



THE INTERPLAY OF MASS LOADING AND ACTIVE SITE ACCESSIBILITY IN MANGANESE OXIDE THIN-FILM ELECTRODES FOR ELECTROCHEMICAL CAPACITOR

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ARTICLE INFO

Article History

Received: January 28, 2026

Reviewed: March 28, 2026

Accepted: April 28, 2026

Published: May 29, 2026

Keywords:

Mn₃O₄,
Thin-film electrodes,
Mass loading,
Supercapacitors,
Electrochemical characterization

ABSTRACT

An easy drop coating method on a microfiber carbon substrate was used to fabricate Manganese Oxide (Mn₃O₄) thin-film electrodes with varying mass loadings. The physical and structural properties of the electrodes were characterized by scanning electron microscopy (SEM), Raman spectroscopy, and X-ray diffraction (XRD), revealing uniform deposition and crystalline structure. The electrochemical performance was evaluated using cyclic voltammetry (CV) and charge-discharge (CD) tests in 1.0 M Na₂SO₄ solution. Results indicate that increasing the mass loading significantly reduces both specific capacitance and coulombic efficiency due to the limited accessibility of active sites in thicker films. The thin-film electrode with 0.7 mg/cm² mass loading demonstrated optimal capacitive behavior within the potential range of -0.1 to 0.9 V. q-plots further confirmed that thicker electrodes hinder ion diffusion, leading to decreased electrochemical efficiency. These findings suggest that controlling mass loading is crucial for optimizing the performance of Mn₃O₄-based supercapacitors. The study provides practical guidelines for designing thin-film electrodes with improved energy storage capability, highlighting the balance between electrode thickness and electrochemical performance for efficient supercapacitor applications.



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I. INTRODUCTION

In recent years, supercapacitors have become attractive power sources because of their vast industrial and domestic application. The supercapacitors whose characteristics lie between those of batteries and capacitors. Supercapacitors have a high specific energy, an accelerated charging and discharging capacity, extended longevity, and eco-friendliness [1-3]. They were considered among the most prominent and excellent candidates for energy storage. The progress of portable equipment and hybrid (and "all-electric") vehicles also require storage devices that allow high energy density to be obtained in a limited volume and that can be released quickly [4]. The effectiveness of supercapacitors is enhanced through the advancement of various electrode materials, which necessitate elevated levels of specific surface area, electrical conductivity, resistance to corrosion, and chemical stability. The primary materials used as supercapacitor electrodes include carbon-based substances, conductive polymers, and metal oxides like manganese oxide, which can store high energy levels [5]. It is a preferred option since manganese oxide has a significant theoretical capacity (1370 F/g) and is inexpensive [2], [6]. However, the experimental-specific capacitance is much lower and is limited to systems with low active mass (mg/cm²) due to the resistivity and high density of the material. To overcome this lack of conductivity and improve storage properties (Increase both power and energy while decreasing resistance), Manganese oxide must be a thin film [7]. Recent studies have confirmed that in addition to the strength of the crystal structure and surface properties, the mass loading/thickness of Mn₃O₄ also significantly affects the electrochemical performance of manganese oxides.

According to [8] proved that the performance of thin electrodes is much higher than that thick electrodes. His work was based on the straightforward redox reaction between Mn^{2+} and MnO_4^- to synthesize high-surface-area manganese oxides. Bong-Ok Park and co-workers [7] reported the cathodic electrodeposition procedure used to create RuO_2 films and demonstrated how decreasing the film thickness causes the electrode's specific capacitance to increase. In [9] Mn_3O_4 thin film electrode produced by spray pyrolysis. The result is that the specific capacitance increases as the layer thickness increases. According to [10] have shown that the mass capacity of MnO_2 strongly depends on the quantity and thickness of the material used to prepare the electrode. This research work focused on electrode materials for supercapacitors. The electrode materials studied are manganese oxides and their association with microfiber carbon paper MCP. To verify the presence of Mn_3O_4 , several produced samples were examined using electrochemical techniques (cyclic voltammetry CV, charge-discharge CD) and physicochemical techniques (scanning electron microscopy SEM, Raman spectra, and X-ray diffraction XRD). The results obtained for the thin electrode (0.7 mg/cm^2) exhibit an impressive particular capability of 232.85 F/g at a scan rate of 5 mV/s . Finally, the goal of this research is to contribute to the investigation and knowledge of the effects of surface and structural properties on electrode materials, especially the impact of mass loading on the electrochemical performance of thin-film manganese oxide electrodes.

II. EXPERIMENTAL

II.1 CHEMICALS

The All chemicals used in this study were of analytical grade and were purchased from Sigma-Aldrich. Potassium permanganate (KMnO_4), sulfuric acid (H_2SO_4), and ethanol (EtOH) were used as received without further purification. Distilled water with a resistivity of $18 \text{ M}\Omega\cdot\text{cm}$ was employed for the preparation of all aqueous solutions. Microfiber carbon paper (MCP), type SC 2050 A, was supplied by Spectracarb. Prior to use, the MCP substrate was treated in concentrated sulfuric acid (H_2SO_4) at 70°C for 4 h to improve surface wettability and adhesion, followed by thorough rinsing with distilled water.

