Engineering single crystalline Mn₃O₄ nano-octahedra with exposed highly active \{011\} facets for high performance lithium ion batteries

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Well shaped single crystalline Mn₃O₄ nano-octahedra with exposed highly active \{011\} facets at different particle sizes have been synthesized and used as anode materials for lithium ion batteries. The electrochemical results show that the smallest sized Mn₃O₄ nano-octahedra show the best cycling performance with a high initial charge capacity of 907 mA h g⁻¹ and a 50th charge capacity of 500 mA h g⁻¹ at a current density of 50 mA g⁻¹ and the best rate capability with a charge capacity of 350 mA h g⁻¹ when cycled at 500 mA g⁻¹. In particular, the nano-octahedra samples demonstrate a much better electrochemical performance in comparison with irregular shaped Mn₃O₄ nanoparticles. The best electrochemical properties of the smallest Mn₃O₄ nano-octahedra are ascribed to the lower charge transfer resistance due to the exposed highly active \{011\} facets, which can facilitate the conversion reaction of Mn₃O₄ and Li owing to the alternating Mn and O atom layers, resulting in easy formation and decomposition of the amorphous Li₂O and the multi-electron reaction. On the other hand, the best electrochemical properties of the smallest Mn₃O₄ nano-octahedra can also be attributed to the smallest size resulting in the highest specific surface area, which provides maximum contact with the electrolyte and facilitates the rapid Li-ion diffusion at the electrode/electrolyte interface and fast lithium-ion transportation within the particles. The synergy of the exposed \{011\} facets and the smallest size (and/or the highest surface area) lead to the best performance for the Mn₃O₄ nano-octahedra. Furthermore, HRTEM observations verify the oxidation of MnO to Mn₃O₄ during the charging process and confirm that the Mn₃O₄ octahedral structure can still be partly maintained after 50 discharge–charge cycles. The high Li-ion storage capacity and excellent cycling performance suggest that Mn₃O₄ nano-octahedra with exposed highly active \{011\} facets could be excellent anode materials for high-performance lithium-ion batteries.

1. Introduction

Nanostructured transition-metal oxides, such as Fe₃O₄, Fe₂O₃, CoO and NiO, have been widely studied as anode materials for lithium ion batteries (LIBs) because of their higher theoretical capacities and higher energy densities than those of conventional graphite anodes (372 mA h g⁻¹).1–7 Hausmannite Mn₃O₄ has attracted more and more attention in the field of rechargeable LIBs because of its high theoretical capacity, low toxicity, thermal stability, low price and natural abundance; in addition to its broad applications in catalysis, molecular adsorption, ion exchange, supercapacitors and magnetic applications.12 However, previous reports on Mn₃O₄ have suggested that this material has poor lithiation activity due to its low electrical conductivity (10⁻² to 10⁻⁸ S cm⁻¹) and poor cycle stability.13 For example, West et al. reported pure Mn₃O₄ with a reversible capacity of just 200 mA h g⁻¹, which is far less than the theoretical capacity of 937 mA h g⁻¹.

To solve these intrinsic drawbacks, two possible approaches have been proposed. One is to prepare Mn₃O₄ composites (or hybrids) with other components to improve the electrode conductivity. This approach is the most widely studied. For example, Fan and Whittingham prepared poly-methylmethacrylate gel modified Mn₃O₄ nanofibers and displayed a charge–discharge capacity of about 450 mA h g⁻¹; yet
the initial coulombic efficiency is very low (26%). Cobalt-doped \( \text{Mn}_3\text{O}_4 \) can exhibit a stable reversible capacity of 400 mA h g\(^{-1}\), but the first coulombic efficiency is as low as 45%. Recent studies show that reduced graphite oxide (RGO) or carbon modified \( \text{Mn}_3\text{O}_4 \) nanostructures (\( \text{Mn}_3\text{O}_4/\text{RGO} \) or \( \text{Mn}_3\text{O}_4/\text{carbon composites} \)) exhibit enhanced electrochemical properties due to the good conductivity and good elastic nature of RGO and carbon. The other approach is the design and synthesis of \( \text{Mn}_3\text{O}_4 \) structures that can provide more electroactive sites to promote the electrochemical reaction. For example, porous \( \text{Mn}_3\text{O}_4 \) exhibits an improved capacity due to its high surface area and the constructed nanostructures can provide a short distance for fast lithium-ion transportation within the structure. Apart from these porous structures, the design of well-defined \( \text{Mn}_3\text{O}_4 \) structures with exposed high surface energy facets should also be beneficial for electrochemical property enhancement.

