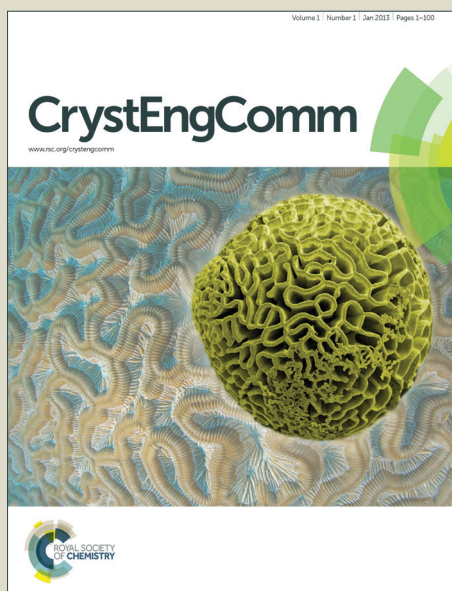


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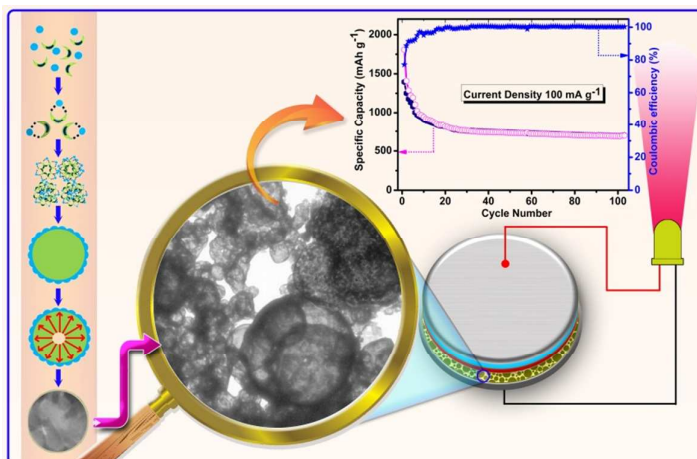
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Graphical Abstract



Ascorbic acid aided inside-out Ostwald ripening promotes the formation of Mn_2O_3 microspheres with a hollow interior surface that exhibits an appreciable capacity of 610 mAh g^{-1} , even after completing 100 cycles.

ARTICLE

Pristine Hollow Microspheres of Mn_2O_3 as Potential Anode for Lithium-Ion Batteries

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Hollow Mn_2O_3 microspheres have been synthesized by a simple and an easy-to-adopt solvothermal method, facilitated by ethanol to obtain the phase pure product at 600 °C. Herein, the ascorbic acid aided inside-out Ostwald ripening promotes the formation of porous microspheres with a hollow interior surface, desirable to allow faster transport of lithium ions and to accommodate the volume changes associated with Mn_2O_3 anode, especially upon extended cycling. Further, an appreciable high surface area of 426.6 m^2g^{-1} has been calculated from BET analysis, which is in favour of imparting excellent electrochemical properties that include high reversible capacity, good cycling stability and an acceptable rate capability. Interestingly, Mn_2O_3 hollow microspheres exhibit 425 mAh g^{-1} under the influence of 1A g^{-1} current density, thus qualifying itself as a high rate anode material, bestowed with the added advantage of appreciable high capacity, extractable under nominal current densities. For instance, without requiring the formation of composite, the as-received Mn_2O_3 anode delivers a steady state capacity of 760 mAh g^{-1} at 50 mA g^{-1} and 610 mAh g^{-1} at 100 mA g^{-1} , especially after completing 100 cycles. The synergistic advantage of microspheres containing hierarchically arranged nanostructures and the hollow interior nature with a better uptake of electrolyte results in obtaining promising electrochemical performance from the currently synthesized Mn_2O_3 anode.

1. Introduction

Lithium-ion batteries, as promising power sources for portable electronics such as mobile phone, laptop, camera etc. have a major dependence on better performing electrode materials. In this regard, the widely exploited graphite anodes suffer from inadmissible irreversible capacity loss, apart from their inherent capacity sealing of 372 mAh g^{-1} , which is inadequate to meet with the high power and energy requirements of next generation e-gadgets. With a view to surpass the inherent intricacies of graphite anode, transition metal oxides such as Co_3O_4 ,¹ Fe_3O_4 ,² NiO ,³ ZnCo_2O_4 ⁴ and Mn_xO_y ^{5,6} are being investigated as probable alternative anodes. Factors such as high capacity, environmental benignity, lower operating potential, structural stability upon extended cycles and feasibility to synthesize the material using a simple and an easy-to-adopt method play a crucial role in recommending any candidate as an alternate to graphite anodes.⁷ Among the upcoming and alternative Mn_xO_y anodes, Mn_2O_3 assumes greater importance, especially due to the high theoretical capacity of 1018 mAh g^{-1} , ecobenign nature, abundant availability of manganese and a relatively lower operating potential. However, critical issues related to the oxidation state of manganese and the possibility of obtaining single phase Mn_2O_3 without co-existing impurities are certain prime factors, due to which Mn_2O_3 anodes are less familiar than MnO_2 .