II.2 MATERIALS PREPARATION

Mn_3O_4 thin films were deposited onto the treated MCP substrate following a drop-coating procedure previously reported in the literature [11]. Different mass loadings of Mn_3O_4 were applied, namely 0.7 , 5.6 , and 26.6 mg/cm^2 , and the resulting electrodes were denoted as MCP- Mn_3O_4 (0.7), MCP- Mn_3O_4 (5.6), and MCP- Mn_3O_4 (26.6), respectively. After deposition, the electrodes were repeatedly rinsed with distilled water to remove residual precursors and then dried under vacuum at 150°C for at least 24 h. The mass loading of each electrode was determined as the mass of Mn_3O_4 per unit area using a high-precision digital balance with a resolution of 0.1 mg . The specific capacitance (C_s , F/g) was calculated from cyclic voltammetry (CV) curves by integrating the charge (Q) according to Equation (1) [11], [12]:

$$C = Q/(\Delta E * m) \quad (1)$$

Where ΔE represents the potential window and m is the mass of the active material. The capacitance derived from constant current charge-discharge (CD) measurements was calculated using Equation (2) [11], [12]:

$$C = I_{td} / (\Delta E_{cc} * m) \quad (2)$$

Where I is the total current, t_d the discharge time, ΔE_{cc} the CC potential drop during constant current discharge.

II.3 MATERIALS CHARACTERIZATION

An X-ray diffractometer model Bruker D8 Advance ($\lambda = 1.54182 \text{ \AA}$ with $\text{Cu-K}\alpha$ radiation) was used to perform the structural characterization of the electrodes at room temperature. The surface of the samples was examined using a JEOL-JSM-7600F analytical scanning electron microscope. Using an alpha 300 R Confocal Raman Microscope and a WITec UHTS 300 spectrometer with a 532 nm laser, the samples' Raman microscopy was captured. In our work, the electrochemical method was performed using a bio-logic potentiostat/electroplating/FRA (SP-300). It is controlled by a Windows computer running EC-Lab® software, allowing selection of electrochemical techniques, parameters of interest, and data processing. A three-electrode glass electrochemical cell immersed in an electrolytic containing a 1 M solution of Na_2SO_4 was used for electrochemical experiments. Electrochemical measurements (cyclic voltammetry CV and charge-discharge CD) were performed by glass electrochemical cell with three electrodes immersed in electrolysis containing the 1 M aqueous solution of Na_2SO_4 at room temperature for all experiments, with a 2 cm^2 ($2 \text{ cm} \times 1 \text{ cm}$) working electrode and only 1 cm^2 was immersed in the electrolyte, the counter electrode and reference electrode being an Pt foil and an Ag/AgCl , respectively.

III. RESULTS AND DISCUSSION

To verify that our Mn_3O_4 is deposited on the MCP, the SEM was used to compare the structural properties of the microfibre carbon paper MCP and MCP- Mn_3O_4 . An SEM picture of the MCP is shown in Figure 1a and Figure 1b. At low magnification, it is noted that the carbon microfibers paper consists of a porous three-dimensional network of carbon microfibers. On the other hand, zooming the MCP image to just one fiber reveals that each carbon microfiber has a smooth, immaculate, and debris-free surface with a diameter of $5 \mu\text{m}$ for each fiber. Figure 1c and Figure 1d show the SEM images of the MCP electrode after Mn_3O_4 deposition. Images confirm the presence of Mn_3O_4 , which is deposited as nano/microparticles on the carbon microfiber. Almost all the MCPs are covered with Mn_3O_4 , given the size of the carbon microfiber ($5 \mu\text{m}$) and the diameter of the objects observed in SEM. At high magnification, we estimate the thickness of the deposition of Mn_3O_4 to about a hundred micro-meter ($1.6 \mu\text{m}$). This observation is interesting because it allows us not only to highlight the presence of Mn_3O_4 but also to have an idea of the amount deposited on the microfiber carbon paper.

We can also see on the SEM images of MCP- Mn_3O_4 that Mn_3O_4 is deposited as nano/microparticles on microfiber carbon paper MCP with sizes between 30 and 50 nm.

