kg at current density 0.5 mA/g. Stability studies shows 80% retentitvity of nano $MnO_2$ electrode after 1000 cycle at scan rate 100 $mVs^{-1}$.EIS studies give values of series resistance and charge transfer resistance. These result shows that the electrochemically deposited nano $MnO_2$ electrode is a good material for supercapacitor application.

 

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**Author's contributions**

Synthesis and characterization were done by S.L.Kadam, S.M. Mane ; Data collection and analysis:S.L.Kadam and S.B.Kulkarni; and the research paper was written by S.L.Kadam and S.B.kulkarni.

**References**

1. Goodenough, J. *Energy Storage Materials*. **2015**, *1*, 158.
2. Xiong, G.;Kundu, A.;Fisher, T.; Thermal effects in supercapacitors; *Springer International Publishing*, **2015**.
3. Ho, M. *NANO: Brief Reports and Reviews, World Scientific Publishing Company*. **2014**, *9*, 6.
4. Zhang, S.; Chen, G.; *Energy Materials*. **2008**, *3*, 3.
5. Jadhav, P.; Suryawanshi, M.; Dalavi, D.; Patil, D.; Jo, E.; Kolekar, S.; Wali, A.; Karanjkar, M.; Kim, J.; Patil, P. *Electrochim. Acta*. **2015,***176*,523.
6. Zhu, T.; Zheng, S.; Chen Y., Luo. *J. Mater.Sci*, **2014**, *49*, 6118.
7. Wang, X.; Fan, X.; Li, G.; Li, M.; Xiao, X.; Yu, A., Chen, Z. *CARBON*. **2015**, *93*, 258.
8. Toupin, M.; Brousse, T.; Belanger, D. *Chem. Mater*. **2004,** *16*, 3184.
9. Padwal, P.; Kadam, S.; Mane, S.; Kulkarni, S . *J. Chin. Adv. Mater. Soc.***2015**, *4*,13.
10. Gund, G.; Dubal, D.; Chodankar, N.; Cho, J.; Romero,P.; Park, C; Lokhande, C. *Scientific Reports.* **2015**, *5*, 12454.

 