Further, problems based on volume expansion, aggregation and intrinsic poor conductivity of Mn_2O_3 deeply affect the electrochemical performance, especially upon cycling, which in turn hampers its wider acceptance as a better performing anode material.⁸

To combat the said issues, one can focus on the synthesis-structure-morphology-performance relationship, which in turn would offer dual benefits such as a gain on the basic understanding of inter-dependence of factors concerned and the possibility of identifying tailor-made compound formulations with customised synthesis approach to arrive at synergistically improved electrochemical behaviour. Of the several attempts made to alleviate the inherent drawbacks of Mn_2O_3 anode, hollow micro-/nanostructure with the dimensionally controlled growth of particles, otherwise known as the formation of particles with desired size and shape with the hollow interior structure attract the attention of recent researchers, as the metal oxide hollow nanostructures are reported to provide high capacity, rate capability and cycling stability.^{9,10,11}

Hollow nanostructured electrode materials are widely used in energy storage and conversion applications,^{12,13,14,15} mainly due to their ability to suppress the volume changes and electrochemical pulverisation of electrode material upon lithiation/delithiation. Because, the hollow or empty interior space effectively manages the strain associated with the aforesaid issues and improves the cycling behaviour with reduced capacity fading. Further, benefits such as high surface

area, low density and short lithium diffusion path render an indispensable importance to hollow micro-/nanostructures, especially when deployed as electrodes in rechargeable lithium-ion cell assembly.¹⁶ In this direction, Mn₂O₃ nanocones,¹⁷ triple shelled Mn₂O₃ nanocubes,¹⁸ porous Mn₂O₃, hierarchical microspheres¹⁹ and Mn₂O₃ hollow nanostructures¹⁰ are reported in the literature, wherein either a stringent synthesis approach or requirement of sequential multi-step reaction is involved.^{20,21,22}

Generally, template assisted hollow spheres and the non-spherical hollow nanostructures pose unsolved issues on tedious synthesis procedure and preservation of shape with high residual stress. Approaches based on Kirkendall effect,²³⁻²⁵ galvanic replacement,²⁶⁻²⁸ chemical etching,²⁹⁻³² thermal decomposition, soft biotemplates³³ and inside-out Ostwald ripening^{34,35} could be exploited to obtain hollow nanostructures. However, morphological uniformity and spheres with hollow interior nature apparently pose challenges in realizing the same, especially through a simplified synthesis approach.³⁷

In this regard, the present communication describes a customised synthesis approach that involves a simple solvothermal method, requiring ascorbic acid as a structure directing additive, facilitating the formation of hollow interior nature *via* Ostwald diffusion process in ethanol medium using manganese acetate as reactant. Thermal decomposition of the as-received white precipitate results in the formation of hollow Mn₂O₃ microspheres, constructed by hierarchically arranged nanostructures. Herein, the in-situ formed manganese ascorbate core shell upon furnace calcination leads to the formation of Mn₂O₃, by removing the residual carbon obtained from ascorbic acid in the form of CO₂, thus forming porous and hollow microspheres of Mn₂O₃.

Quite different from the reported range of capacity, the currently synthesized Mn₂O₃ hollow microsphere anode delivers a capacity as high as 760 and 610 mAh g⁻¹, even after completing 100 cycles respectively under the influence of 50 and 100 mA g⁻¹. Further, an appreciable capacity of 425 mAh g⁻¹ has been obtained at 1A g⁻¹ current density, thus surpassing the reported anodes of similar category. The combination of permeable thin shells and the effective role of hollow interior in offering better tolerance against the structural strain and volume change are responsible for the synergistically improved electrochemical performance of Mn₂O₃ anode in terms of rate capability and high capacity, which is the significance of the present study. Further, this communication offers an understanding on the type of reaction mechanism involved and the role of synthesis approach upon structure, morphology and the electrochemical properties of Mn₂O₃.

2. Experimental Section

2.1. Preparation of Mn₂O₃

Hollow Mn₂O₃ micro spheres were prepared by solvothermal method. In this, ascorbic acid, Mn(OAc)₂·4H₂O (Alfa Aesar) and C₂H₅OH (Alfa Aesar) were used as received without further purification. Ascorbic acid (2 mmol) and manganese acetate (1 mmol) were added to 35 ml of ethanol, and the mixture was stirred magnetically at room temperature, to form white colour precipitate. Then, the content of the beaker was transferred to a 50 ml Teflon-lined stainless steel autoclave and heated at 120 °C for 24 h. Subsequently, the autoclave was cooled to room temperature and the dense white colour precipitate thus obtained was washed with distilled water and

acetone several times. The resulting material was dried at 70 °C for 10 h in vacuum. Then, the dried material was calcined at 600 °C for 2 h with a heating rate of 2 °C min⁻¹ to obtain Mn₂O₃ hollow microspheres.