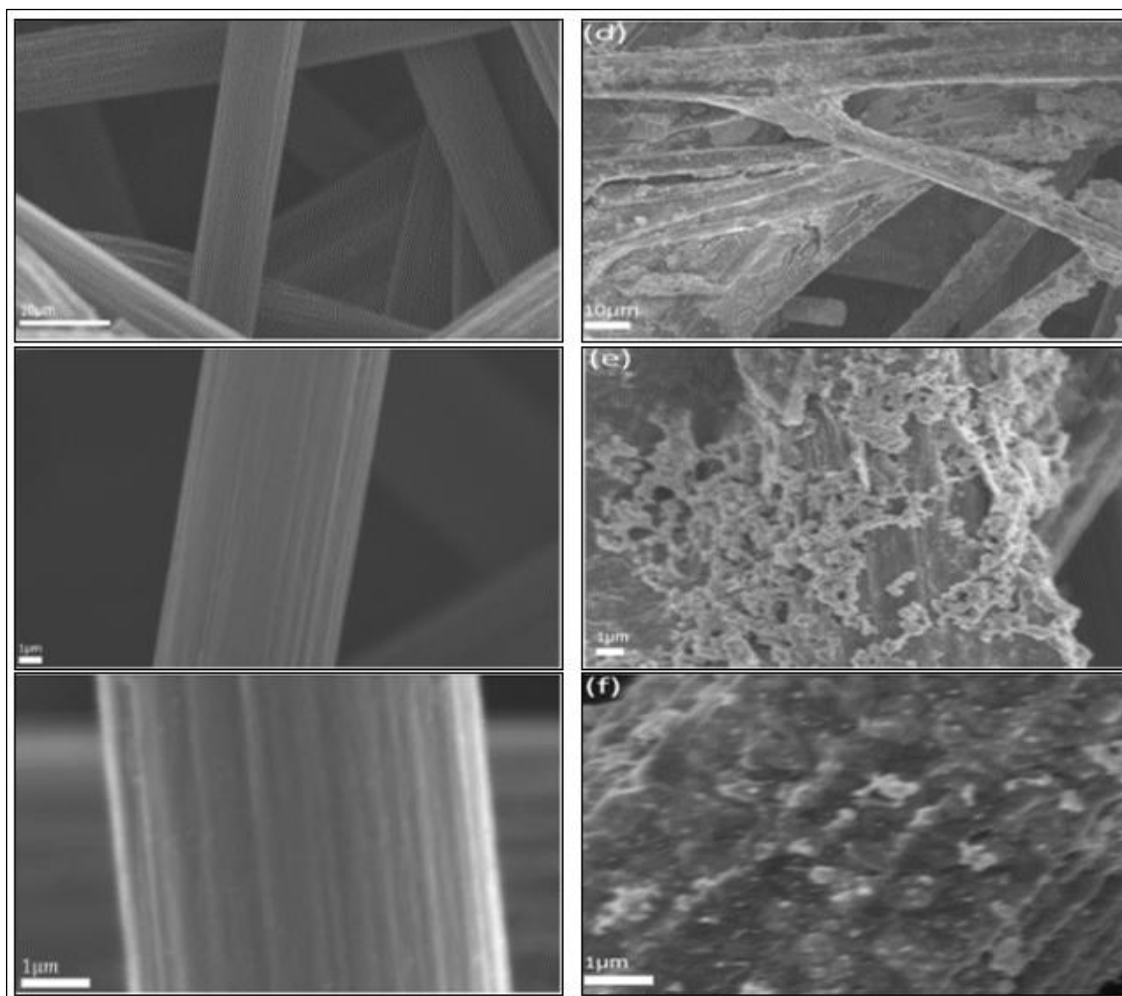


Figure 1: SEM images of carbon microfibers MCP and MCP- Mn_3O_4 (0.7).
Source: Authors, (2026).

The X-ray diffraction patterns of MCP and MCP- Mn_3O_4 are presented in Figure 2. Compare the MCP and MCP- Mn_3O_4 spectrum. DRX diagrams of MCP substrate are characterized by different peaks corresponding to the reported graphite [13]. However, The MCP- Mn_3O_4 electrode has peaks at $31,84^\circ$, $33,07^\circ$, $36,57^\circ$, $37,26^\circ$, $43,74^\circ$, $51,91^\circ$, $55,94^\circ$, $55,94^\circ$, $59,94^\circ$ et $62,16^\circ$, which correspond to the (200), (103), (211), (004), (220), (105), (303), (321), (224) and (400) tetragonal structure planes of Mn_3O_4 nanoparticles (JCPDS Card #24-0734) [14]. Scherrer's formula and the diffractogram of MCP- Mn_3O_4 can be used to determine the average crystallite size (Dhkl). This formula leads us to the conclusion that the particle's Mn_3O_4 typical crystallite size is approximately 115 nm. The crystalline parameters of MCP- Mn_3O_4 are $a = 5.85 \text{ \AA}$ and $c = 9.5 \text{ \AA}$ [15]. To supplement the results obtained in SEM and XRD, to comprehend the carbon structures of the carbon microfiber and to corroborate the existence of the Mn_3O_4 phase (major phase) already observed by XRD, Raman spectroscopy analyses were performed.

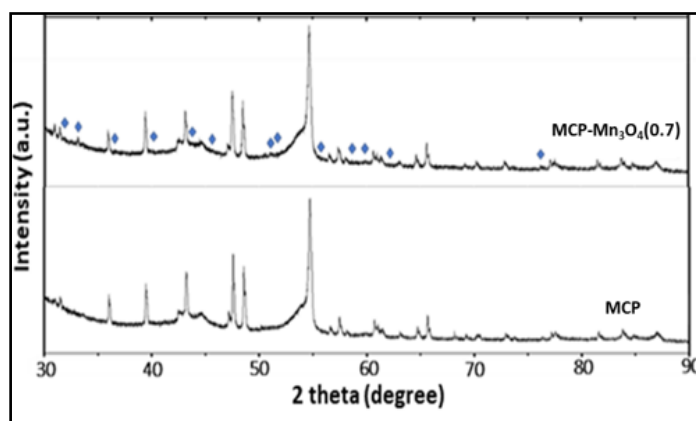


Figure 2: XRD patterns of MCP, and MCP- Mn_3O_4 (0.7) electrodes.
Source: Authors, (2026).

The superposition of the Raman spectra obtained from MCP and MCP-Mn₃O₄ in the 200 cm⁻¹ to 3500 cm⁻¹ frequency range is shown in Figure 3. The two Raman spectra present in the same region (200-3500 cm⁻¹), the three prominent peaks at 1357.61, 1584.9, 2707 cm⁻¹ for MCP and 1355, 1584, 2720 cm⁻¹ for MCP- Mn₃O₄ attribute to bands D, G and 2D respectively. Specific vibrations of pure crystalline Mn₃O₄ are responsible for a noticeable peak in the spectra of MCP- Mn₃O₄ that may be found about 653 cm⁻¹ [16].

