

# Potentiodynamically deposited nanostructured manganese dioxide as electrode material for electrochemical redox supercapacitors

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## Abstract

Amorphous nanostructured hydrated electrochemical manganese dioxide (EMD) was potentiodynamically deposited on stainless steel (SS). Electrolyte medium used for the deposition was 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.5 M MnSO<sub>4</sub>·5H<sub>2</sub>O. The scan rate of deposition was varied between 50 and 200 mV s<sup>-1</sup>. The EMD deposited SS electrodes were characterized by cyclic voltammetry (CV) in 0.1 M Na<sub>2</sub>SO<sub>4</sub> for electrochemical redox supercapacitors. The specific capacitance (SC) of EMD increases by increasing the scan rate of deposition. For EMD deposited at 200 mV s<sup>-1</sup>, a maximum SC of 482 F g<sup>-1</sup> was obtained from cyclic voltammetry at a scan rate of 10 mV s<sup>-1</sup>. For the same electrode, a SC value of 275 F g<sup>-1</sup> was obtained even at a high scan rate of 150 mV s<sup>-1</sup>, indicating high power characteristics of the material. The SC was found to increase with the increase in thickness of EMD. Long cycle-life and stability of EMD were also demonstrated.

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**Keywords:** EMD; Potentiodynamic deposition; Supercapacitors

## 1. Introduction

Electrochemical supercapacitors are a kind of charge-storage devices, which possess high power density, excellent reversibility and have long cycle-life compared to batteries [1,2]. Because of these properties, supercapacitors have attracted increased interest during the last few years with projected applications, which include load leveling for batteries in hybrid vehicles, burst power generation and memory back-up devices. For example, in hybrid vehicles, battery supplies energy during the normal functioning of the device and a capacitor, which is in series with the battery, supplies energy during acceleration, hill climbing, etc. for short durations. Two basic types of electrochemical capacitors can be realized using different charge-storage mechanisms: [1,2] (i) electrical double-layer capacitors (EDLCs), which utilize the capacitance arising from charge separation at an electrode/electrolyte interface and (ii) supercapacitors or ultracapacitors, which utilize the charge-transfer pseudo capacitance arising from reversible Faradaic reactions occurring at the electrode surface.

High surface area carbon-based systems (surface area greater than 2000 m<sup>2</sup> g<sup>-1</sup>) come under the category of EDLCs, because the non-Faradaic capacitance of the electrical double-layer is directly proportional to the surface area accessible by the electrolyte. For activated carbon, a specific capacitance (SC) value of more than 200 F g<sup>-1</sup> has been reported in aqueous electrolyte media [3,4]. On the other hand, the electrodes of electrochemical redox supercapacitors consist of electroactive materials with several oxidation states. These types of capacitors are under extensive investigation in the recent times because of high capacitive and high energy characteristics. Since the pseudo capacitance comes from the reversible redox transitions of the electroactive materials, transition metal oxides [5–14] and conducting polymers [15,16] with various oxidation states are considered to be promising materials for the applications of redox supercapacitors. Recently, hydrous RuO<sub>2</sub> has been extensively studied [5,6] as an active electrode material for supercapacitors as it possesses capacitance as high as 720 F g<sup>-1</sup> in aqueous acidic electrolytes. Although RuO<sub>2</sub> gives high specific capacitance, it has disadvantages of high cost and toxic nature. In view of finding an inexpensive alternate to RuO<sub>2</sub>, recently hydrous manganese oxide prepared by both chemical and electrochemical routes was found to possess capacitive characteristics with acceptable