3. Physical Characterisation

The crystal structure of the material was characterised by Bruker D8 Advance X-ray diffractometer using Ni-filtered Cu K α radiation (λ = 1.5406 Å). Fourier transform infrared spectroscopy (FT-IR) studies of the samples were carried out by Bruker Tensor 27 FT-IR Spectrometer using KBr pellet. Thermogravimetry analysis (TGA) was performed from room temperature to 750 °C in air using SDT Q600 thermogravimetric analyser. The Scanning electron microscopy (SEM) images of the samples were captured with JEOL JSM6480LV system and Transmission electron microscopy (TEM) images of sample were obtained from Tecnai 20 G2 (FEI make). Field emission scanning electron microscopy (FESEM) images and Elemental mapping of the samples were obtained with FESEM (Zeiss Field Emission Scanning Electron Microscope). X-ray photoelectron spectroscopy (XPS, MULTILAB 2000 Base system with X-Ray, Auger and ISS attachments) was used to characterize the surface composition of the sample. The Brunauer- Emmett-Teller surface area of the product was determined by using Quantachrome, NOVA version 11.02.

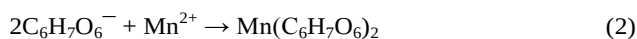
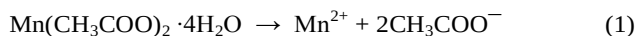
4. Electrochemical Characterisation

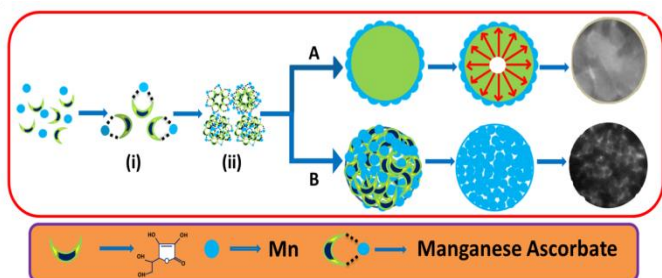
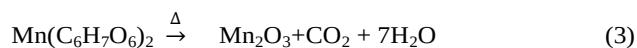
Electrochemical measurements were carried out using CR2032 type coin cells, wherein copper foil has been used as the current collector and lithium metal as counter and reference electrode. A solution consisting of 1.0 M LiPF₆ dissolved in 1:1 (v/v) mixture of ethylene carbonate (EC)/ dimethyl carbonate (DMC) serves as the electrolyte. The electrode was prepared by mixing Mn₂O₃ hollow microspheres (70 wt%) as the active material, conductive carbon (Super-P) (20 wt%) and polyvinylidene fluoride binder (10 wt%). Using N-methyl-2-pyrrolidone as solvent, the mixture was made as slurry and coated on copper foil. The coated electrode was dried in oven at 80 °C to evaporate NMP, hot roll pressed to ensure better adherence and cut in to circular discs of 15.5 mm diameter to act as anode in the coin cell assembly. Cyclic voltammetry (CV) was recorded with VMP3 multichannel potentiostat-galvanostat system (Biologic Science Instrument) in the potential window of 0.01-3.0 V and at the scan rate of 0.1mV s⁻¹. The charge-discharge behaviour was investigated with Arbin battery cycler. Electrochemical impedance spectroscopy (EIS) measurements are carried out on a Biologic VSP electrochemical work station in the frequency ranging from 10 KHz to 100 mHz with an amplitude voltage of 10 mV at room temperature.

5. Result and Discussion

5.1. Characterisation of hollow Mn₂O₃ micro spheres

Addition of ascorbic acid and manganese acetate in ethanol leads to the formation of hollow spheres of Mn₂O₃, according to the following equations.





Scheme 1. Synthesis of hollow and porous Mn_2O_3 microspheres

Herein, two different and possible mechanisms could be ascertained, based on the schematic representation (Scheme 1) of formation of Mn_2O_3 hollow microspheres. One possibility is that, a template-free formation of hollow structure, aided by the inside-out Ostwald ripening is responsible for the formation of hollow microsphere with the desired interior cavity as the final product by following the path A. In other words, the white colour solution that contains manganese ascorbate (i) upon autoclave cooking forms colloidal aggregates (ii), which in turn undergoes a thermodynamically favoured and spontaneous evacuation of energetically less stable part of the core material that contains energetically less stable components. The continuous inside-out diffusion of less dense and poorly crystallised particles from the central part of the colloidal mass leads to a sequential re-deposition of the colloidal particles on the outer surface of the aggregates, thus responsible for the formation of void volume at the center. As a result, hollow microspheres of Mn_2O_3 are obtained, wherein the carefully selected heating rate of $2^\circ\text{C}/\text{min}$ ensures the maintenance of hollow sphere morphology with admissible inhomogeneity based on the size of the individual spheres. On the other hand, as indicated by path B, the combination of in-situ formed acetic acid and the added ethanol to form an emulsion may be enunciated as the reason for the formation of nanostructured particles. Herein, the added ascorbic acid may render carbon wiring and control the growth of the individual particles. However, prolonged drying at 70°C for 10 h may lead to the aggregation of nanoparticles to form microspheres, wherein carbon wiring around the particles of the active material is believed to get maintained. But the same upon furnace calcination will undergo thermal decomposition, during which the carbon wiring is expected to disappear to form the admissibly disintegrated and porous assembly of nanoparticles present in Mn_2O_3 microspheres.

