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Review

Recent advances in Mn-based oxides as anode materials for lithium ion batteries

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It is of great interest to develop new electrode materials for lithium-ion batteries (LIBs), because the available electrode materials may not meet the high-energy demands for electronic devices, especially good cyclic and rate performance demands. Mn-based oxides have received substantial attentions as promising anode materials for LIBs due to their high theoretical specific capacities, low charge potential vs. Li/Li$^+$, environmental benignity and natural abundance. Herein, the preparations of Mn-based oxide nanomaterials with various nonostructures and chemical compositions, and their application as negative electrodes for LIBs are reviewed. It covers MnO, Mn_3O_4, Mn_2O_3, MnO_2, $CoMn_2O_4$, $ZnMn_2O_4$ and their carbonaceous composites/oxides supports with different morphologies and compositions. The aim of this review is to provide an in-depth and rational understanding of the relationships among the chemical composition, morphologies and electrochemical properties of the Mn-based anode materials and how the electrochemical performance can be improved using materials engineering strategies. Special attention has been given to the discussion on some challenges and bottlenecks in the areas of practical applications of Mn-based oxides in LIB full cells.

1. Introduction

After entering the 21st century, the calling for more energy and a cleaner environment has forced a lot of countries to invest large amounts of money in developing the environmental friendly energy storage systems.[1] Rechargeable lithium-ion batteries (LIBs) have the advantages of high energy density, long cycle life and memory-free effect over the lead-acid battery, nickel–cadmium battery and nickel–metal hydride battery, making them widely applied in portable electronic and electric tool market.[2-4] In the near future, they are expected to play even more important roles in electric vehicles (EVs) and plug-in hybrid electric vehicles (PHEVs).[4] However, they currently still fail in meeting the demands dictated by powering of both EVs and HPEVs or by the large-scale energy storage systems for renewable energies. Therefore, a significant improvement in the lithium storage capacity is in imminent demand for LIBs to enhance their feasibility on the aforementioned large scale applications.

The charge/discharge mechanism of LIBs is based on the rocking-chair concept. A typical commercial LIB consists of a cathode (e.g., $LiCoO_2$) and an anode (*e.g.*, graphite), together with an electrolyte-filled separator that allows lithium (Li) ions transfer but prevents electrodes from direct contact. When the battery is charging, Li ions deintercalate from the cathode and intercalate into the anode. Conversely, the Li ions intercalate into the cathode via the electrolyte during discharging. During

charge/discharge, Li ions flow between the anode and the cathode, enabling the conversion of chemical energy into electrical energy and the storage of electrochemical energy within the battery. The reactions in the typical battery are $LiCoO_2 + 6C \leftrightarrow Li_{1-x}CoO_2 + Li_xC_6$ (0 < x < 1).[5-8]

The energy density of the LIBs depends on the capacities and operating potentials of the respective electrode materials. Searching for such electrode materials that can yield higher capacity and energy density, e.g. cathode materials with higher operating voltages ($\geqslant$4.0 V vs Li/Li$^+$)[9-12] and anode materials with lower operating voltages ($\leqslant$1.0 V vs Li/Li$^+$), and are of less environmental cost is essential to achieve this goal.[8] Research on anode materials for LIBs has been directed towards new materials that involves three different mechanisms: (1) intercalation−deintercalation mechanism, e.g. compounds with a two-dimensional (2-D) layer structure[13] or three-dimensional (3-D) network structure[14] that can reversibly intercalate/deintercalate Li$^+$ into/out of the lattice; (2) elements (M) that can form alloys with Li metal (Li$_x$M), e.g. Si,[15-17] Sn/SnO$_2$,[18-23] Ge,[24] Sb,[25] Zn,[25] In, Bi, and Cd[27]; and (3) materials that can act as anode with the so-called redox or "conversion" reaction with Li.[28] These materials are mainly oxides, fluorides, oxyfluorides, sulfides, nitrides and phosphides.[29] As the consequence, a large number and wide variety of metal-containing oxides, including binary and complex oxides have been explored for Li cycling.[8,30-32] In

addition, the modern nanotechnology has been employed to prepare many metal oxides with various morphologies and structures for Li cycling as anode materials for LIBs.[7] As a result, the research on metal oxides as anodes for LIBs has been enhanced and enriched very significantly in recent years.[8]