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values of specific capacitance [7–11]. A SC of  $130 \text{ F g}^{-1}$  was reported [11] at a scan rate of  $5 \text{ mV s}^{-1}$ , for  $\text{MnO}_2$  synthesized by sol–gel method. However, pure  $\text{MnO}_2 \cdot n\text{H}_2\text{O}$  prepared by chemical co-precipitation method exhibits poor capacitive characteristics due to the high resistance of bulk  $\text{MnO}_2 \cdot n\text{H}_2\text{O}$ . Because of these disadvantages of chemical synthesis, electrochemical anodic deposition of amorphous non-stoichiometric manganese oxide ( $\text{MnO}_x \cdot n\text{H}_2\text{O}$ ) with acceptable specific capacitance, high specific power, excellent stability, is under extensive investigation in the last couple of years. Chang and Tsai [7] have reported hydrous manganese oxide synthesized by potentiostatic method at anodic potentials of 0.5–0.95 V versus SCE. A SC value of  $240 \text{ F g}^{-1}$  was reported [7] at a scan rate of  $5 \text{ mV s}^{-1}$ , for manganese oxide deposited at 0.5 V versus SCE.

In the present study, we report the application of electrochemical manganese dioxide (EMD) as an electrode material for redox supercapacitors. EMD has been potentiodynamically deposited onto a stainless steel (SS) substrate from an electrolyte solution consisting of 0.5 M  $\text{H}_2\text{SO}_4$  + 0.5 M  $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ . The scan rate of deposition was varied between 50 and  $200 \text{ mV s}^{-1}$ . Nanowhiskers of EMD have been synthesized by using high scan rate of  $200 \text{ mV s}^{-1}$ . SC values as high as  $482 \text{ F g}^{-1}$  at a scan rate  $10 \text{ mV s}^{-1}$  and  $275 \text{ F g}^{-1}$  at a high scan rate of  $150 \text{ mV s}^{-1}$  were obtained for EMD deposited at a high scan rate of  $200 \text{ mV s}^{-1}$ . These values of capacitance are much higher than the values reported in the literature for manganese oxide material synthesized by other methods.

## 2. Experimental

$\text{H}_2\text{SO}_4$ ,  $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4$  were purchased from Aldrich. All the solutions were made using double-distilled water. The EMD has been deposited onto a commercially pure stainless steel (SS) (grade 304) foil of 0.2 mm thickness by potentiodynamic deposition. Before deposition, a  $1 \text{ cm} \times 10 \text{ cm}$  SS foil was polished with emery paper to a rough finish, washed free of emery particles and then air dried. The area of SS used for potentiodynamic deposition was  $1 \text{ cm}^2$ . An electrolyte solution of 0.5 M  $\text{H}_2\text{SO}_4$  + 0.5 M  $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$  was used for the potentiodynamic deposition of EMD. The electrochemical cell used in this study is a four electrode cell having provisions for working electrode, reference electrode and two auxiliary electrodes. The working electrode (SS or EMD/SS) is placed symmetrically between two Pt auxiliary electrodes. A saturated calomel electrode (SCE) was used as reference electrode and all potentials in the present study are reported against the SCE. The deposition of EMD was carried out potentiodynamically between the potential limits of 0.5 and 1.5 V at various scan rates. Subsequent to deposition, the electrodes are washed with distilled water and dipped in a beaker containing distilled water which was stirred by using a magnetic paddle. Subsequent to cleaning, these electrodes were dried in a conven-

tional oven at room temperature for about 12 h. The mass of EMD was measured by Sartorius micro-balance model BP211D. Subsequently, the electrodes were dipped in 0.1 M  $\text{Na}_2\text{SO}_4$  solution before characterizing them in the same solution. The X-ray diffraction patterns of the samples were observed by Rigaku X-ray diffractometer model R1NT2100 using a Cu  $\text{K}\alpha$  source. The microstructure of the samples was recorded by JEOL scanning electron microscope model JSM-6340F and cyclic voltammetry (CV) was recorded using a Hokuto Denko model HSV-100.

## 3. Results and discussion

### 3.1. Deposition and nanostructure of EMD

Electrochemical deposition techniques are known to have better control over the properties of the deposited material than the chemical synthesis. Electrochemical manganese dioxide (EMD) is expected to have better electrochemical activity for most applications than chemical manganese dioxide (CMD). Potentiodynamic deposition of EMD on Ti, platinumized Ti or Pb substrates was studied by Rodrigues et al. [17]. They have also studied the kinetics and mechanism of electrodeposition of manganese oxide. In the present study, the same method of deposition was followed to deposit EMD onto an inexpensive SS substrate at various scan rates between 50 and  $200 \text{ mV s}^{-1}$ .