Of the two possibilities, the formation of microsphere with a hollow interior, resulting from the inside-out Ostwald ripening (via. path A) is believed to take place, as the second possibility (path B) does not justify the formation of hollow interior nature of Mn_2O_3 microspheres. Hereagain, the surface crystallisation of diffused out colloids renders the formation of outer shell with a desired thickness, thus facilitating the facile intercalation/deintercalation of lithium ions. Further, the

thermal decomposition upon furnace heating is believed to be responsible for the formation of porous surface, resulting from the escape of CO_2 from the shell. In other words, the in-situ formed ascorbate shell expels CO_2 upon furnace heating, and the resultant product with no carbon content is better seen from the energy dispersive spectroscopy (EDS) and related elemental mapping analysis, which are discussed in the forthcoming explanation.

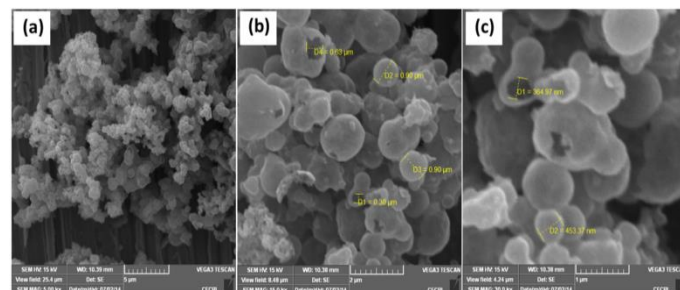


Fig. 1 SEM images of hollow and porous Mn_2O_3 microspheres

Morphology of the chosen precursor and the formed Mn_2O_3 hollow microspheres as final product has been characterised by SEM (Fig. S1 and Fig. 1). From the recorded images, it is quite clear that unlike the final product (Fig. 1), the precursor contains no porous surface and the presence of solid or dense spherical particles of $1\text{--}2\ \mu\text{m}$ size of the precursor with a smooth surface are evident in Fig. S1a and b. On the other hand, the furnace heated product, obtained after solvothermal treatment is found to possess twin advantages, viz., hollow interior and porous surface (Fig. 1). The formation of porous and hollow micro spheres with an inlet cleavage point to admit facile transport of ions and easy percolation of electrolyte is the significance of the present study (Fig. 2).

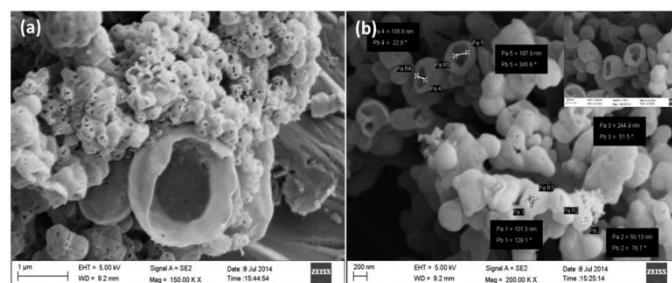


Fig. 2 FESEM images of Mn_2O_3 microspheres with a hollow interior structure

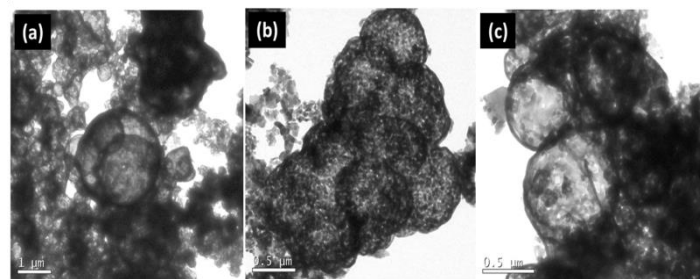


Fig. 3 TEM images of hollow Mn_2O_3 microspheres formed out of nano crystalline spherical assembly

The volume expansion related issues and the required lithium ion transport kinetics are believed to get addressed due to the presence of hollow interior structure (Fig. 2) and the porous microsphere, consisting of nano crystalline spherical assembly are evident from the recorded high magnification FESEM and TEM images of the final product obtained (Fig. 2 and 3). Further, the hollow interior could be identified from the difference in the intensity of the TEM images showing a pale interior and a dark curvature of the spherical particles. The thickness of the spherical shell is ~ 65 nm and the diameter of the interior cavity is ~ 850 nm (Fig. 3), as understood from the TEM results of Mn_2O_3 microspheres.