Generally, well-defined structures with exposed high surface energy facets lead to more interesting and exciting properties. For example, Zhang \textit{et al.}\(^9\) prepared \( \text{Mn}_3\text{O}_4 \) micro-octahedra with a size range of 1–3 \( \mu \text{m} \) by using the hydrothermal method. The micro-octahedra presented excellent sensing characteristics for acetone. Jiang \textit{et al.}\(^11\) prepared \( \text{Mn}_3\text{O}_4 \) nano-octahedra with a size of around 160 nm by using an ethylenediaminetetraacetic acid disodium salt assisted hydrothermal route, which exhibited a high specific capacitance of 322 F g\(^{-1}\). Our group\(^22\) introduced a simple hydrothermal method using polyethylene glycol as a reductant and shape-directing agent for the fabrication of \( \text{Mn}_3\text{O}_4 \) nano-octahedra. The results showed that \( \text{Mn}_3\text{O}_4 \) nano-octahedra were well-shaped with a mean size of about 150 nm; they exhibited anomalous magnetic properties and high superior photodecomposition activity due to the exposed \{011\} facets. These enhanced properties suggest that \( \text{Mn}_3\text{O}_4 \) nano-octahedra with exposed \{011\} facets could potentially exhibit good electrochemical performance for LIBs.

As far as we know, there are no reports on well-defined nano-octahedra as electrode materials for LIBs. Therefore it is interesting to investigate whether and how the exposed high surface energy facets of \( \text{Mn}_3\text{O}_4 \) affect the electrochemical performance as observed in other physical and chemical properties. Furthermore, nanoscale \( \text{Mn}_3\text{O}_4 \) nano-octahedra can have a higher surface area and provide more electroactive sites to promote the electrochemical reaction. For example, a smaller size can improve the electrode surface contact with the electrolyte and provide a short distance for fast lithium-ion transportation within the particles. Hence, it is of prime interest to study the electrochemical properties of differently sized \( \text{Mn}_3\text{O}_4 \) nano-octahedra with exposed \{011\} facets to LIBs.

Here we synthesized differently sized \( \text{Mn}_3\text{O}_4 \) nano-octahedra with exposed \{011\} facets as anode electrode materials for LIBs. We controlled the synthesis to reduce the octahedral size and to retain the good octahedral shape of the particles. Four different sizes (350 nm (MO1), 150 nm (MO2), 100 nm (MO3) and 40 nm (MO4)) were prepared with different amounts of exposed \{011\} facets. The results show that the exposed high energy \{011\} facets can greatly affect the electrochemical performance. Moreover, MO4 with the smallest size possesses more \{011\} facets and active sites to enter into contact with the electrolyte and provide a short distance for fast lithium-ion transportation within the particles. The synergy of the highly active \{011\} facets and the size dependence from the \( \text{Mn}_3\text{O}_4 \) nano-octahedra results in the best electrochemical performance for MO4, which demonstrates a high initial charge capacity of about 907 mA h g\(^{-1}\) and delivers an excellent rate capability with a high charge capacity of 350 mA h g\(^{-1}\) when cycled at 500 mA g\(^{-1}\).

2. Experimental section

All the reactants and solvents were of analytical grade and used without any further purification.

2.1 Synthesis of differently sized \( \text{Mn}_3\text{O}_4 \) nano-octahedra and irregular \( \text{Mn}_3\text{O}_4 \) particles

For the synthesis of MO1, 1.0 g of KMnO\(_4\) was dispersed in 50 mL distilled water and then stirred for 15 min; subsequently, 10 mL diethylene glycol (DEG) was slowly added into the above solution and stirred for another 20 min. Finally, the resulting suspension was transferred to a Teflon-lined stainless steel autoclave (100 mL) and was tightly sealed and maintained at 160 °C for 8 h, then allowed to cool to room temperature.

The synthesis of MO2 followed the procedure of our previous work.\(^{25}\) 0.105 g of KMnO\(_4\) was completely dissolved in 30 mL distilled water to form a purple-black solution. Polyethylene glycol (PEG200) (30 mL) was then added to the solution and stirred for 30 min at room temperature until a suspension was formed. The suspension was then poured into a Teflon-lined stainless steel autoclave (100 mL), which was subsequently sealed and maintained at 120 °C for 8 h, then allowed to cool to room temperature.

The synthesis of MO3 was similar to the synthesis procedure of MO2 with a slight modification: the amount of KMnO\(_4\) was changed to 0.5 g, the volume of PEG200 was increased to 40 mL and the reaction temperature was 130 °C, other conditions remained similar to the MO2 case.