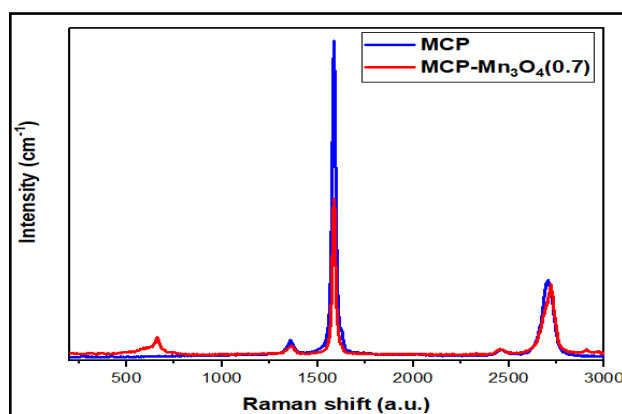


Figure 3: Raman spectra of MCP, and MCP- Mn₃O₄ (0.7) electrodes.
Source: Authors, (2026).

Cyclic voltammetry tests were carried out to examine and comprehend the electrochemical behaviour of the various synthesized materials. These materials were subjected to electrochemical experiments at ambient temperature using a neutral 1 M Na₂SO₄ aqueous electrolyte, highlighting the effects of manganese oxide deposition and mass loading on microfiber carbon paper MCP. Mass loading is the mass of Mn₃O₄ in MCP- Mn₃O₄. Voltammograms were recorded in the -0.1 to 0.9 V/Ag/AgCl potential range. Figure 4a compares the cyclic voltammograms of the MCP and MCP- Mn₃O₄ electrodes recorded in a 1 M Na₂SO₄ electrolyte at a scanning speed of 10 mV / s. We can see that the signal obtained varies greatly depending on the material tested. At first, the MCP has extremely low currents compared to the MCP- Mn₃O₄. This very low capacitance of the MCP is directly linked to its very low electronic conductivity. Additionally, the MCP- Mn₃O₄ electrode's cyclic voltammograms had a rectangular shape through the 1V investigated potential window. This rectangular voltammogram for MCP- Mn₃O₄ shows that the system behaves nearly optimally in terms of capacitance. This result demonstrates and confirms that manganese oxide is present and deposited on the microfiber carbon paper. Figure 4b shows a superposition of cyclic voltammograms (CVs) for various electrodes studied (0.7, 5.6 and 26.6 mg) in a 1M Na₂SO₄ solution. The shape of the voltammogram clearly shows that the sample with an active mass of 0.7 mg has a higher capacitance than the other samples. The same observation is also noted for the appearance of the corresponding CV, which is very rectangular compared to the others. This suggests a difference in electrochemical behavior among these three samples.

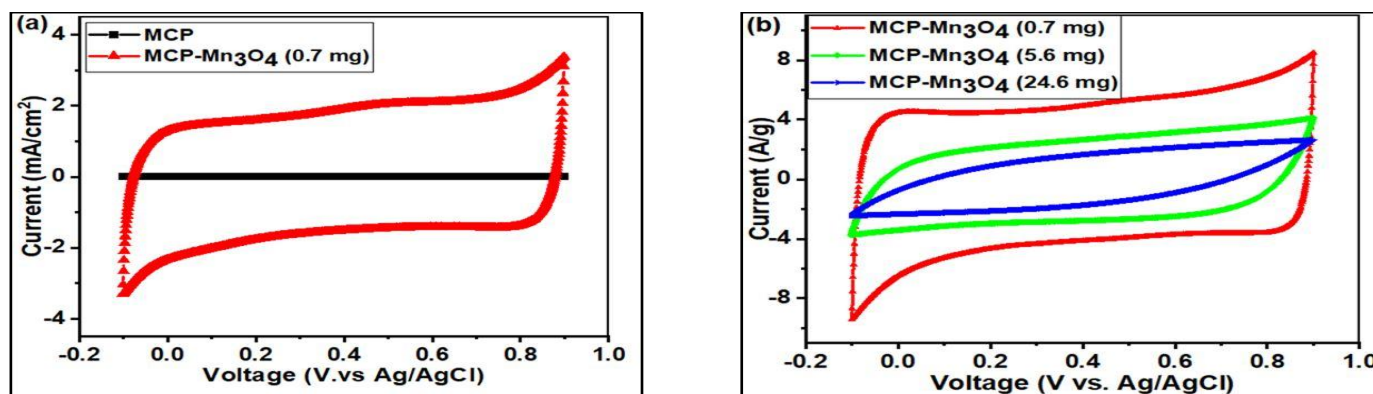


Figure 4: (a) Cyclic voltammograms of MCP and MCP- Mn₃O₄ (0.7) electrodes in 1 M Na₂SO₄ aqueous solution at a potential scan rate of 20 mV/s, (b) cyclic voltammograms in 1 M Na₂SO₄ aqueous solution of MCP- Mn₃O₄ (0.7), MCP- Mn₃O₄ (5.6) and MCP- Mn₃O₄ (24.6) electrodes in 1 M Na₂SO₄ aqueous solution at a potential scan rate of 20 mV/s.