The XRD patterns of the EMD deposited SS samples at various scan rates (not shown) have resembled those reported in the literature [17] indicating that EMD deposited at various scan rates is highly amorphous. Fig. 1 shows the SEM images of EMD prepared at three different scan rates. It is seen from Fig. 1a that the morphology of EMD prepared at a low scan rate of  $50 \text{ mV s}^{-1}$  consists of large spherical grains. As the scan rate of deposition increases to  $100 \text{ mV s}^{-1}$  (Fig. 1b), the morphology completely changed to highly amorphous (grassy kind of structure) and highly porous structure. The porosity still increases by increasing the scan rate to  $200 \text{ mV s}^{-1}$  (Fig. 1c). Under higher magnification of 200 000 times (Fig. 1d), the structure is composed of nanowhiskers or small nanowires of EMD with diameter in the range of 7–8 nm and length in the order of 50–60 nm. The morphology of this deposit clearly shows highly nanostructured and three-dimensional network. This type of highly amorphous and highly porous structures are expected to produce high SC values when used for capacitor applications.

### 3.2. Capacitive behavior of EMD/SS electrodes

Cyclic voltammetry is considered to be an ideal tool to indicate the capacitive behavior of any material. A large magnitude of current and a rectangular type of voltammogram, symmetric in anodic and cathodic directions, are the indications of ideal capacitive nature of any material. Fig. 2