MO4 was prepared by a special method: 0.316 g of KMnO\(_4\) was dispersed in 30 mL distilled water and stirred for 15 min. Subsequently, 40 mL DEG was slowly added into the above solution and stirred for another 30 min, then the dark-yellow solution was transferred into a thermostatic oil bath and heated to 140 °C with vigorous stirring. Finally, 2 mL ethylenediamine was quickly added into the flask. After 4 h stirring, the mixture was cooled to room temperature.

For comparison, the irregular shaped \( \text{Mn}_3\text{O}_4 \) nanoparticles with a size of about 40 nm were prepared following the procedure of previous report.\(^{26}\) 1 mmol of Mn(CH\(_3\)COO)\(_2\)·4H\(_2\)O was added into 20 mL distilled-water. When it was dissolved completely, 28 mg of PEG200 was introduced into the solution, followed by slowly adding 20 mL of NaOH aqueous solution (0.2 M) under stirring. The mixed solution was transferred to a Teflon-lined stainless steel autoclave (100 mL) and heated at 180 °C for 12 h.
All the products were washed with ethanol and water repeatedly until the organic reagents were washed out. Finally, the obtained precipitate was dried in air at 40°C for 12 h.

2.2 Material characterization

X-ray diffraction patterns (XRD) were obtained using a Bruker diffractometer at 40 kV, 40 mA, with Cu Kα radiation (λ = 1.54056 Å). The morphology of the as-prepared materials was detected by field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800) at 5 kV. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) were performed on a JEOL JEM-2100F with an acceleration voltage of 200 kV. High resolution high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was performed on a FEI Titan 80-300 “cubed” microscope fitted with a double aberration-corrector in TEM mode as well as in STEM mode, a monochromator and a GIF Quantum energy filter. An acceleration voltage of 120 kV was used to avoid radiation damage. The Brunauer–Emmett–Teller (BET) specific surface area of the samples was analyzed by nitrogen adsorption in a Micromeritics Tristar II 3020 nitrogen adsorption–desorption apparatus according to the BJH method from the N₂ adsorption isotherms.

2.3 Electrochemical characterization

The working electrodes were prepared by mixing 70 wt% of the as-synthesized Mn₃O₄ nano-octahedra, 20 wt% of acetylene black, and a 10 wt% polytetrafluoroethylene (PTFE, 60 wt%) binder. Electrochemical measurements were carried out via a CR2025 coin type cell using lithium pellets as the counter electrode and the reference electrode, a 1 M solution of LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC)(1:1 w/w) as an electrolyte. The cells were assembled in an argon-filled glovebox. The galvanostatic charge–discharge cycling was studied in a potential range of 0.1–3 V vs. Li/Li⁺ with a multichannel battery testing system (LAND CT2001A). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were performed on the electrochemical workstation (Autolab PGSTAT 302N) at the voltage of 0–3 V and the frequency range from 100 kHz to 100 mHz, respectively.

3. Results and discussion

The as-synthesized products were first characterized by X-ray diffraction (XRD). Fig. 1 shows the XRD patterns of MO1, MO2, MO3 and MO4, respectively. All peaks can be indexed to Mn₃O₄ as a tetragonal spinel with a space group I₄₁/amd (JCPDS no. 80-0382). No other crystalline phases are observed. The strong diffraction peaks of the XRD patterns indicate that all the as-obtained products are well crystallized. The broadening of the peaks in the XRD patterns indicates that the product has nanoscale dimensions. And the broader peaks of MO4 indicate that this product has the smallest size among the four products.

The field-emission scanning electron microscopy (FESEM) images in Fig. 2 show the general morphology of the four samples. Fig. 2a displays the SEM image of MO1, demonstrating the very well-shaped nano-octahedra with an average size of 350 nm. The as-prepared MO2 also shows a nano-octahedra morphology with a particle size of about 150 nm (Fig. 2b). MO3 (Fig. 2c) and MO4 (Fig. 2d) have a size of about 100 and 40 nm, respectively. It is clear that very small nano-octahedra with a size of about 40 nm can be obtained. Although the size is as small as 40 nm, the nano-octahedra are still well-shaped and monodispersed and no agglomeration occurs under our synthesis conditions. The nano-octahedra have exposed {011} facets, in agreement with our previous work.