Source: Authors, (2026).

Figure 5a,b,c represent the voltammograms of the MCP- Mn₃O₄ (0.7), MCP- Mn₃O₄ (5.6) and MCP- Mn₃O₄ (24.6) electrodes at scanning speeds from 5 mV/s to 100 mV/s, further to the evolution of the specific capacitance of materials as a function of the kinetics (Figure 5d) of the synthesized electrodes with different mass loadings (0.7, 5.6, 24.6 mg), as the scanning speed increases, there is an increase in the current for MCP- Mn₃O₄ (0.7) without significant change in the form of the cyclic voltammetry, even with high-speed scanning. This indicates that there are low contact resistances and ideal capacitive behavior. When the scan rates increase (Figure 5b, c), the voltammograms lose their rectangular shape and take on a resistive profile. Indeed, at high-speed scanning, problems linked to the limitation of the diffusion of ionic species in the porosity of the material and/or of the percolation of the charges up to the collector appear. Ionic species have less time to diffuse correctly within the composite material, and faradaic reactions linked to the presence of Mn₃O₄ are more difficult to carry out [17].

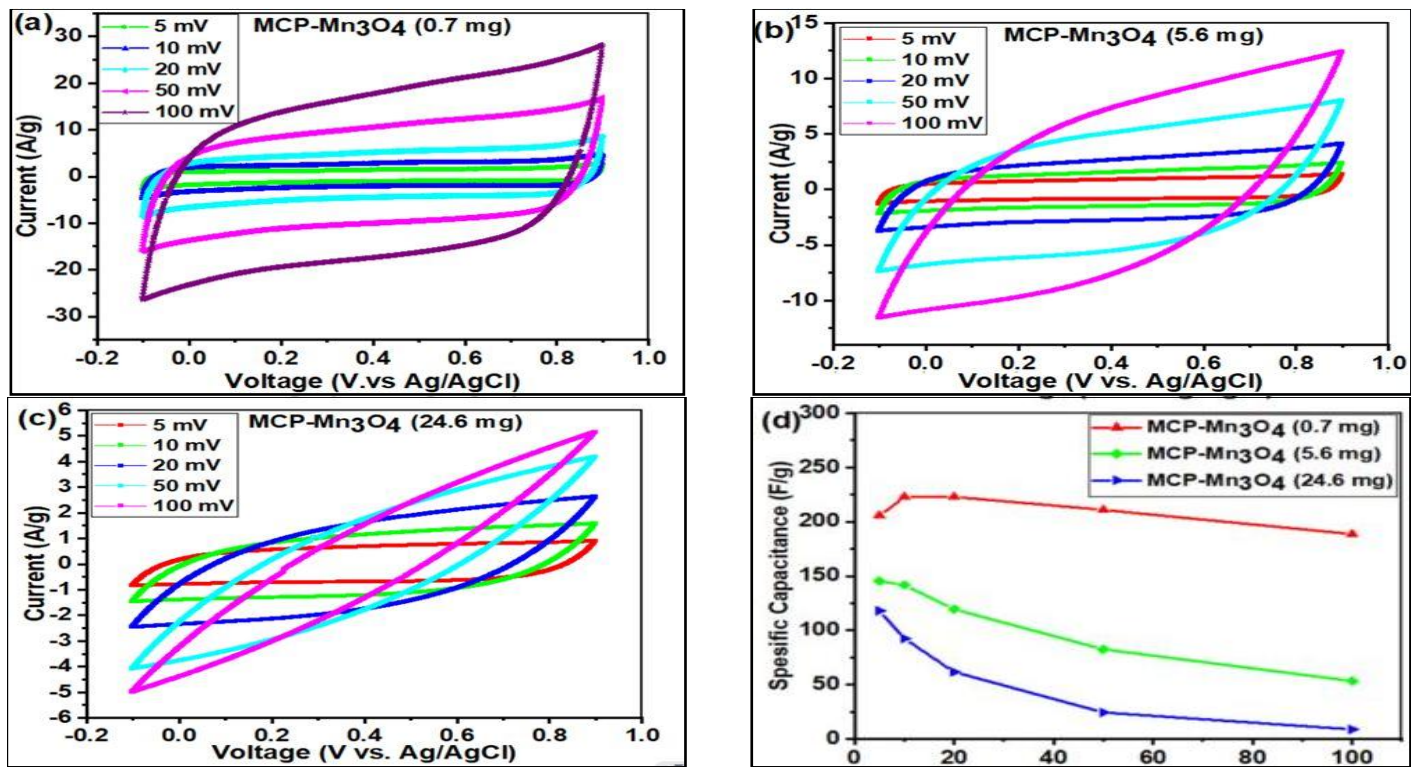


Figure 5: Cyclic voltammograms in 1 M Na₂SO₄ aqueous solution at different potential scan rate for (a) MCP- Mn₃O₄ (0.7) (b) MCP- Mn₃O₄ (5.6) (c) MCP- Mn₃O₄ (24.6) electrodes (d) variation of the specific capacitance as a function of a scan rate for MCP- Mn₃O₄ (0.7), MCP- Mn₃O₄ (5.6) and MCP- Mn₃O₄ (24.6) electrodes in 1 M Na₂SO₄ aqueous solution.

Source: Authors, (2026).