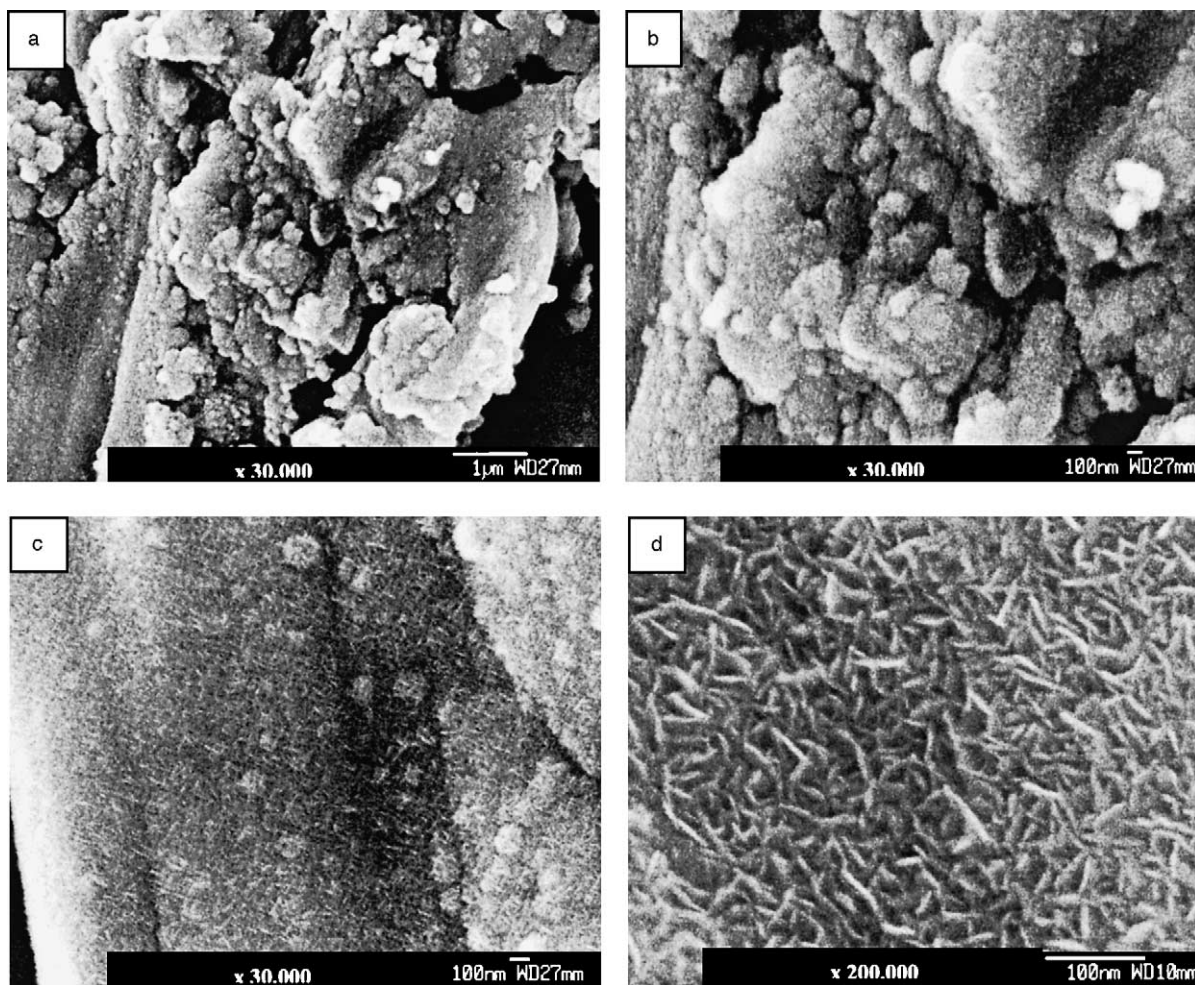


Fig. 1. SEM images (at 30,000 times magnification) of EMD prepared by potentiodynamic method at a scan rate of (a) 50 (b) 100 (c) 200 mV s<sup>-1</sup>. The SEM image of EMD prepared at 200 mV s<sup>-1</sup> is shown in (d) at a higher magnification of 200,000 times.

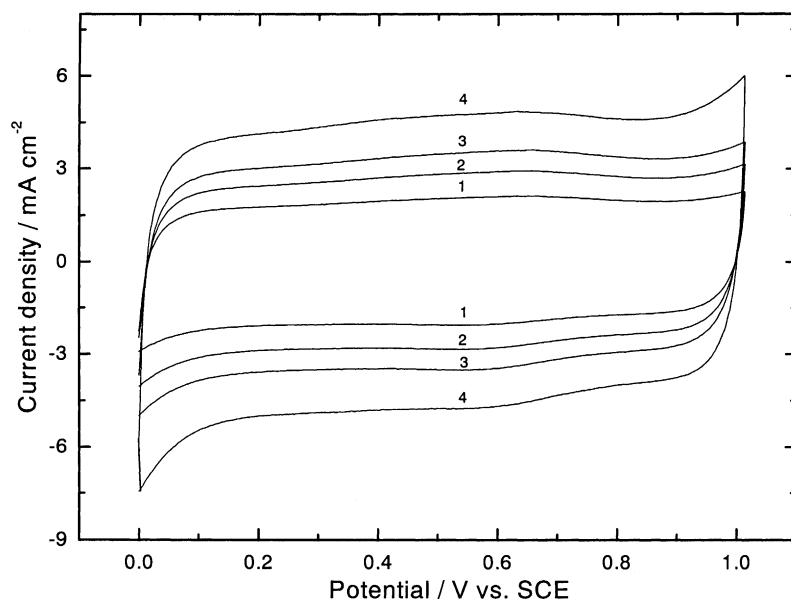


Fig. 2. Cyclic voltammograms of EMD/SS electrodes in 0.1 M Na<sub>2</sub>SO<sub>4</sub> electrolyte at a scan rate of 100 mV s<sup>-1</sup>. EMD was prepared by potentiodynamic method at a scan rate of (1) 50 mV s<sup>-1</sup> (2) 100 mV s<sup>-1</sup> (3) 150 mV s<sup>-1</sup> and (4) 200 mV s<sup>-1</sup>. Mass of EMD = 0.2 mg cm<sup>-2</sup>.