Transmission electron microscopy (TEM) was performed to reveal the Mn₃O₄ nano-octahedra in more detail. Fig. 3a shows a typical TEM image of an individual nano-octahedron of MO1, which shows an edge length of about 350 nm. The corresponding corner is depicted in the HRTEM image (Fig. 3b), which exhibits well-resolved lattice fringes of 0.235 nm corresponding to the (004) plane and 0.246 nm corresponding to the (022) plane. The corresponding electron diffraction (ED) pattern clearly demonstrates the zone axis of [100] (Fig. 3c). The HRTEM image clearly illustrates that the exposed facets for nano-octahedra are {011}, which is consistent with our previous result. Fig. 3d–f show the TEM characterizations of MO2.
one nano-octahedron with a size of about 150 nm; imaged along [021], it exhibits a highly symmetric configuration of the nano-octahedron with smooth surfaces (Fig. 3f). Fig. 3e shows the corresponding HRTEM of the corner. The well-resolved lattice fringes with an interplanar spacing of 0.288 nm and 0.308 nm correspond to the (200) and (1\textendash12) planes, respectively. Fig. 4g–i show the TEM and HRTEM images and the corresponding ED pattern of MO3 along the c-axis (Fig. 3i). The nano-octahedron is about 100 nm and the lattice fringes with an interplanar spacing of 0.288 nm correspond to the (200) and (020) planes. Fig. 3j displays one nano-octahedron of MO4 with a size of 40 nm imaged along the [011] direction (Fig. 3j). The HRTEM image in Fig. 3k exhibits well-resolved lattice fringes of 0.288 nm and 0.494 nm, corresponding to the (020) plane and (101) plane, respectively. All HRTEM images reveal a clear lattice structure and the ED patterns exhibit sharp diffraction spots, accentuating the single crystalline nature of all the nano-octahedra with exposed \{011\} facets.

These results clearly show that differently sized Mn$_3$O$_4$ nano-octahedra with exposed \{011\} facets can be successfully synthesized. The size of the Mn$_3$O$_4$ nano-octahedra can be controlled by changing the amount of KMnO$_4$, alcohols and temperature.

It has been reported that self-assembly of colloidal particles into aggregated particles with a well-defined crystallographic orientation can result in the formation of different micro/nanostructures, which depends on the concentration of solute in the solution and the synthesis temperature.$^{27}$ Furthermore, according to the Stokes–Einstein equation, $D = \text{constant}/\eta$, as the concentration of the solute increases, the viscosity ($\eta$) of the liquid phase increases and thus the diffusion rate ($D$) of the nanoparticles decreases. Compared to the preparation procedure of MO2, the synthesis system of MO1 has a higher solute concentration that leads to fast supersaturation and the temperature of reaction is also higher, therefore the nucleation and crystal growth are faster. Moreover, the utilization of 10 mL DEG in 50 mL water for MO1 synthesis leads to a lower viscosity than 30 mL PEG in 30 mL water used in the MO2 synthesis, which generates higher fluidity for the solute to directional aggregation.$^{29}$ Thus MO1 has a larger size than MO2. The synthesis system for MO3 utilizes a more viscous liquid although a higher concentration of the solute was used. The more viscous system will affect the solute convection and is not beneficial to crystal growth, so the size of MO3 is smaller than that of MO2. Similar to MO3, 30 mL water and 40 mL organic solvent were used in the synthesis of MO4, but the reaction was carried out in a thermostatic bath instead of an autoclave system, which has lower power to force the crystal growth. Moreover, less solute was used in the synthesis of MO4, which led to slow crystal growth. Therefore, MO4 has a smaller size than MO3. Based on our previous work and experimental observations, it is believed that very small nanoparticles are first formed at the beginning of the reaction, then the small nanoparticles agglomerate to form larger nanoparticles under directional aggregation, finally single crystalline Mn$_3$O$_4$ nano-octahedra are obtained by an Ostwald ripening mechanism.$^{25}$

Fig. 4a shows a schematic nano-octahedron with exposed \{011\} facets. Fig. 4b shows the tetragonally distorted spinel...
structure of Mn$_3$O$_4$, which clearly displays Mn$^{2+}$ ions at the tetrahedral sites and Mn$^{3+}$ ions at the octahedral sites. Fig. 4c displays the atomic arrangement of the {011} facets along the [100] direction. Along the {011} planes Mn and O atom layers alternate: either the surface is completely covered with manganese or the surface is completely covered with oxygen. Spherical aberration corrected HAADF-STEM, which has been proved to be powerful in providing comprehensive information of electrode materials for Li-ion batteries at the atomic scale,$^{30,31}$ was used to obtain directly an image of the atomic structure of the Mn$_3$O$_4$ nano-octahedra. Fig. 4d shows a HAADF-STEM image of the MO4 sample along the [100] direction, in which heavy elements such as Mn(n) and Mn(m) can be clearly observed. This image along the [100] direction is also in good agreement with the crystal structure in Fig. 4b. HAADF line profiles of selected areas along the (010) plane (blue) and (011) plane (red) are shown in Fig. 4e and f, respectively. This gives a much clearer picture of the Mn(n), Mn(m) and O positions, consistent with the crystal structure in Fig. 4b and c. This study confirms again that, whatever their particle size, the Mn$_3$O$_4$ nano-octahedra contain exposed highly active {011} facets with the alternating Mn and O atom layers on the surface. As the Mn$_3$O$_4$ nano-octahedra with exposed {011} facets have already demonstrated anomalous magnetic properties and greatly superior photodecomposition activity, it is expected that the exposed highly active {011} facets of the Mn$_3$O$_4$ nano-octahedra may also have a remarkable effect on the electrochemical performance.