The results of Figure 5d make it abundantly evident that the electrochemical performance of the produced electrodes is influenced by the amount of mass deposited. The higher the mass deposited, the more the specific capacities decrease. Consequently, a high mass has a negative impact on electrochemical performance. For example, with MCP- Mn₃O₄ (0.7) and MCP- Mn₃O₄ (24.6), the capacity decreases from 222.85 F/g to 92.43 F/g at scanning speeds of 10 mV/s, respectively. Devaraj and Munichandraiah have shown similar behavior in their manganese oxides [18]. In addition, as soon as the scanning speed is increased from 5 to 100 mV/s, MCP- Mn₃O₄ (0.7) retains 85% of its specific capacitance (from 222.85 to 188.57 F/g). However, only 37.65% and 9.54% of the specific capacity of MCP- Mn₃O₄ (5.6) and MCP- Mn₃O₄ (24.6) electrodes remained, respectively. This demonstrates that the electrode MCP- Mn₃O₄ (0.7) also has the highest and most stable capacities as the scan rates increase. These results confirm those described in the literature, highlighting a drop in the capacitances of manganese oxides during the increase in the active mass and therefore during the film thickness [19]. Therefore, the performance of the produced electrodes' electrochemical reactions is adversely impacted by the increase in the mass of manganese oxides deposited on MCP. Compared to other electrodes, the MCP-Mn₃O₄ (0.7) electrode has a high specific capacitance value and can sustain a high current density. According to Equation (2), we can calculate the specific capacities of the MCP- Mn₃O₄ (0.7), MCP- Mn₃O₄ (5.6) and MCP- Mn₃O₄ (24.6) electrodes at different current densities from the discharge time. These measurements were made for six current values (Figure 6b). It is clear that for the three electrodes, as the charge/discharge current increases, the specific capacity decreases slightly. When applying a 1 mA/cm² current density, the profiles clearly show that the specific capacity of MCP- Mn₃O₄ (0.7) (287.63 F/g) is greater than MCP- Mn₃O₄ (5.6), MCP- Mn₃O₄ (24.6) (133.06 and 106.67 F/g).

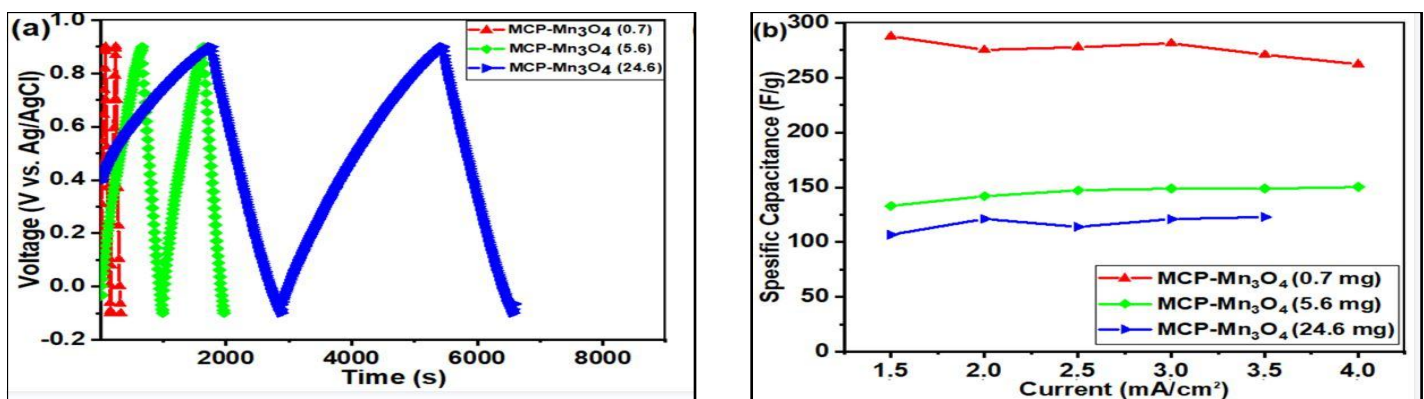


Figure 6: (a) Charge–discharge curve in 1M Na₂SO₄ aqueous solution of MCP- Mn₃O₄ (0.7), MCP- Mn₃O₄ (5.6) and MCP- Mn₃O₄ (24.6) electrodes at a current of 2 mA/cm², (b) variation of the specific capacitance of MCP- Mn₃O₄ (0.7), MCP- Mn₃O₄ (5.6) and MCP- Mn₃O₄ (24.6) electrodes as a function of applied current.

Source: Authors, (2026).

In an aqueous electrolyte (1 M Na_2SO_4), voltammetric charge data extracted from cyclic voltammetry measurements is performed at different scan rates. These data can be analyzed using the approach developed by Ardizzone [20], [21] and by Trasatti [21-23]. They have been shown that with decreasing scanning speed the charge of the voltameter q^* decreases (v) (increases with $(v)^{-1/2}$). The commonly accepted explanation for the dependence of q^* on v is the presence of Na^+ or SO_4^- in the boundaries of pores, grains, and cracks. In cyclic voltammetry, the measured capacity $q(v)$ varies inversely with the potential scan rate v . When the scan rate is increased, the contribution of the least accessible sites decreases, and the reliance of q^* on v is typically explained by the presence of Na^+ or SO_4^- within the confines of pores, fractures, and grains. As a result, the electrode's outer surface is where the majority of protons are consumed at high scanning speeds. This limits proton access to surfaces that are difficult to access from the electrode. Thus, electrochemical reactions occur only on surfaces easily accessible to protons (the external active surface). Figure 7a shows a plot of q as a function of the opposite of the square root of the scanning speed ($v^{-1/2}$). It is possible to calculate the outer capacity (C_{ou}) by the extrapolation of $v^{-1/2}$ to infinity, this is coupled to the charge in the most accessible active area. A plot of q^* versus the square root of the scanning speed ($v^{1/2}$) is shown in Figure 7b. Conversely, the total capacitance (C_T) will be determined by extrapolating q^* to $v = 0$, which concerns all the inner and outer active sites; the difference between the two capacitances (C_{ou} and C_T) indicates the capacitance associated with the internal active surface charge (C_{in}).

