Mixed valence nanostructured Mn_3O_4 for supercapacitor applications

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Abstract. Nanostructured Mn_3O_4 with an average crystallite size of ~ 19 nm was synthesized through a microwave-assisted chemical route. Structural characterization was carried out using X-ray diffraction analysis and transmission electron microscopy. Observed change in the ratio of lattice constants, c/a for the sample compared with single-crystalline Mn_3O_4 points to the presence of Mn^{4+} ions at the octahedral sites. This is attributed to the presence of cation vacancies. X-ray photoelectron spectroscopic studies confirm the presence of Mn^{4+} ions. Specific capacitance value of 665.08 F g^{-1} was obtained for symmetric supercapacitor with Mn_3O_4 active material at slow scan rate. Reasonably high power and energy density values, viz., 4.27 kW kg^{-1} and $4.36 \times 10^{-2} \text{ Wh kg}^{-1}$, respectively, were obtained for charge–discharge cycles at a constant current of 12.74 mA cm^{-2} .

Keywords. Nanomaterials; transition metal oxides; mixed valence; electrochemical capacitors; XPS.

1. Introduction

Nanostructured transition metal oxides exhibit physical and chemical properties much varied from those of their bulk counterparts and hence are of interest for many device applications. In many of these oxides, cations can have more than one valence state and such systems are employed as active materials in pseudocapacitance-based supercapacitors.^{1,2} For supercapacitor applications, oxides of manganese are preferred owing to their outstanding structural flexibility and environmentally benign nature.^{3,4} Hausmannite, Mn_3O_4 , is one of the most stable oxides of manganese and has normal spinel structure with a tetragonal distortion along the c -axis.^{5,6} In Mn_3O_4 , Mn^{2+} and Mn^{3+} ions occupy the tetrahedral and octahedral sites, respectively, and the structure can be represented as $[\text{Mn}^{2+}(\text{Mn}^{3+})_2\text{O}_4]$. Many reports on the synthesis and characterization of nanostructured Mn_3O_4 through different routes for supercapacitor applications have appeared in the literature.^{7–9} Specific capacitance as high as 314 F g^{-1} under low scan rates makes the material a potential candidate for supercapacitor applications.^{8–10} Advantages of Mn_3O_4 as a supercapacitor electrode material include good efficiency, long-term performance, low cost, environmental compatibility and good corrosion stability.^{7,11} This paper reports on the synthesis of nanostructured Mn_3O_4 through a novel microwave-assisted two-step chemical method and its structural characterization using X-ray diffraction (XRD) analysis, transmission electron microscopy (TEM) and Brunauer–Emmett–Teller (BET) surface area analysis. X-ray photoelectron spectroscopy (XPS) is used for analysing the valence states of manganese. The performance of the sample

as an active material in a symmetrical coin-type electrochemical supercapacitor is evaluated.

2. Experimental

All the chemicals used were of analytical grade purchased from Merck, India and were used without further purification. Ethanolic solution of manganese acetate, $(\text{CH}_3\text{COO})_2\text{Mn} \cdot 4\text{H}_2\text{O}$ (0.2 M), was refluxed for 3 h at 100°C . The resultant solution was treated with microwave power using a Electrolux EM 18EG70SL (1000 W) oven for 15 min at 40% power to obtain an organometallic precursor $(\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 6\text{C}_6\text{H}_{13}\text{OH})$ in the form of a loose light brown powder. The precursor was dried in a hot air oven at 100°C . Thermogravimetric analysis (TGA) of the precursor was carried out in the temperature range 50 – 550°C in air at a heating rate of 5°C using a METTELER TOLEDO S R System. The TGA curve (figure 1) of the organometallic precursor shows that the decomposition occurs in the temperature range 200 – 300°C . Decomposition of the precursor was done at 300°C for 2 h in a muffle furnace. Manganese oxide was obtained as a loose brown powder.

The XRD pattern of the oxide was recorded in a Philips XPERT-PRO powder diffractometer employing $\text{Cu K}\alpha$ ($1.54056 \text{ \AA}$) radiation in the 2θ range 20 – 80° . The particle size and size distribution were studied using a PHILIPS CM 200 transmission electron microscope (TEM). The specific surface area was measured by a Gemini 2375 conventional volumetric apparatus according to the Brunauer–Emmett–Teller (BET) method. The pore size distribution was estimated from the adsorption branch of the isotherm, by the Barrett–Joyner–Halden (BJH) method.