The electrochemical properties of Mn$_3$O$_4$ nano-octahedra with different particle sizes have been determined. Fig. 5a shows the charge and discharge profiles of the different Mn$_3$O$_4$ nano-octahedra: MO1, MO2, MO3 and MO4 as anode materials for the first cycle at a current density of 50 mA g$^{-1}$ and cycled between 3.0 and 0.1 V vs. Li/Li$^+$. The cyclic voltammetry (CV) curves of the four samples at a scan rate of 0.2 mV s$^{-1}$ in the potential range from 0 V to 3 V were also obtained (see Fig. S1 in the ESI†). The general features of the discharge–charge profiles are consistent with other transition metal oxide anodes that undergo conversion reactions, especially for manganese oxides.$^{13}$ For each sample in the first discharge, there is an obvious voltage slope ranging from 1.6 V to 0.37 V, consistent with two broad cathodic peaks at about 0.86 V and 1.25 V, as shown in Fig. S1,$^\dagger$ which can be ascribed to the irreversible reaction between Li$^+$ and Mn$_3$O$_4$ and the formation of a solid electrolyte interphase (SEI) due to the decomposition of the electrolyte solvent.$^{13,14}$ The voltage plateau at about 0.37 V reflects the Mn reduction reaction: Mn$_3$O$_4$ + 8Li$^+$ + 8e$^-$ $\rightarrow$ 3Mn(0) + 4Li$_2$O.$^{35,36}$ The specific discharge capacities of MO1, MO2, MO3 and MO4 in the first cycle are 1097 mA h g$^{-1}$, 1009 mA h g$^{-1}$, 1127 mA h g$^{-1}$ and 1504 mA h g$^{-1}$, respectively, higher than the theoretical capacity of 937 mA h g$^{-1}$, which can be attributed to the decomposition of the electrolyte and the formation of the SEI layer on the surface of the electrode.$^{7,18}$

The first charge curves show a well-defined voltage plateau of around 1.2 V, which corresponds to the reversible oxidation of manganese metal. During this process, approximately 6 electrons per formula unit of initial Mn$_3$O$_4$ are removed by the end of this plateau, consistent with the oxidation of each Mn to MnO.$^{13}$ According to previous reports,$^{13,21,29}$ an additional shoulder peak appearing around 2.2 V should correspond to the further oxidation of MnO to Mn$_2$O$_4$, but this is not observed in the first charge curves of MO1, MO2 and MO3, hence the first

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**Fig. 5**  (a) The first charge–discharge profiles of MO1, MO2, MO3 and MO4 at 50 mA g$^{-1}$ in the voltage range of 0.1 V–3 V; (b) the second charge–discharge profiles of MO1, MO2, MO3 and MO4 at 50 mA g$^{-1}$ in the voltage range of 0.1–3 V; (c) cycling performance of MO1, MO2, MO3 and MO4 at 50 mA g$^{-1}$; (d) coulombic efficiency of MO1, MO2, MO3 and MO4 at 50 mA g$^{-1}$; (e) charge–discharge capacities of MO3 and MO4 at various rates; (f) electrochemical impedance spectra of the electrodes of MO1, MO2, MO3 and MO after 10 cycles. The inset in (f) is the corresponding circuit diagram according to the EIS results.
specific charge capacities of the three MOs (535 mA h g\(^{-1}\) for MO1, 486 mA h g\(^{-1}\) for MO2 and 543 mA h g\(^{-1}\) for MO3) are much lower than the theoretical capacity (937 mA h g\(^{-1}\)), indicating that MnO is not converted into Mn\(_2\)O\(_4\) completely. However, the shoulder peak around 2.2 V is observed in the charge profile of MO4 and the charge capacity approaches 907 mA h g\(^{-1}\), which is very close to the theoretical capacity of a fully reversible conversion reaction. The redox reactions of MO4 were further confirmed by CV curves shown in Fig. S1.† From the curves, a broad oxidation peak around 2.2 V in the first/second curve of MO4 can be clearly observed, while it cannot be seen in the first/second cycles of MO1, MO2 and MO3, respectively, which is consistent with the charge curves in Fig. 5a and b. In the second discharge curves, only one voltage plateau around 0.5 V can be observed, which is consistent with the CV curves (Fig. S1†), indicating that the lithiation reaction of the second cycle is easier. This is often the feature of a single phase reaction. However, the tendency of the second charge profiles of all the samples is still very similar to the first ones, indicating the good reversibility of all the samples after the first discharge. Moreover, MO4 shows the highest second charge capacity of 886 mA h g\(^{-1}\), which is still very close to the first charge capacity (907 mA h g\(^{-1}\)), indicating its excellent capacity retention capability.