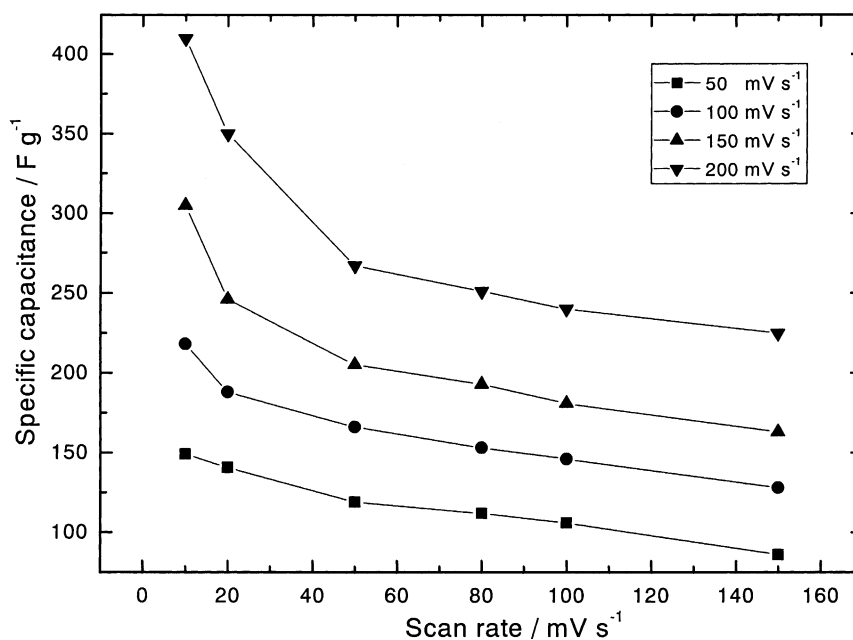


Fig. 3. Specific capacitance of EMD/SS electrodes calculated from CV against the scan rate. EMD was prepared by potentiodynamic method at various scan rates (indicated in the inset) to a mass of  $0.2 \text{ mg cm}^{-2}$ .

shows the typical CV (at  $100 \text{ mV s}^{-1}$  scan rate) of EMD/SS electrodes prepared potentiodynamically at four different scan rates. The thickness (mass per unit area) of EMD was  $0.2 \text{ mg cm}^{-2}$ . It is clear from Fig. 2 that there are no redox peaks in the range between 0 and 1 V. All the curves were rectangular in shape and exhibit mirror-image characteristics which indicate capacitive behavior. A large magnitude of current in CV could not be attributed to double-layer processes. Similar CVs were observed at all the other scan rates.

These results indicate ideal capacitive behavior of EMD. The values of specific capacitance calculated from the CVs ( $100 \text{ mV s}^{-1}$  scan rate) are 106, 145.6, 180.7,  $240.9 \text{ F g}^{-1}$  with EMD deposited at a scan rate of 50, 100, 150 and  $200 \text{ mV s}^{-1}$ , respectively. Fig. 3 shows the variation of SC with the scan rate of CV for EMD deposited at various scan rates, to a thickness value of  $0.2 \text{ mg cm}^{-2}$ . The CVs are rectangular and symmetrical even at a high scan rate of  $150 \text{ mV s}^{-1}$  (not shown), indicating excellent reactivity, high