For evaluating the performance of the sample as an active material, a coin-type symmetric electrochemical cell

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Figure 1. TGA of the organometallic precursor.

was fabricated. Electrodes of the electrochemical symmetric capacitor were prepared by mixing the active material (well ground Mn_3O_4 sample) with 15 wt% acetylene black and 5 wt% polytetrafluoroethylene (PTFE) of the total electrode mass. PTFE acts as a binder. One to two drops of 1-methyl-2-pyrrolidinone was then added to this composite to form a homogeneous mixture, which was pasted on the surface of two stainless-steel coins. A Whatman glass filter paper wetted with 6 M potassium hydroxide (KOH) electrolyte was stacked in between the two electrodes to form the symmetric capacitor. Electrochemical (EC) measurements were performed using a Bio-Logic Model VMP3 16 Channel Electrochemical Workstation. Cyclic voltammograms (CVs) were recorded in the voltage range 0–1 V at different scan rates, viz., 0.01, 0.05, 0.1, 0.5, 1, 5, 10 and 20 mV s^{-1} . Electrochemical impedance of the cell in the frequency range 1 Hz–600 kHz was also measured. Galvanostatic charge–discharge behaviour of the cell at different fixed currents, viz., 1.27, 6.37 and 12.74 mA cm^{-2} was examined by chronopotentiometry in the potential range 0–0.8 V. The charge–discharge cycles were repeated for testing the stability.

XPS analysis was performed using a SPECS make X-ray photoelectron spectrometer with $\text{AlK}\alpha$ source (1.48671 keV) under an operating pressure of 6×10^{-8} mbar. XPS survey scan was carried out in the energy range 0–1400 eV. The Mn 3s, 2p and O 1s XPS spectra were recorded at slow scan rates in the range 75–100, 635–660 and 525–538 eV, respectively. All the measurements were carried out with C 1s binding energy as an internal standard.

3. Results and discussion

3.1 TGA, XRD and TEM analyses

The TGA curve of the organometallic precursor is shown in figure 1. The curve shows two distinct mass loss regions.

Figure 2. XRD pattern of nanostructured Mn_3O_4 .

The first mass loss ($\sim 6.95\%$) occurs at 50°C , which is due to the evaporation of ethanol present in the precursor. The second mass loss ($\sim 46.69\%$) occurs in the temperature range of 220 – 300°C and can be attributed to the decomposition of the precursor. From the differential curve, it is found that the rate of decomposition is maximum at 280°C . The decomposition of the precursor was done at 300°C to obtain the oxide as a loose powder. The TGA curve does not show any marked weight loss in the temperature range 300 – 550°C which means that the oxide formed is stable in the temperature range.

The XRD pattern of the sample shown in figure 2 can be indexed to that of the tetragonal phase of Mn_3O_4 (JCPDS-ICDD pattern number 80-0382, space group 14_1). Two additional peaks with $d = 2.2381$ and 2.5754 Å are, respectively, the (200) and (111) peaks of cubic MnO phase (JCPDS-ICDD pattern number 78-0424, space group $\text{Fm}3\text{m}$). Thus the procedure result in the synthesis of Mn_3O_4 with trace amounts of MnO . The average crystallite size estimated from the four most intense XRD peaks using the Scherrer equation, after correcting for instrumental error is 17.28 ± 4.90 nm.^{12,13} Williamson–Hall analysis was done to separate the size and strain contributions to XRD line broadening.^{14,15} The average crystallite size after applying correction for strain broadening is 19.35 ± 3.64 nm and the r.m.s. microstrain is 1.53×10^{-3} .

The precise values of lattice constants estimated from the XRD peaks are, respectively, $a = 5.723 \pm 0.0005$ and $c = 9.379 \pm 0.0010$ Å.¹⁶ These values are slightly smaller than those corresponding to single-crystalline Mn_3O_4 , viz., $a = 5.765$ and $c = 9.442$ Å. The unit cell volume is 307.19 Å³ which is smaller than that for single-crystalline Mn_3O_4 , viz., 313.81 Å³. Also, the c/a ratio is 1.6388 which is slightly higher than that for single-crystalline Mn_3O_4 (1.6378) JCPDS-ICDD pattern number 80-0382, space group 14_1 . In Mn_3O_4 , the tetragonal distortion is due to Jahn–Teller effect owing to the presence of Mn^{3+} (d^4) at the octahedral sites.