The cycling performances of MO1, MO2, MO3 and MO4 were measured at a current density of 50 mA g\(^{-1}\) with a voltage range from 3.0 V to 0.1 V, as shown in Fig. 5c. The capacity loss after the initial cycle may mainly be caused by the formation of a SEL.\(^{14-40}\) The further capacity loss is normally dependent on the path length and volume change for lithium insertion–deinsertion.\(^{41}\) Consistent with Fig. 4b, MO1, MO2 and MO3 deliver second discharge capacities of about 479 mA h g\(^{-1}\), 450 mA h g\(^{-1}\) and 459 mA h g\(^{-1}\), respectively, while MO4 shows a much higher discharge capacity of about 935 mA h g\(^{-1}\), indicating its great lithium-ion storage capability. When cycled for 50 cycles, the discharge capacities of MO1 and MO2 decline to 169 mA h g\(^{-1}\) and 210 mA h g\(^{-1}\), respectively, but the discharge capacity of MO3 still remains at about 400 mA h g\(^{-1}\), with a 12.8% specific capacity loss. Although the MO4 sample displays somewhat slightly lower cycling stability compared to the MO3 sample, MO4 still delivers a very high stable lithium-ion storage capacity of about 500 mA h g\(^{-1}\), which is much higher than most of the pure Mn\(_2\)O\(_4\) materials reported.\(^{14-18,20,24,26}\)

The coulombic efficiency of MO1, MO2, MO3 and MO4 is also displayed in Fig. 5d. It clearly shows that MO4 delivers a high initial coulombic efficiency of 60.3%, higher than MO1, MO2 and MO3 (48.8%, 48.1% and 48.2%, respectively). Moreover, MO4 displays a very great coulombic efficiency, higher than 94% from the second cycle and it tends to approximately 100% after 25 cycles.

The rate capability of MO3 and MO4 was evaluated at current densities of 50 mA g\(^{-1}\), 100 mA g\(^{-1}\) and 500 mA g\(^{-1}\) with a voltage range from 3.0 V to 0.1 V, as shown in Fig. 5e. Clearly, MO4 has a higher discharge capacity than MO3 at each current density. At 50 mA g\(^{-1}\), the reversible capacity of MO4 reaches about 800 mA h g\(^{-1}\). When cycled at 500 mA g\(^{-1}\), the reversible capacity is still higher than 350 mA h g\(^{-1}\). Remarkably, when the current density returns to 50 mA g\(^{-1}\), the reversible capacity can return again to 700 mA h g\(^{-1}\), indicating great rate capability and cycling stability.

Note that the Mn\(_2\)O\(_4\) nano-octahedra with a larger size display a worse cycling performance, while those with a smaller size show a better cycling performance. This result indicates that the high lithium storage capability and great rate capability of MO4 may be partly related to the smallest particle size that contains the highest surface area. As can be predicted, the decrease in particle size should lead to a higher surface area. N\(_2\) adsorption–desorption measurements confirm this tendency that the Mn\(_2\)O\(_4\) nano-octahedra give a surface area of 3 m\(^2\) g\(^{-1}\) for MO1, 9 m\(^2\) g\(^{-1}\) for MO2, 12 m\(^2\) g\(^{-1}\) for MO3, and 23 m\(^2\) g\(^{-1}\) for MO4 (the nitrogen adsorption–desorption isotherms are shown in Fig. S2 in the ESI†). The high surface area of MO4 can provide more active sites leading to the best performance. Additionally, the small particle size of MO4 can facilitate the rapid Li-ion diffusion at the electrode/electrolyte interface and result in easier intercalation and deintercalation of Li\(^+\) within the nano-octahedron leading to the best cycling performance.