Among the metal oxides as anode materials for LIBs, Mn-based oxides have obvious advantages because of their high specific capacities, lower toxicity, cost, and operating voltage (average discharge and charge voltages of 0.5 V and 1.2 V vs. Li/Li$^+$, respectively) comparing with the iron,[33-35] cobalt[36-38] and Ni-based oxides.[39-40] Table 1 listed the experimental values of the plateaus potential and theoretical specific capacities associated with conversion reactions in Mn-based oxides.[41-45] In a Li/Mn$_x$O half-cell, the electrochemical processes can be summarized by the equation below:

$$MnO_x + 2xLi^+ + 2xe^- \leftrightarrow Mn + xLi_2O$$

This reaction for Li storage in Mn-based oxides based on the "conversion mechanism" has four major obstacles for practical applications:[29] (1) the strong structural reorganization that takes place to accommodate the chemical changes and induces large volume changes, resulting in severe particle agglomeration and unsatisfactory cycling performance; (2) low rate performance arising from their low conductivity; (3) an unacceptable large voltage hysteresis, in term of round-trip energy density loss, which is observed between the discharge and charge steps; and (4) a virtually ubiquitous large coulombic inefficiency observed in the first cycle.

[Table 1]

Different strategies have been proposed to resolve the aforementioned problems of Mn-based anodes, and four of them are widely practiced. The first strategy is to fabricate nanosized particles so as to shorten the diffusion length for electrons and lithium ions.[46] The second strategy is to synthesize Mn-based oxides with porous structure, which contains porous 1-D nanorods/nanowires[47] and hollow nanotubes,[48] 2-D nanoflakes,[49] and 3-D hollow or hierarchical porous nanostructures.[50] The vacant space provided by the hollow or porous structures can accommodate the structural strain and favor fast Li$^+$ insertion/extraction kinetics by enabling electrolyte uptake through the nanoparticles, leading to improved rate and cycling performance. The third strategy is to introduce a considerable proportion of carbon into the Mn-based oxides to form homogenous oxides/carbon nanocomposites.[46] It has been suggested that the carbon–based materials can provide a cushion effect against the volume strain because of their elastic feature. Meanwhile, the carbon-based materials could also increase the electrical conductivity of the nanocomposites which is essential to the rate performance and cyclability. Furthermore, the carbon is also active at the low voltages at which some of the conversion reactions occur, thereby partially compensating the decrease in capacity associated with the dilution of the active phase. The fourth strategy is to optimize the electrodes by adjusting the ratios of active materials, binders and conductive agents or choosing novel binders/conductive agents.[51] It has also been documented

that proper selection of the ratios of the active materials, conductive agents and binders would be an significant advantage for the improvement of the rate and cyclic performance for metal oxides-based[52] and other anode materials.[51] Because of the potential application of nano-scale Mn-based oxides as anode materials for LIBs, it is of great importance to have a more detailed discussion on this kind of metal oxides with various nanostructures, chemical compositions and their electrode fabrication processes.