A decrease in the c -value indicates the possible presence of Mn^{4+} (d^3) at the octahedral site which does not contribute to Jahn–Teller effect.^{17,18} The presence of Mn^{4+} ions at the octahedral sites could be due to cation vacancies at the octahedral sites which leads to the transformation of Mn^{3+} ions into Mn^{4+} ions.^{17,18} The decrease in the value of a is probably due to the increase in the positive valence state at the octahedral site.

TEM image, selected area electron diffraction (SAED) pattern and the particle size distribution are shown in figure 3. The particle size distribution can be approximated by a lognormal profile and the average particle size estimated is 29.52 ± 4.62 nm. The distinct spots superimposing on the smooth rings in the SAED pattern indicate the presence of some relatively large crystallites. Thus the XRD and TEM analyses conclude that the microwave-assisted synthesis technique is successful in synthesizing nanostructured Mn_3O_4 with the traces of MnO. Larger value of particle size estimated from TEM analysis in comparison with the average crystallite size estimated from XRD analysis indicates the possibility of agglomeration in the sample.

3.2 Surface area analysis

The N_2 sorption isotherm for the sample is shown in figure 4a. The sorption profile is intermediate between the types II and IV of the Brunauer–Deming–Deming–Teller (BDDT) classification.¹⁹ The incipient hysteresis loop appears at a relative pressure of about 0.4 and the pores

become filled at higher pressures due to the uptake of adsorbate. The existence of mesoporosity, i.e., pores with diameter in the range 20–500 Å is identified from the adsorption and desorption curves of the hysteresis.¹⁹ From the surface area plot shown in figure 4b, the specific surface area of the material is calculated using the equation, $S = (V_m Na)/(m \times 22,400)$, where V_m is the volume of gas adsorbed at STP, N Avagadro's number, a the effective cross sectional area of one adsorbate molecule in square meters and m the mass of the material in grams. The BET surface area for the sample is estimated to be $12 \text{ m}^2 \text{ g}^{-1}$. The average particle size estimated from the specific surface area is about 98.76 nm which is much larger than the size estimated from XRD and TEM analyses. This means that only about 20% of maximum possible surface area is available for N_2 adsorption. Figure 5 shows the pore size distribution with diameter of the pores in the range 19–150 Å. This figure reveals that the sample is mesoporous with the maximum number of pores in the 20–30 Å range.

3.3 XPS analysis

The XPS survey scan of the material in the range of 0–1400 eV shown in figure 6a revealed the absence of any impurities, except the contaminant carbon. Carbon contamination is quite common and it can be used as an internal standard. The energy levels of Mn 3s, Mn 2p and O 1s obtained are in agreement with the previously reported values.²⁰ The Mn 3s, Mn 2p and O 1s peaks are broad due to multiple

Figure 3. TEM image of the nanostructured Mn_3O_4 together with SAED pattern and particle size distribution.

Figure 4. (a) Isotherm plot and (b) BET surface area plot of nanostructured Mn_3O_4 .

Figure 5. BJH adsorption dV/dD pore volume of nanostructured Mn_3O_4 .

splitting.²⁰ The oxidation states of Mn in the external layers can be obtained by analysing the Mn 3s and Mn 2p XPS spectrum which are shown in figures 6b and c, respectively. The doublet separation of Mn 3s could reveal the presence of different valence states of Mn ions.^{20,21} The binding energy of Mn 3s level is 89.39 eV and the multiple splitting is 5.78 eV.^{20–22} The magnitude of splitting of Mn 3s peak is proportional to the number of unpaired electrons in the d orbital and hence is different for Mn^{2+} , Mn^{3+} and Mn^{4+} .^{20,22} The two branches of Mn 3s peaks were deconvoluted assuming a Gaussian profile for each component. It was found that each peak actually correspond to three component peaks. The

observed splitting of Mn 3s doublets shown in figure 6b is 6.44, 5.59 and 4.76 eV, which are exactly in agreement with experimentally observed relative values of Mn^{2+} , Mn^{3+} and Mn^{4+} , respectively.^{20,23–28} The spin–orbit splitting for Mn^{2+} , Mn^{3+} and Mn^{4+} ions in the present case are listed in table 1 along with the previously reported values.^{20,23–28}