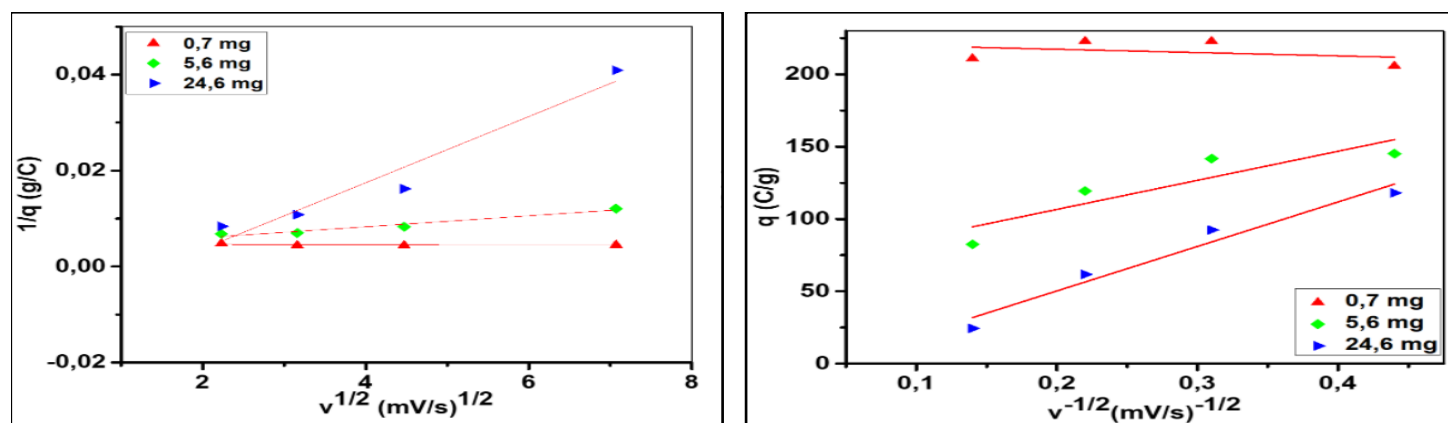


Figure 7: Variation of the voltammetric charge (q) for the sweep rate v : (a) extrapolation of (q) to $v = \infty$ from the q vs $v^{-1/2}$ plot gives the outer charge q_{ou} , (b) extrapolation of q to $v = 0$ from $1/q$ vs $v^{1/2}$ plot gives the total charge q_T .

Source: Authors, (2026).

It is therefore possible to determine the contribution of each of the outer and inner layers to the total capacity. In the case of MCP- Mn_3O_4 (0.7), the total capacity is approximately equal to the outer layer, which underlines the importance of the accessibility of the active sites for a power electrode. In addition, by increasing the amount of Mn_3O_4 on the MCP electrode, the limited accessibility of the surface-active sites in thick electrodes was measured by measuring a decrease in the value of q_{ou} (Table 1).

Table 1: Distribution of Outer (q_{ou}) and Inner (q_{in}) Charge Contributions as a Function of Mn_3O_4 Mass Loadin.

Électrode	q_{ou}	q_T	q_{in}	q_{in}/q_T	q_{ou}/q_T
MCP- Mn_3O_4 (0.7)	219	222	3	0.013	0.98
MCP- Mn_3O_4 (5.6)	77	243	166	0.68	0.31
MCP- Mn_3O_4 (24.6)	4	333	329	0.98	0.012

Source: Authors, (2026).

The increased number of inaccessible sites caused by the electrode film's growing thickness accounts for the decrease in the outer layer's contribution. Figure. 8 shows a schematic representation of the impact of the thickness of an active material film on-site accessibility.

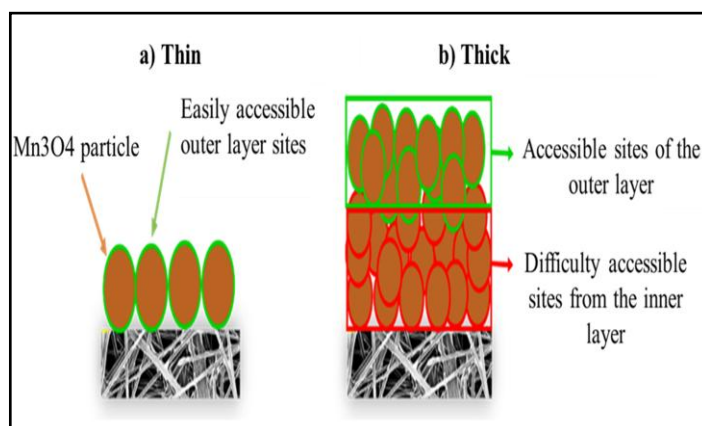


Figure 8: Schematic representation of the number of easily accessible sites in the electrode a) thin and b) thick.