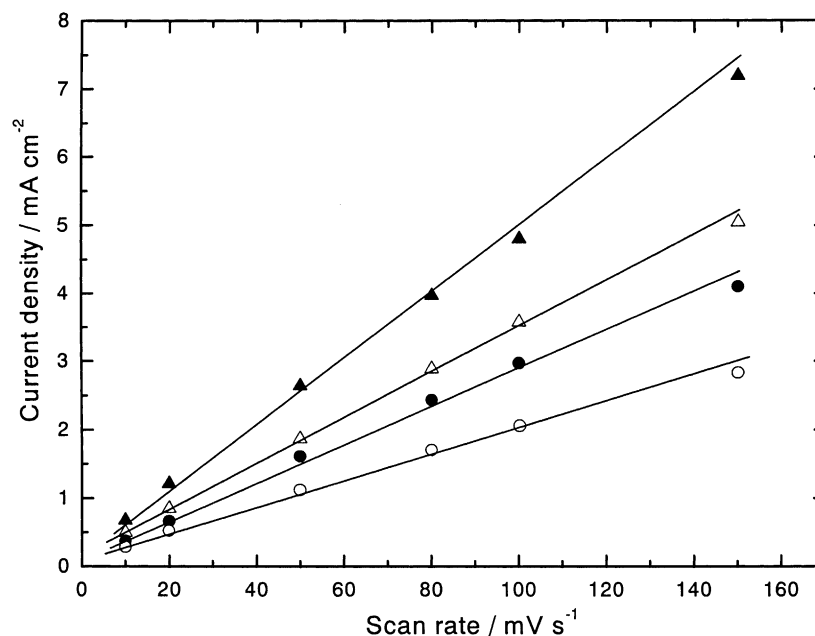


Fig. 4. Cyclic voltammetric current density versus applied scan rate for EMD/SS electrodes. EMD was prepared by potentiodynamic method at a scan rate of (○)  $50 \text{ mV s}^{-1}$  (●)  $100 \text{ mV s}^{-1}$  (△)  $150 \text{ mV s}^{-1}$  and (▲)  $200 \text{ mV s}^{-1}$ . Mass of EMD =  $0.2 \text{ mg cm}^{-2}$ .

Table 1

Comparison of SC values obtained in the present study with the values reported in the literature for manganese oxide prepared by other methods

Material	Reference number	Scan rate of CV ( $\text{mV s}^{-1}$ )	SC ( $\text{F g}^{-1}$ )
Hydrous manganese oxide prepared by potentiostatic (at 0.5 V vs. SCE) method	[7]	5	240
Amorphous manganese oxide prepared by galvanostatic method at a current density of $3.7 \text{ mA cm}^{-2}$	[8]	20	220
$\text{MnO}_2$ synthesized by sol-gel method	[11]	5	130
Nanowhiskers of EMD potentiodynamically deposited on SS at a scan rate of $200 \text{ mV s}^{-1}$	Present studies	20	432
		150	275

reversibility and high specific power of EMD. For an ideal capacitor, the relationship between the capacitive current ( $i$ ) and the cyclic voltammetric scan rate ( $\nu$ ) can be expressed as:

$$i = C \times \nu \quad (1)$$

where  $C$  is the capacitance. Hence, from Eq. (1), voltammetric currents should vary linearly with the scan rate. Fig. 4 shows variation of voltammetric current with the applied scan rate for EMD deposited at various scan rates. It is seen from Fig. 4 that the current varies linearly with the scan rate over a wide range between 10 and  $150 \text{ mV s}^{-1}$  for all the electrodes, indicating high power properties of all the EMD electrodes prepared by various scan rates. Also, it is interesting to note from Figs. 3 and 4 that the cyclic voltammetric current density and hence, the specific capacitance increases with the increase in scan rate of deposition of EMD. Specific capacitance as high as  $410 \text{ F g}^{-1}$  was obtained at a

scan rate of  $10 \text{ mV s}^{-1}$  for EMD prepared at a scan rate of  $200 \text{ mV s}^{-1}$ . Table 1 shows the comparison of the SC values obtained in the present study with some values reported in the literature for manganese oxide. It is clear that the SC values reported in the present study are much higher than the reported values.

The reason for such a high capacitance could be as follows: The deposition of EMD occurs between the potentials of 1.2–1.5 V versus SCE. The deposition occurs continuously in galvanostatic and potentiostatic methods. In the case of potentiodynamic method, there is a break in the deposition between each potentiodynamic cycle and the deposition is discontinuous. This phenomenon is expected to produce porous deposit than the galvanostatic and potentiostatic methods. Moreover, at higher scan rates of deposition, the resident time of the electrode between 1.2 and 1.5 V is very less, resulting in lower deposition per each potentiodynamic scan and highly porous deposits of EMD. Hence