Intrigued by the porous nature of hollow microspheres, the porosity and surface area of Mn_2O_3 microspheres were determined from BJH model and BET method respectively (Fig. S2). Nitrogen adsorption-desorption isotherms were recorded at 77 K for Mn_2O_3 in the range of relative pressure P/P_0 from 0.1 to 1.0. The hollow spheres of Mn_2O_3 exhibit type IV isotherm, which is a typical and characteristic property of Mn_xO_y oxide electrodes. The average pore size of 15 nm (Inset of Fig. S2) and the mesoporous nature of currently synthesized Mn_2O_3 hollow microspheres correspond to a BET surface area of $426.6 \text{ m}^2\text{g}^{-1}$ and a pore volume of $0.106 \text{ cm}^3\text{g}^{-1}$ respectively. Herein, the observed larger surface area of the Mn_2O_3 electrode material would be desirable in facilitating fast lithium ion transport kinetics and enhanced electrolyte contact area, which is noteworthy.^{37,38}

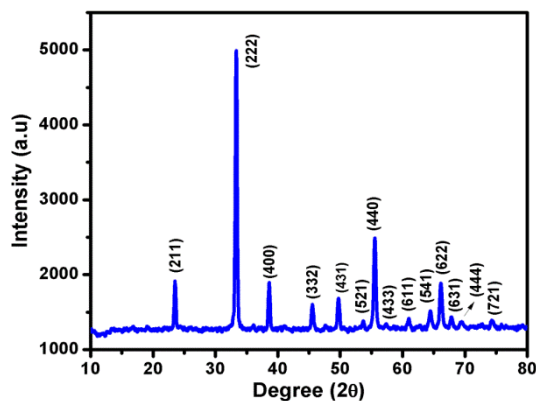


Fig. 4 XRD pattern evidencing the crystalline nature of hollow Mn_2O_3 microspheres

The formation and phase purity of Mn_2O_3 micro spheres have been investigated by XRD. While the XRD pattern of the precursor (Fig. S3) correspond to the presence of amorphous phase, the bragg peaks of the final product (Fig. 4) correspond to the formation of crystalline Mn_2O_3 . Particularly, a striking similarity in the search match analysis has been observed with respect to JCPDS No: 41-1442 with a cubic structure and $Ia\bar{3}$ space group. The calculated lattice parameter value of $a = b = c = 9.4065 \text{ \AA}$ is in agreement with Mn_2O_3 with a cubic structure.^{17,39} Absence of additional peaks confirms the formation of phase pure Mn_2O_3 without any undesirable impurities.

TGA behavior of the precursor that has been used to prepare the title compound was recorded by subjecting the same to a heat treatment varying from ambient temperature to 750°C with a heating rate $10^\circ\text{C}/\text{min}$. The results obtained is appended in Fig. 5. An approximate weight loss of 16 wt% is noticed around 180°C that corresponds to the removal of absorbed and occluded water molecules present in the meta stable colloidal aggregate, prior to the Ostwald diffusion process. On the other hand, the presence of sharp and endothermic peak around $200\text{--}350^\circ\text{C}$ range corresponds to the occurrence of inside-out diffusion of ions along with the liberation of CO_2 to form MnO_2 with the desired physical characteristics.⁴⁰ Finally, the furnace heating at 600°C results in the formation of Mn_2O_3 with the release of excess oxygen and removal of residual carbon, wherein no significant weight loss is anticipated. As a result, a flat profile is observed after 350°C , thus evidencing the formation of MnO_2 at 350°C and that of the final product (Mn_2O_3) obtained upon prolonged heating of MnO_2 up to 600°C .^{40,41}

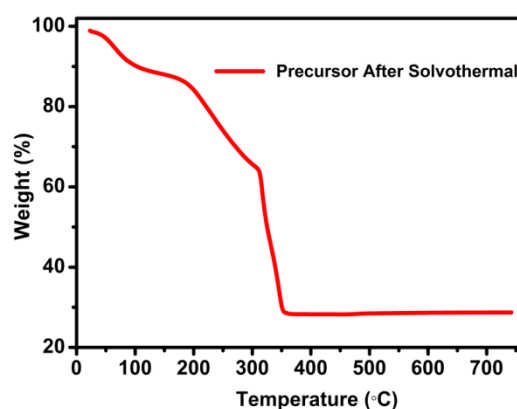


Fig. 5 TGA behavior of precursor recorded after solvothermal treatment

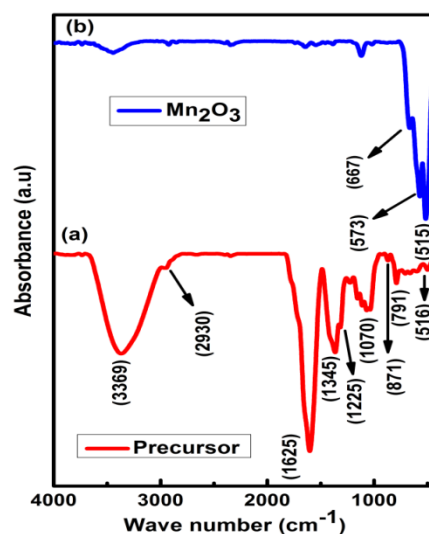


Fig. 6 FTIR spectra of (a) precursor and (b) hollow Mn_2O_3 microspheres

Fig. 6 displays the FT-IR spectra of the precursor and the hollow Mn_2O_3 microspheres recorded in the detection range of