Source: Authors, (2026).

Figure 9a shows the CV of the MCP- Mn_3O_4 (0.7) electrode before and after cycling. After 1000 cycles, the CV of MCP- Mn_3O_4 (0.7) may lose their rectangular shape at the level of the positive potential (between 0.4 and 0.9 V, repression current decreases), and MCP- Mn_3O_4 (0.7) has a specific capacity of 80.28%, offering excellent material stability over the entire range of cycle numbers (Figure 9b).

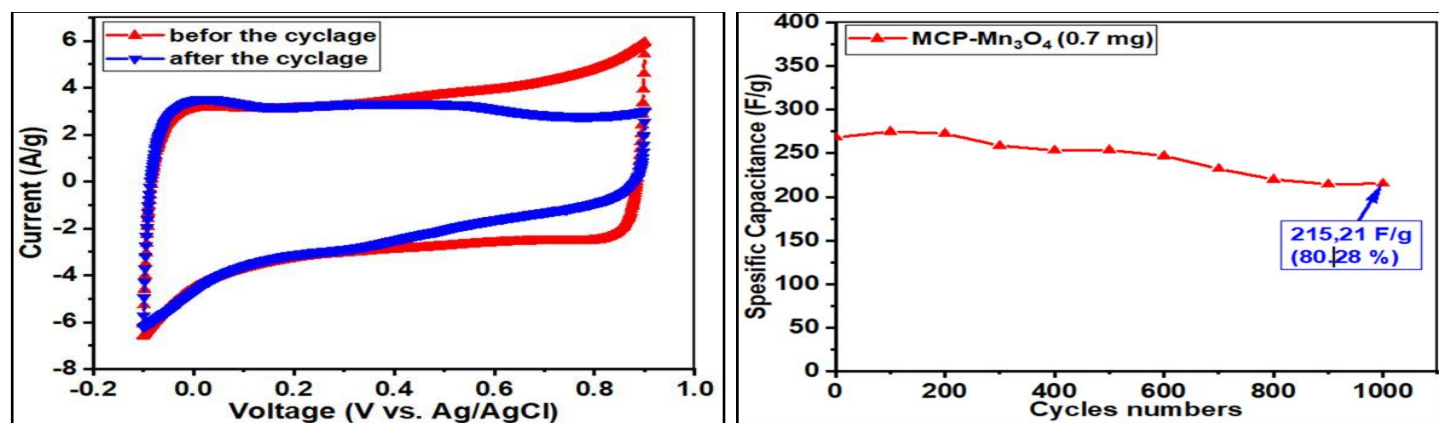


Figure 9: (a) Variation of the specific capacitance of a MCP- Mn_3O_4 (0.7) electrode as a function of cycle numbers. Electrolyte: 1 M Na_2SO_4 aqueous solution, charge and discharge at a current of 4.5 mA/cm^2 (b) Cyclic voltammograms of CP- Mn_3O_4 (0.7) electrodes in 1 M Na_2SO_4 aqueous solution at a potential scan rate of 20 mV/s .

Source: Authors, (2026).

IV. CONCLUSIONS

Various mass loadings of MCP- Mn_3O_4 electrodes are fabricated using a drop-casting method using spontaneous reduction of MnO_4^- ions at a temperature of 150°C in acidic media. According to X-ray diffraction data, the Mn_3O_4 thin film possessed a tetragonal crystal structure (JCPDS Card #24-0734). At ambient temperature, in a neutral aqueous electrolyte of 1 M Na_2SO_4 , the electrochemical behavior of the thusly produced MCP- Mn_3O_4 electrodes with varying mass loadings was investigated and understood. The voltage range between -0.1 and 0.9 V/Ag/AgCl showed outstanding pseudocapacitive behavior in all MCP- Mn_3O_4 electrodes. With increasing mass loading, the specific capacitance value continues to decline, reaching a maximum of 232 F/g for 0.7 mg cm^{-2} mass loading of Mn_3O_4 . This indicates that there are low contact resistances, ideal capacitive behavior fast ion diffusion in the electrode MCP- Mn_3O_4 (0.7). All results proved that the thinner mass loading MCP- Mn_3O_4 is useful for electrochemical supercapacitor applications.

V. AUTHOR'S CONTRIBUTION

Conceptualization: Zineb Nabti and Tarik Bordjiba.

Methodology: Zineb Nabti, Reda Bekhakhecha and Tarik Bordjiba.

Investigation: Zineb Nabti, and Tarik Bordjiba.

Discussion of results: Zineb Nabti, and Tarik Bordjiba.

Writing – Original Draft: Zineb Nabti.

Writing – Review and Editing: Zineb Nabti, Reda Bekhakhecha and Tarik Bordjiba.

Resources: Zineb Nabti, Reda Bekhakhecha and Tarik Bordjiba.

Supervision: Tarik Bordjiba, Zineb Nabti.

Approval of the final text: Zineb Nabti, Reda Bekhakhecha and Tarik Bordjiba.

VI. ACKNOWLEDGMENTS

The authors would like to thank the laboratories of the University of 8 May 1945 Guelma for providing the facilities and equipment necessary to carry out this research.

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