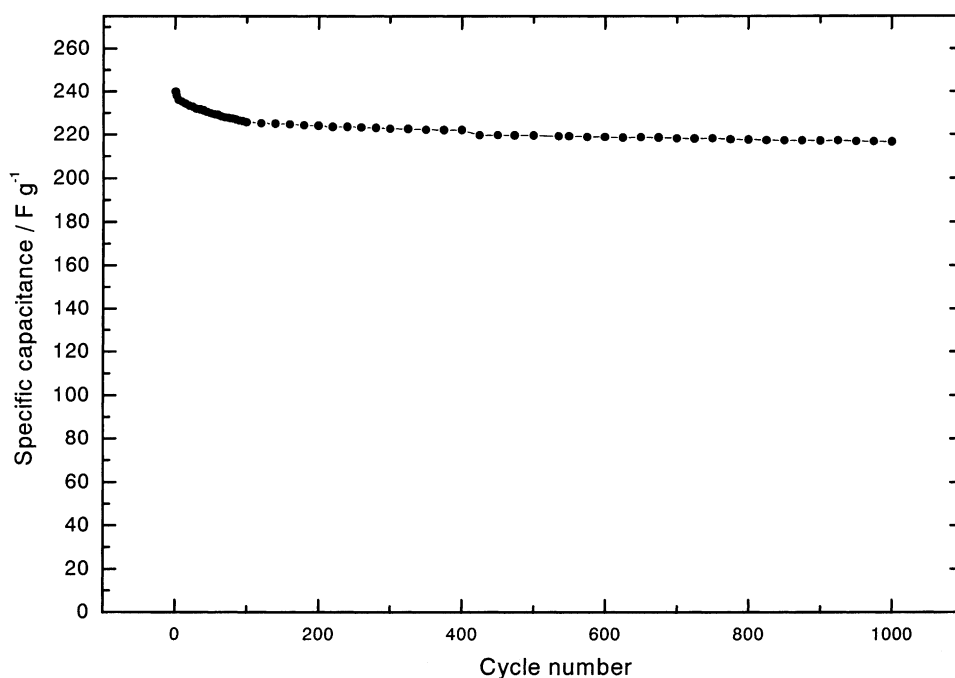


Fig. 5. Cycle-life data of EMD/SS electrode. Specific capacitance was calculated from CV at a scan rate of  $100 \text{ mV s}^{-1}$ . EMD was prepared at a scan rate of  $200 \text{ mV s}^{-1}$  to a mass of  $0.2 \text{ mg cm}^{-2}$ .

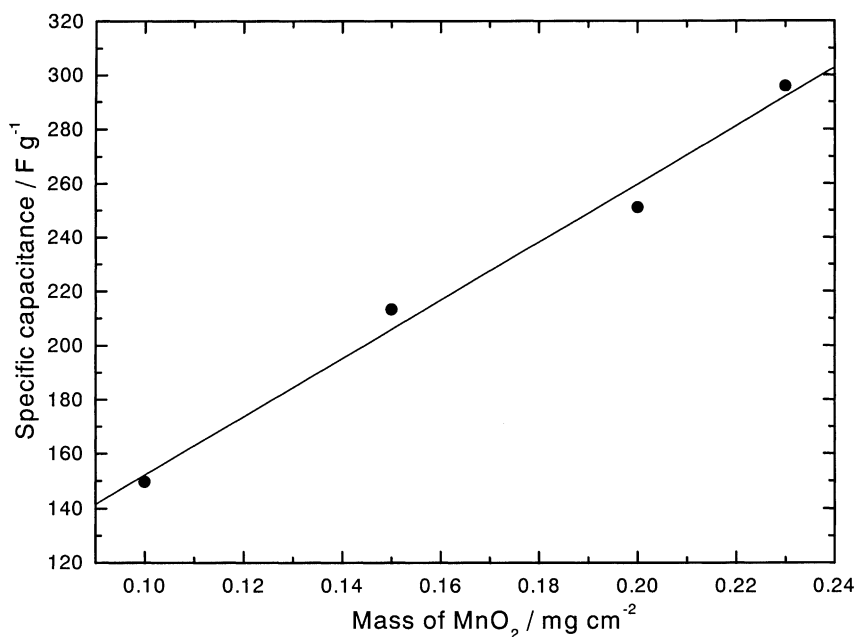


Fig. 6. Variation of specific capacitance (at a scan rate of  $100 \text{ mV s}^{-1}$ ) as a function of mass of EMD. EMD was prepared by potentiodynamic method at a scan rate of  $200 \text{ mV s}^{-1}$ .