400–4000 cm^{-1} . Peaks corresponding to ascorbic acid will normally appear at 1670 and 1330 cm^{-1} , due to the presence of stretching vibrations of C–C double bond and enol-hydroxyl groups, respectively.^{42,43} The said peaks with a small shift to the extent of 1625 and 1345 cm^{-1} have been observed in the currently recorded FTIR spectra of the precursor (Fig. 6a). Similarly, broad band centered at 3369 and a peak at 2930 cm^{-1} are due to the presence of hydroxyl groups and C–H stretching mode respectively. Further, the presence of three peaks around 512, 871 and 1225 cm^{-1} may be correlated to the presence of M–O, C–C and CH_2 groups of manganese ascorbate (Fig. 6a).⁴⁴ Interestingly, formation of Mn_2O_3 is understood from the appearance of new bands at 575 and 667 cm^{-1} , which could be attributed to the M–O bonds of Mn_2O_3 (Fig. 6b).^{9,45}

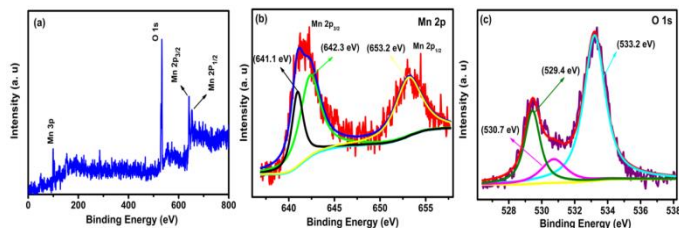


Fig. 7 XPS results of hollow Mn_2O_3 microspheres (a) survey spectrum, (b) Mn 2p and (c) O 1s spectra

In order to get further information about the purity and chemical composition of the sample, we carried out X-ray photoelectron spectroscopy (XPS). Fig. 7a shows the XPS survey spectrum of Mn_2O_3 hollow microspheres, in which characteristic peaks due to the presence of Mn and O are found to exist. Fig. 7b displays the high-resolution Mn 2p spectrum, wherein two peaks with the binding energy values of 641.5 and 653.3 eV indicate the presence of Mn 2p_{3/2} and Mn 2p_{1/2} signals. The spin energy separation between these peaks is 11.7 eV, which is matching with that of standard Mn_2O_3 .⁴⁶ O 1s spectrum after deconvolution shows three peaks positioned at 529.4, 530.7 and 533.2 eV (Fig. 7c), corresponding to the presence of oxygen in binary oxide thus confirming the presence of Mn_2O_3 .^{47–49}

Fig. S4 illustrates the EDX spectrum of the precursor and the final compound Mn_2O_3 obtained as hollow microspheres. Presence of Mn, O and C in the precursor (Fig. S4a–d) and the corresponding presence of Mn and O in the final product (Fig. S4e–g) evidences the absence of carbon in Mn_2O_3 obtained as the end product. Hence, the earlier explanation on the possible removal of residual carbon from the manganese ascorbate core shell to form a porous final product could be substantiated and better understood from the elemental mapping and EDX analyses.

6. Electrochemical Characterization of Mn_2O_3 anode

6.1. Cyclic Voltammetry

Fig. 8 shows the cyclic voltammetry (CV) behavior of Mn_2O_3 anode material recorded in the voltage range of 0.01 to 3.0 V versus Li/Li^+ at a sweeping rate of 0.05 mV s^{-1} at room temperature. First cycle CV behavior displays the presence of broad peak at 1.8 V, which may be ascribed to the reduction of Mn^{3+} to Mn^{2+} and the small peak at 0.69 V corresponds to the irreversible decomposition of the electrolyte to form a solid

electrolyte interface (SEI). The high current peak located at 0.13 V is due to the further reduction of Mn^{2+} to Mn^0 . In the reversible cycling process, two oxidation peaks are visible at 1.2 and 2.3 V corresponding to Mn^0 to Mn^{2+} and Mn^{2+} to Mn^{3+} reactions.^{50,51} After the initial CV cycle, the subsequent cycling behavior of Mn_2O_3 anode exhibits two reduction and oxidation peaks, corresponding to the aforesaid redox pairs.

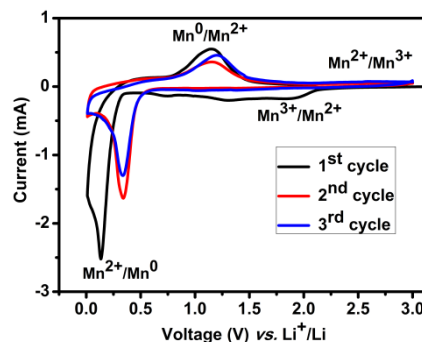
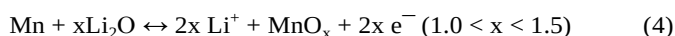
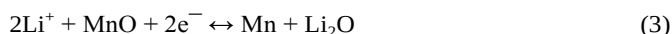
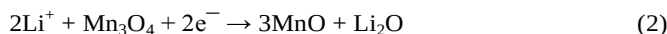
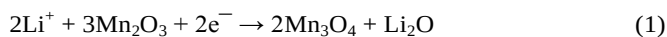


Fig. 8 CV behavior of hollow Mn_2O_3 microsphere anode recorded at a scan rate of 0.05 mV s^{-1} in the voltage range of 0.01–3.0 V vs Li^+/Li