To further investigate the kinetic differences of the four samples, the electrochemical impedance spectroscopy (EIS) results of the electrodes after 10 cycles were also obtained based on the modified equivalent circuit,\(^{42,43}\) as shown in Fig. 5f. All the curves display a semicircle in the high-frequency region, which is corresponding to the charge-transfer resistance (R\(_{ct}\)) through the electrode/electrolyte interface, and an inclined line, which is related to solid-state diffusion of Li ions in the electrode materials. From Fig. 5f, it can be observed that the charge transfer resistance of MO4 is the smallest, indicating that MO4 has higher electronic conductivity than the other three samples, which is beneficial for the improvement of electrochemical performance. Moreover, it can be found that when the size is smaller, the R\(_{ct}\) is smaller. This may be ascribed to higher specific surface area of smaller particles that can fully contact with the electrolyte, which facilitates the charge transfer in the electrode.

As aforementioned, Pasero et al. introduced pure Mn\(_2\)O\(_4\) particles with a reversible capacity of only 200 mA h g\(^{-1}\) at 10 cycles.\(^{37}\) Wang reported that pure Mn\(_2\)O\(_4\) nanoparticles showed a capacity less than 300 mA h g\(^{-1}\), which further decreased to ~115 mA h g\(^{-1}\) after only 10 cycles.\(^{38}\) Nam prepared pure Mn\(_2\)O\(_4\) nanoparticles of approximately 14 nm, which showed a low coulombic efficiency of less than 90% and a capacity lower than 150 mA h g\(^{-1}\) after 10 cycles.\(^{39}\) Liu synthesized nanosized Mn\(_2\)O\(_4\) particles with the same size as our sample MO4, which delivered a discharge capacity of only 400 mA h g\(^{-1}\), and quickly decreased to 100 mA h g\(^{-1}\) after 50 cycles, exhibiting very poor cycling performance.\(^{40}\) In our case, the discharge capacity of MO4 can still be maintained at around 500 mA h g\(^{-1}\) after cycling for 50 cycles, exhibiting excellent cycling performance, which is much better than many of the pure Mn\(_2\)O\(_4\) particles reported before.\(^{13,15,19,24}\) In comparison with the previous Mn\(_2\)O\(_4\) nanoparticles, the major difference is that our samples have a special morphology, a clear octahedral shape with exposed highly active \{011\} facets. As shown in Fig. 4, the Mn\(_2\)O\(_4\) nano-octahedra are composed of highly active \{011\} facets with...
alternating Mn and O atom layers on the surface. The conversion reaction of Mn₃O₄ and Li involves the formation and decomposition of the amorphous Li₂O and the multi-electron reaction: \[ \text{Mn}_3\text{O}_4 + 8\text{Li}^+ + 8e^- \rightarrow 4\text{Li}_2\text{O} + 3 \text{Mn} \]. The alternating Mn or O atom layers on the \{011\} facets may make the conversion reaction more easy, resulting in a higher capacity and a better cycling performance. In particular, the small size MO₄ octahedra can contain the largest number of highly active \{011\} facets, demonstrating the best electrochemical properties among the different sized Mn₃O₄ nano-octahedra.

The kinetics of the electrochemical lithium insertion/extraction reactions of the Mn₃O₄ nano-octahedra was further studied and the irregular shaped Mn₃O₄ nanoparticles were also prepared. The results show that the irregular shaped Mn₃O₄ nanoparticles also have a tetragonal spinel structure with the same size of MO₄ (about 40 nm) (Fig. S3a and 3b†). The BET specific surface area of irregular shaped Mn₃O₄ is measured to be 43 m² g⁻¹, which is almost double of MO₄. (The nitrogen adsorption/desorption isotherms are shown in Fig. S4 in the ESL†) Fig. 6a depicts the cycling performance of the irregular shaped Mn₃O₄ nanoparticles between 0.1 and 3 V at a current density of 50 mA g⁻¹ for 50 cycles. This result is very similar to the previous report.²⁴ It shows that the Mn₃O₄ nanoparticles deliver a high initial discharge capacity of 1770 mA h g⁻¹ due to the high surface area, which quickly decreases to 132 mA h g⁻¹, with a much poorer cycling performance and low initial coulombic efficiency of 54.2%, showing a much worse cycling performance than that of MO₄ even with a higher specific surface area. To further understand the reason for the big difference of the cycling performance between the irregular shaped Mn₃O₄ nanoparticles and MO₄, the EIS results of Mn₃O₄ nanoparticles and MO₄ are displayed in Fig. 6b, which shows that the charge transfer resistance \( R_{ct} \) of the irregular shaped Mn₃O₄ nanoparticles is larger than MO₄’s. In fact, the \( R_{ct} \) of the irregular shaped Mn₃O₄ nanoparticles is larger than those of MO₂ and MO₃. This result indicates that the nano-octahedral structure is beneficial for the charge transfer through the electrode/electrolyte interface, which can lead to the improvement of electrochemical performance.