The Mn 2p peak (figure 6c) is broad due to multiple splitting. Hausmannite Mn_3O_4 belongs to class II of mixed valence compounds in which the interaction between different ion sites is feeble.^{20,23–25} Owing to the difference in binding energy of ions, the XPS spectrum of hausmannite has a larger doublet separation of Mn $2p_{1/2}$ and Mn $2p_{3/2}$ spin–orbit levels than the simple oxides.²⁰ The binding energy value of Mn $2p_{3/2}$ is 641.58 eV and the spin–orbit splitting between Mn $2p_{3/2}$ and Mn $2p_{1/2}$ is 12.15 eV.^{20–27,29} The binding energy values of Mn^{2+} , Mn^{3+} and Mn^{4+} in the Mn $2p_{3/2}$ peak are 641.14, 642.62 and 644.10 eV, respectively, while the corresponding peaks for Mn $2p_{1/2}$ appears at 652.37, 653.14 and 654.77 eV. These values are in agreement with the previously reported values.^{20–29} The presence of multiple valence states for the cation is also evident from the O 1s analysis.^{21,28,29} The O 1s peak can be resolved into three components due to the three different oxidation states of cation as shown in figure 6d.^{20,21,28,29} These correspond to the presence of lattice oxygen bonded to Mn^{2+} , Mn^{3+} and Mn^{4+} in Mn_3O_4 . The peaks appearing at 529.56 and 530.07 eV, respectively, correspond to Mn^{3+} and Mn^{2+} in Mn_3O_4 while the peak at 531.50 eV is associated with the presence of Mn^{4+} ions.^{20,21,28,29} Thus the XPS analysis conclusively establishes the presence of Mn^{4+} together with Mn^{2+} and Mn^{3+} ions in the sample.

3.4 Study of electrochemical response

3.4a Current–potential studies: Figure 7 shows the cyclic voltammograms at different scan rates ranging from 0.01 to 20 mV s^{-1} . Current increases with the potential and reaches a maximum value at 1 V and also decreases with the decrease in the potential. The shape of the CVs is quasirectangular, which confirms that the electrochemical reaction in Mn_3O_4 electrodes have reversibility with KOH electrolyte.⁹ It was found that the current density increases with an increase in the scan rate and reaches maximum for 20 mV s^{-1} . This shows that the voltametric current density is directly proportional to the scan rates of CV, which indicates the behaviour of an ideal capacitor.^{10,30} Moreover, there is no distortion in the curves at higher scan rates, which also confirms good electrochemical behaviour of the active material.³¹ The average current density during the charging part of the CVs as a function of scan rate is shown in figure 8. It is found that the average current density increase with scan rate. This is similar to the results for Mn_3O_4 thin films with average crystallite sizes of 29⁷ and 15 nm¹⁰ synthesized through chemical bath deposition with Na_2SO_4 electrolyte in the potential range -0.1 to 0.9 V reported by Dubal *et al.*^{7,10}

Figure 6. (a) Survey spectrum, (b) Mn 2s spectrum, (c) Mn 2p spectrum and (d) O 1s spectrum of nanostructured Mn₃O₄.

Table 1. Result of deconvolution of the Mn 2p, 3s and O 1s XPS spectra and comparison with reported values.

Manganese ions	Mn ²⁺		Mn ³⁺		Mn ⁴⁺		Reference
	Obtained value (eV)	Reported value (eV)	Obtained value (eV)	Reported value (eV)	Obtained value (eV)	Reported value (eV)	
Binding energy of Mn 2p _{3/2}	641.14	640.6 641.0 640.9 640 640.84	642.62	641.9 641.9 641.8 641.2	644.10	642.2 642.6 642.5 643.1	Oku <i>et al</i> ²³ Castro and Polzonetti ²⁵ Foord <i>et al</i> ²⁷ Wang <i>et al</i> ²⁹
Splitting of Mn 3s	6.44	5.8 6.1 6.1 6.48 5.8 — 5.79	5.59	5.2 5.4 5.5 — — 5.2 5.41	4.71	4.7 4.5 4.5 4.72 4.6 4.7 4.78	Moses Ezhil Raj <i>et al</i> ²⁰ Ragupathy <i>et al</i> ²⁸ Oku <i>et al</i> ²³ Castro and Polzonetti ²⁵ Foord <i>et al</i> ²⁷ Moses Ezhil Raj <i>et al</i> ²⁰ Murray <i>et al</i> ²⁴ Ragupathy <i>et al</i> ²⁸ Chigane and Ishikawa ²¹
Binding energy of O 1s	530.07	530.8 529.83	529.56	529.4 529.67	531.50	530.8 529.48	Wang <i>et al</i> ²⁹ Chigane and Ishikawa ²¹

Figure 7. Cyclic voltammograms of the symmetric capacitor using nanostructured Mn_3O_4 at different scan rates.