Interestingly, the perfect overlapping of CV peaks indicates the excellent cycling and structural reversibility of Mn_2O_3 anode upon progressive cycling process. However, the slight decrease in the peak current value of the second cycle in comparison with that of the first cycle infers the occurrence of irreversible capacity loss, which is not unusual. Based on the said points, the lithium insertion and extraction process of Mn_2O_3 anode could be summarized as follows.^{44,52}



6.2. Charge-Discharge Studies

Fig. 9a and b depict the charge-discharge profile and the cycling performance of Mn_2O_3 anode, investigated under the influence of 50 mA g^{-1} current density. It is evident from the charge-discharge behavior of the first cycle of Mn_2O_3 anode (Fig. S5) that a decrease from 3.0 V to the first plateau at 1.8 V, corresponding to a capacity of 261 mAh g^{-1} is due to the conversion of Mn_2O_3 to Mn_3O_4 . The second plateau at about 1.2 V, corresponding to the conversion of Mn_3O_4 to MnO and the subsequent larger plateau around 0.3 V, due to the formation of Mn^{2+} from Mn^0 attribute to a capacity of 219 and 1664 mAh g^{-1} respectively. As a result, an initial discharge capacity of 2144 mAh g^{-1} has been exhibited by Mn_2O_3 anode. Such a high discharge capacity value, which is twice the theoretical capacity of Mn_2O_3 (1018 mAh g^{-1}) is believed to be due to the initial and irreversible decomposition of the electrolyte to form SEI, (especially at lower operating voltage) along with the formation of Li_2O that aids the metal/ Li_2O interfacial charging process.^{53–55} The subsequent oxidation of metal to Mn^{2+} and Mn^{3+} is better understood from the charging

plateaus at about 1.0 and 2.1 V, corresponding to a total capacity of 1559 mAh g⁻¹. As a result, an inferior coulombic efficiency of 71 % has been exhibited initially by the Mn₂O₃ hollow sphere anode, which upon progressive cycling exhibits significantly increased coulombic efficiency behavior to the extent of 98.6 %. Similarly, despite the initial drop in the capacity value, a progressive and steady-state capacity of ~770 mAh g⁻¹ has been delivered by Mn₂O₃ anode up to 100 cycles (Fig. 9a), which is noteworthy.

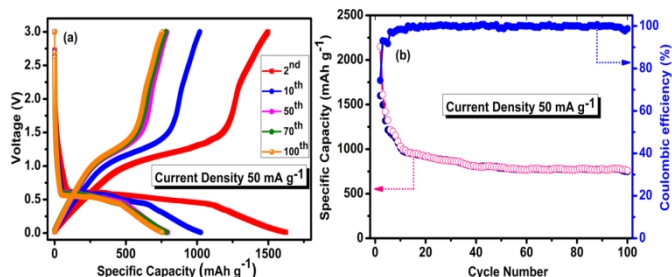


Fig. 9 (a) Charge-discharge profile and (b) cycling performance along with coulombic efficiency of hollow Mn₂O₃ microspheres investigated as anode under a current density of 50 mA g⁻¹ in the voltage range of 0.01-3.00 V vs Li⁺/Li

Based on the encouraging result obtained with 50 mA g⁻¹ current density, the title anode was subjected to a current density of 100 mA g⁻¹. Hereagain, an appreciable capacity of 750 mAh g⁻¹ at the end of 30 cycles and about 610 mAh g⁻¹ at the 100th cycle have been exhibited (Fig. 10a) by the currently synthesized Mn₂O₃ anode, irrespective of the higher initial capacity of 1800 mAh g⁻¹ (Fig. 10b). Our capacity values are higher than the reported value,¹⁸ thus validating the suitability of solvothermally synthesized Mn₂O₃ hollow sphere anode for its potential application in rechargeable lithium batteries.

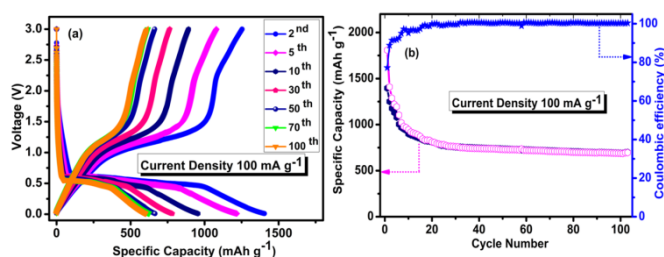


Fig. 10 (a) Charge-discharge profile and (b) cycling performance along with coulombic efficiency of hollow Mn₂O₃ microsphere anode at a current density of 100 mA g⁻¹ in the voltage range of 0.01-3.00 V vs Li⁺/Li