EMD deposited by potentiodynamic method at high scan rate is expected to result in larger values of specific capacitance than the EMD prepared by potentiostatic, galvanostatic methods and potentiodynamic method at low scan rates. The important advantage of EMD used in the present study is the percentage decrease of specific capacitance by increasing the CV scan rate from  $10$  to  $150 \text{ mV s}^{-1}$ . When the scan rate was increased to  $150 \text{ mV s}^{-1}$ , the capacitance of EMD was reduced to about 54% of that measured at  $10 \text{ mV s}^{-1}$  irrespective of the scan rate used for the deposition of EMD. This decrease of 54% is much less than the value reported in the literature [7] for the same material deposited by using potentiostatic method.

The cycle-life test of EMD capacitors was performed by subjecting a EMD/SS electrode deposited at  $200 \text{ mV s}^{-1}$  for longer number of cyclic voltammetric scans. The cycling was performed at a scan rate of  $100 \text{ mV s}^{-1}$  for 1000 cycles. Fig. 5 shows the variation of specific capacitance as a function of cycle number. There is a little decrease in the

value of specific capacitance in the first 100 cycles and then the specific capacitance value remained almost constant. A decrease of 10% of the specific capacitance was observed after 1000 cycles. This decrease in the value of specific capacitance is very less compared to the value reported in the literature [11].

### 3.3. Effect of thickness of EMD on specific capacitance

For the purpose of studying the effect of thickness (mass per unit area) of EMD on the value of specific capacitance, EMD was deposited on to SS to various thickness values at a scan rate of  $200 \text{ mV s}^{-1}$ . The thickness of the film was controlled by the number of cycles and the charge corresponding to the last voltammetric cycle of deposition of EMD. Fig. 6 shows the variation of specific capacitance (calculated at  $100 \text{ mV s}^{-1}$ ) as a function of mass of EMD. Electrical parameters calculated at various scan rates and various thickness values of EMD are given in Table 2. It

Table 2

Specific capacitance values (calculated from CV at various scan rates) of EMD/SS as a function of thickness (mass per unit area) of EMD. EMD was prepared at a scan rate of  $200 \text{ mV s}^{-1}$

Scan rate of CV ( $\text{mV s}^{-1}$ )	Thickness			
	0.10 ( $\text{mg cm}^{-2}$ )	0.15 ( $\text{mg cm}^{-2}$ )	0.20 ( $\text{mg cm}^{-2}$ )	0.23 ( $\text{mg cm}^{-2}$ )
10	256.5	364.0	410.0	482.0
20	220.5	306.0	350.0	430.7
50	167.0	233.0	266.5	327.5
80	158.4	217.3	250.2	306.2
100	150.0	213.0	240.0	295.0
150	141.4	202.0	225.0	275.0

is interesting to note from Table 2 that the values of specific capacitance increases with an increase in thickness of EMD. The method of preparation of EMD plays an important role for this increase in specific capacitance with an increase in thickness of EMD. The use of high scan rate for the potentiodynamic deposition leads to the formation of microporous EMD. As a consequence, the electrolyte could seep into the micropores of oxide electrode-material giving increased SC with an increase in thickness of EMD.

#### 4. Conclusions

Nanostructured and amorphous EMD was deposited on to SS electrode by potentiodynamic method at high scan rates. Electrolyte solution used for the deposition was 0.5 M  $\text{H}_2\text{SO}_4$  + 0.5 M  $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ . EMD/SS electrodes were characterized by cyclic voltammetry in 0.1 M  $\text{Na}_2\text{SO}_4$  for electrochemical redox supercapacitor. A SC as high as  $482 \text{ F g}^{-1}$  was obtained (at  $10 \text{ mV s}^{-1}$ ) with EMD deposited at a high scan rate of  $200 \text{ mV s}^{-1}$ . The capacitance was found to increase with the increase in scan rate of deposition of EMD. High power density, high stability of the material was demonstrated.

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