To confirm the stability of the nano-octahedral structure, the morphology of the electrodes after electrochemical cycling was studied, as shown in Fig. 7. These SEM images clearly show that after cycling for 50 cycles at 50 mA g⁻¹, the nano-octahedral structure can still be maintained in the electrodes.

As mentioned above, there is an additional shoulder peak around 2.2 V in the charge curve of MO₄. In the previous work, this peak was assigned to the further oxidation of MnO to Mn₃O₄ as proposed in Li’s and Gao’s studies.¹³,²³ However, it is found that the shoulder peak weakens with continuous cycling; after deep cycling for 50 cycles, the shoulder peak becomes very weak (Fig. S6 in the ESL†), indicating the gradually irreversible oxidation of MnO to Mn₃O₄. This is also a reflection of the decrease of the specific capacity of MO₄ (Fig. 5c). To further investigate the crystal structure of the electrode after cycling, some more detailed information of MO₄ after 50 discharge-charge cycles was revealed by high resolution TEM observations. Fig. 8 shows the HRTEM images of MO₄ after 50 discharge-charge cycles. The images are not as clear as the sample MO₄ shown in Fig. 3 due to some organics or amorphous materials covering the surface of the nano-octahedra. The interplanar spacings of the intersecting lattice fringes in Fig. 8a are measured to be 0.288 nm and 0.308 nm, which correspond to the (200) and (1-12) planes of Mn₃O₄ (JCPDS no. 80-0382), while the interplanar spacing of the lattice fringes in Fig. 8b is measured to be 0.256 nm, which corresponds to the (111) plane of MnO (JCPDS no.: 78-0424). This result demonstrates that after 50 discharge-charge cycles, the electrode structure is...
becomes the mixture of MnO and Mn$_3$O$_4$. To the best of our knowledge, this is the first time to verify the previously proposed transformation of MnO to Mn$_3$O$_4$ during the oxidation process.$^{1,2,3}$ Therefore, after deep cycling at 50 mA g$^{-1}$ for 50 cycles, not only the morphology of MO4 is maintained, but also the crystal structure of Mn$_3$O$_4$ is partly maintained. The revertible crystal structure of Mn$_3$O$_4$ indicates that the octahedral shape with $\{011\}$ facets of Mn$_3$O$_4$ should be beneficial for the high performance of MO4.

From the above results, it can be seen that the good cycling performance of MO4 is not only related to the smallest size resulted high surface area, but also the exposed highly active $\{011\}$ facets effectively improving the kinetics of charge transportation and Li ion diffusion. The synergy of high surface area and exposed $\{011\}$ facets demonstrates the best electrochemical performance for MO4. This result may result in a significant concept on guiding the deep research between the exposed active facets and the electrochemical properties in the future.

4. Conclusion

Well shaped single crystalline Mn$_3$O$_4$ nano-octahedra with different sizes have been successfully prepared. The electrochemical properties of Mn$_3$O$_4$ nano-octahedra as anode materials for lithium ion batteries have been investigated. The results show that the smallest sized Mn$_3$O$_4$ nano-octahedra demonstrate the best cycling performance with a discharge capacity of 500 mA h g$^{-1}$ after 50 cycles at a current density of 50 mA g$^{-1}$. The smallest sized Mn$_3$O$_4$ nano-octahedra also show excellent coulombic efficiency (nearly 100%) and good rate capability with a charge–discharge capacity of 350 mA h g$^{-1}$ when cycled at 500 mA g$^{-1}$. The exposed highly active $\{011\}$ facets with alternating Mn and O atom layers facilitate the easier conversion reaction between Mn$_3$O$_4$ and Li, resulting in a high Li-ion storage capacity, an excellent rate capability and low charge transfer resistance. In addition, the smallest size of Mn$_3$O$_4$ nano-octahedra ensures more active sites that come into full contact with the electrolyte, facilitate the rapid Li-ion diffusion at the electrode/electrolyte interface and provide short distances for fast lithium-ion transportation within the particles. The synergy of high surface area and exposed $\{011\}$ facets demonstrates the best electrochemical performance for MO4.

The HRTEM observations verify the transformation of MnO to Mn$_3$O$_4$ during the oxidation process and demonstrate that MO4 can partly maintain the octahedral structure after 50 discharge–charge cycles. Our results demonstrate that the Mn$_3$O$_4$ nano-octahedra with exposed highly active $\{011\}$ facets could be promising anode materials for high performance lithium ion batteries. By engineering the particle size of Mn$_3$O$_4$ nano-octahedra, we can enhance their electrochemical properties.

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