6.3. Rate capability and Electrochemical Impedance Spectroscopy (EIS) studies

Further, with a view to investigate and to qualify the title anode for rated capacity behavior (Fig. 11), cell containing Mn₂O₃ anode has been subjected to discharge under various current densities in the sequential order of 50, 100, 200, 400, 500, 600, 700, 800 mA g⁻¹ and 1 A g⁻¹ and subsequently switched back to 50 mA g⁻¹ current density. In particular, a minimum of 5 cycles was performed at every chosen current density and thus after completing the 50th cycle under the influence of 1 A g⁻¹, the cell

was switched back to a lower current density 50 mA g⁻¹ with a view to understand the ability of Mn₂O₃ anode to resume the capacity, especially after experiencing series of high current densities. The cell shows a gradually decreasing capacity pattern of 2350 (50 mA g⁻¹), 1169 (100 mA g⁻¹), 1031 (200 mA g⁻¹), 735 (500 mA g⁻¹) and 425 mAh g⁻¹ (1 A g⁻¹) with the increasing current density values. More interestingly, the cell exhibits a capacity of about 851 mAh g⁻¹, especially when subjected to 50 mA g⁻¹ after having experienced a high current density of 1 A g⁻¹. This is an evidence of better capacity retention behavior of Mn₂O₃ anode. The observed capacity values under different current density conditions are either comparable with or superior than the reported values,^{18,44,50,52} thus enunciating the suitability of currently synthesized Mn₂O₃ anode for rate capability behavior.

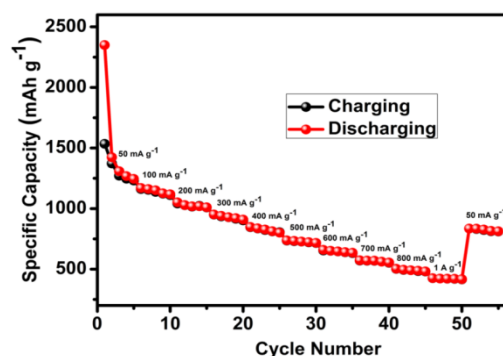


Fig. 11 Rate capability of hollow microspheres of Mn₂O₃ as anode in the voltage range of 0.01-3.00 V vs Li⁺/Li

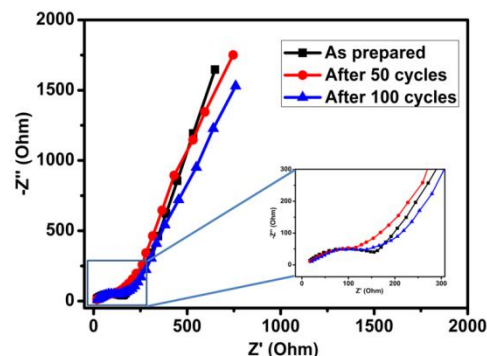


Fig. 12 Electrochemical impedance spectroscopy of Mn₂O₃ hollow microsphere anode recorded after different cycles performed at 50 mA g⁻¹; Inset: Zoomed view

A careful analysis of the impedance behavior of the as fabricated cell with those of cells after completing 50 and 100 cycles clearly evidences (Fig. 12) the decreasing R_{ct} values against increasing cycle number. Such a decrease in R_{ct} value, viz., 165, 117 and 125 Ω observed respectively for the cells after completing 0, 50 and 100 cycles clearly demonstrates the facile transport of lithium ions without any notable hindrance.^{56,57} The advantages of porous and hollow microspheres in ensuring better uptake of electrolyte, presence of hollow interior space that provides the buffering effect against the anticipated volume expansion related to manganese

based oxide anodes and the presence of core shell structure, tagged with the desired connectivity pattern to offer long term cycling and structural stability upon progressive cycling could be better understood from the observed EIS behavior of Mn_2O_3 anode.

7. Conclusions

To sum up, we have demonstrated a facile solvothermal synthesis approach, wherein the added ascorbic acid in ethanol medium facilitates the inside-out Ostwald ripening process to form porous and hollow microspheres of Mn_2O_3 . The hierarchically arranged nanostructures to form microspheres, hollow interior nature and the high surface area of currently synthesized Mn_2O_3 anode facilitate better uptake of electrolyte and faster transport kinetics of lithium ions to exhibit appreciable electrochemical properties. The hollow microsphere of Mn_2O_3 anode deliver a steady state reversible capacity of 760 mAh g^{-1} at 50 mA g^{-1} and 610 mAh g^{-1} at 100 mA g^{-1} , apart from tolerating a high current density of 1 A g^{-1} , under which a nominal capacity of 425 mAh g^{-1} has been exhibited. More specifically, formation of hollow microspheres addresses the inherent volume change issues associated with Mn_2O_3 anodes, especially through the hollow interior driven buffering activity and the hierarchically arranged nanostructures with preferred connectivity renders appreciable cycling and structural stability to the title anode. Role of synthesis method in preparing Mn_2O_3 with desired morphology and the suitability of thus formed Mn_2O_3 hollow microsphere anode for high capacity and rate capability applications are better understood from this study.

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Notes

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Electronic Supplementary Information

Fig. S1 shows SEM images of precursor and **Fig. S2** represents the N_2 adsorption-desorption isotherm of hollow Mn_2O_3 microspheres. **Fig. S3** displays the XRD pattern of precursor evidencing the amorphous nature and **Fig. S4** is the EDX and elemental mapping results of precursor (a-d) and the final product Mn_2O_3 (e-g). **Fig. S5** shows the first charge-discharge profile of Mn_2O_3 hollow micro sphere anode at a current density of 50 mA g^{-1} .

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