The capacitance, C of the symmetric capacitor was calculated using the equation $C = I/(dV/dt)$, where I is the average current in amperes and dV/dt the voltage scanning rate.^{10,32} The specific capacitance (C_s) was estimated as $C_s = 4C/M$ where M is the average mass of the symmetric electrodes.³² The capacitance values were also measured from the area under the CVs using the formula, $C = \int (I/V)dt$.³³ The specific capacitance values estimated from the two methods are nearly equal. The average of the specific capacitance at each scan rate estimated using the above two equations are shown in figure 8. Maximum specific capacitance of 1330.16 F g^{-1} was obtained at a scan rate of 0.01 mV s^{-1} , while it is 39.58 F g^{-1} at 5 mV s^{-1} . At 20 mV s^{-1} the specific capacitance is 8.67 F g^{-1} .

Ghodbane *et al*³⁴ had reported specific capacitance of 14 F g^{-1} for nanostructured Mn_3O_4 at a scan rate of 5 mV s^{-1} with $0.5 \text{ M K}_2\text{SO}_4$.³⁴ Dubal *et al*¹⁰ had reported specific capacitance values in the range of $314\text{--}245 \text{ F g}^{-1}$ for Mn_3O_4 thin films ($1.23 \mu\text{m}$ thickness) as an active material with $1 \text{ M Na}_2\text{SO}_4$ electrolyte at scan rates in the range $5\text{--}100 \text{ mV s}^{-1}$.¹⁰ Also Xing *et al*⁸ had reported specific capacitance of 172 F g^{-1} (rate not mentioned) for nanocrystalline Mn_3O_4 sample with a particle size of 6.2 nm .⁸ Sankar *et al*³¹ had obtained maximum specific capacitance of 135 F g^{-1} for nanostructured Mn_3O_4 with an average crystallite size of 15 nm synthesized through the

Figure 8. Average current density and average specific capacitance with scan rate.

microwave-assisted reflux method at a scan rate of 2 mV s^{-1} using 1 M NaNO_3 electrolyte.³¹ The decrease in specific capacitance with increase in scan rate was also reported by Sankar *et al*.³¹ Sankar *et al*³¹ also reported a specific capacitance of 94 F g^{-1} for Mn_3O_4 with an average size of 50 nm with 6 M KOH electrolyte.⁹ Misnon *et al*³⁵ had reported a specific capacitance of 294.6 F g^{-1} for

nanoflower-like MnO_2 with 1 M KOH electrolyte at the scan rate of 2 mV s^{-1} .³⁵ But Mn_2O_3 nanospheres exhibit a specific capacitance of $40\text{--}50 \text{ F g}^{-1}$ with 6 M KOH electrolyte at the scan rate of 5 mV s^{-1} .³⁶

In the present case, high values of specific capacitance was obtained for smaller scan rate 0.01 mV s^{-1} while at higher scan rates the specific capacitance is rather low. These values are much smaller than that reported for hydrous RuO_2 , viz., $\sim 720 \text{ F g}^{-1}$.^{37,38} The low value of specific surface area estimated from BET analysis indicates that the entire surface area is not available probably due to the presence of closed pores. At low scan rates the ions in the KOH electrolyte are completely occupying the available sites in the inner and outer surfaces of the active material of the electrode, because the ions have enough time to occupy all the available sites in the active material.^{9,31} Moreover the ionic conductivity and mobility of the K^+ ions in aqueous solution increases the propagation of ions at low scan rates.⁹ At higher scan rates, due to restricted rate of movement during charge–discharge through the electrolyte, the ions in the electrolyte have difficulty to diffuse into the available sites in the inner and outer surface of the active electrode material.^{9,31} Thus the interaction between the active material and electrode is reduced at higher scan rates.^{9,31} It is to be analysed whether the capacitance can be improved at higher scan rates if the active material is in the form of thin film as in the study reported by Dubal *et al.*¹⁰ In a recent report, Sankar *et al.*⁹ had studied the performance of nanostructured Mn_3O_4 as the active material in supercapacitor with different electrolytes.⁹ It was found that 6 M KOH was the most suitable electrolyte giving maximum specific capacitance.⁹ But the smaller value specific capacitance at higher scan rates obtained for the present sample with 6 M KOH electrolyte, it is clear that the suitable electrolyte and specific capacitance could depend on the synthesis route, morphology, type, concentration of defects, etc. Therefore, for improving the specific capacitance at higher rates, other electrolytes such as Na_2SO_4 , polymer gel-type electrodes will be explored in the near future.^{10,42}

3.4b Electrochemical impedance spectral analysis: The electrochemical impedance measurement was carried in the frequency range of 1 Hz–600 kHz was carried out and the Nyquist plot is shown in figure 9. Three distinct regions corresponding to different frequency ranges are evident from the inset of figure 9.⁴⁰ In the Nyquist plot, the intersection made on the real axis in the high frequency region corresponds to the solution resistance (R_s). One depressed semi-circle observed in the higher to medium frequency region represents the charge transfer resistance at the electrode–electrolyte interface.^{9,31} The appearance of a spike in the low frequency region is a characteristic of the supercapacitor. The spike represents the resistance offered during the diffusion of ions into the electrode material, the Warburg impedance, W .^{9,31} The phase angle of spike is greater than 45° in the

Figure 9. Nyquist plot of the symmetric supercapacitor.

low frequency region, which is the characteristic of ion diffusion into the porous structure of the electrode.^{9,31,40} The vertical line in this frequency range in the Nyquist plot shows the purely capacitive nature of the Mn_3O_4 electrode.⁴⁰

3.4c The charge-discharge analysis: Figure 10 shows the galvanostatic charge–discharge curves at three different fixed currents, viz., 1.27, 6.37 and 12.74 mA cm^{-2} . It can be noted that the rate of charging and discharging decreases with increase in the fixed current. The charge–discharge curve is almost symmetrical for all the curves, which indicate the high reversibility and reactivity of the active material.^{8,40} At the beginning of the discharge curve, a small potential or IR drop is found which is due to the internal resistance of the electrode material.^{9,31} This internal resistance includes the contact resistance between the electrode material and the electrolyte, the resistance of the electrolyte and charge transfer.^{9,31} It is also clear from the figure 10 that the internal resistance of the electrochemical cell increases with increase in the charging current.⁹ The time period of one charge–discharge cycle for 1.27, 6.37 and 12.74 mA cm^{-2} are, respectively, 669.2, 93.6 and 36.8 ms. The power density was estimated using the relation $P = E/tM = Q\Delta V/tM$, where P , E , Q , ΔV , t and M are the power density, energy density, charge, voltage, time for charging/discharging and mass of the active material used.^{40,41} The estimated power density values for 1.27, 6.37 and 12.74 mA cm^{-2} currents are, respectively, 0.42, 2.28 and 4.27 kW kg^{-1} and the corresponding energy densities are 7.89×10^{-2} , 5.95×10^{-2} and $4.36 \times 10^{-2} \text{ Wh kg}^{-1}$. These values are comparable to those reported for the manganese oxide-based active materials for supercapacitors.⁴² It was observed that there is no variation in the value of energy and power density after fifty charge–discharge cycles.

Figure 10. Chronopotentiograms for the symmetric capacitor at different fixed currents.

4. Conclusion

Nanostructured Mn_3O_4 with an average crystallite size of ~ 19 nm was synthesized through a microwave-assisted chemical route. The average particle size estimated from the TEM analysis is ~ 29 nm. Brunauer–Emmett–Teller (BET) analysis gives a specific surface area of $12 \text{ m}^2 \text{ g}^{-1}$ and reveals the mesoporous nature of the sample. The presence of Mn^{4+} ions at the octahedral sites were identified from the decreased value of c/a and it is verified from XPS analysis. Cyclic voltammetry studies in the potential range 0–1 V indicate that the material can be used as an electrode for supercapacitors applications. The power density and energy density values estimated from the chronopotentiograms recorded at different constant currents also support the possible use in the field of supercapacitors. The improvement in the performance of the supercapacitor by using the active material in thin film form and with different electrolytes will be attempted in the near future. Further, the possible detrimental effect of the presence of trace amount of MnO and the possibility of formation of MnOOH in the presence of alkaline medium will also be investigated as a future work.

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