Cabana et al.[29] gave an excellent review on the different conversion reactions of metal oxides, sulfides, nitrides, phosphides, and fluorides in 2010, in which the development of the Mn-based oxides as anode materials for LIBs before 2010 had been extensively reviewed. Wu et al.[30] gave a another good review on a topic of metal oxides as anode materials for LIBs in 2012. Reddy et al.[8] reviewed the detailed development of metal oxides and oxysalts as anode materials for LIBs. Some advances in Mn-based oxides as anode materials for LIBs in recent years have also been found in these three papers. In addition, these three excellent review papers demonstrated that the research field of metal oxides as anode materials is a very active and important area of LIBs. Although some recent advances on this topic have been reviewed in aforementioned papers, continuous updating is still required to reflect the fast developments of the strategies for the electrochemical performance improvement of Mn-based oxides and their research statuses. In order to obtain better understanding of the research statuses of this topic, this review mainly discusses the recent developments, current status and the major strategies for the performance enhancement of Mn-based oxides with various structures and chemical compositions. The oxides reviewed in this work include MnO, Mn$_3$O$_4$, Mn$_2$O$_3$, MnO$_2$, CoMn$_2$O$_4$ and ZnMn$_2$O$_4$ as well their carbon/metal oxides-based composites. The key challenges and opportunities in their future developments and applications are also discussed. Given the rapid development and broad field of Mn-based oxides, the authors apologize for the inevitable oversights of some important contributions.

2.   Binary Mn-based Oxides as anode materials

Mn-based binary oxides have been widely investigated as anode materials for LIBs in the past decades after the works of Tarascon et al. in 2000.[28] Many binary Mn-based oxides including MnO, Mn$_3$O$_4$, Mn$_2$O$_3$, MnO$_2$ and their carbon-based nanocomposites with different nano-structures have found useful applications in LIBs.[8]

2.1 MnO and its nanocomposites

Although the MnO has a high theoretical capacity of 755.6 mAh g^{-1} that is twice the capacity of graphite, and a lower electromotive force (1.032 V vs Li/Li$^+$) than other TMO anodes such as Fe$_2$O$_3$, Co$_3$O$_4$, NiO, CuO, and so forth, only few examples on the Li cyclability of the pure MnO anode material have been reported in recent years.[46,49,53,54] This may attributed to the fact that manganese is one of the first row transition

metals which is very difficult to be reduced into a metallic state.[29] Zhong *et. al.*[46] investigated the commercial MnO powders as anode active materials for LIBs. According to the results of *ex- situ* XRD, TEM and galvanostatic intermittent titration technique, they suggested that lithium is stored reversibly in MnO through conversion reaction and interfacial charging mechanism. In addition, they found that a layer of the solid electrolyte interphase with a thickness of 20–60 nm is covered on MnO particles after full insertion. The cyclic performance of MnO is significantly improved after decreasing particle size. Following this work, MnO in the forms of microspheres,[53] nanoflakes[49] and thin-film[54] as anode materials to improve their cycling and rate performance have been reported. In 2011, Zhong *et al.*[53] synthesized porous MnO microspheres by decomposing $MnCO_3$ under argon atmosphere at 600 °C for 1 h. The as-prepared MnO material shows a reversible capacity of 800 mAh g^{-1} and an initial coulombic efficiency of 71%. It can deliver 600 m Ah g^{-1} at a rate of 400 mA g^{-1}. They further confirmed the conversion reaction mechanism by Mn K-edge X-ray absorption near edge structure (XANES) spectra and extended X-ray absorption fine structure (EXAFS), indicating that pristine MnO is reduced to Mn^0 after discharging to 0 V and a part of reduced Mn^0 is not oxidized to Mn^{2+} after charging to 3 V. Li *et al.*[49] developed a novel method for the preparation of porous MnO nanoflakes on nickel foam (Figs. 1a-d) by a reduction of hydrothermal synthesized MnO_2 precursor in hydrogen. The porous MnO nanoflakes showed good capacity retention capability and rate performance (Fig. 1e), with a capacity of 568.7 and 708.4 mA h g^{-1} at the 2nd and 200th charge–discharge cycle at a current density of 246 mA g^{-1} and 376.4 mA h g^{-1} at a current density as high as 2460 mA g^{-1}, respectively. Thin films of MnO were successfully deposited on Cu foils by radio-frequency (RF) sputtering under the Ar:H$_2$ (95:5 vol%) reduction atmosphere at 500 °C.[54] The films with a thickness of about 0.5 mm exhibit an initial coulombic efficiency of 75% and a reversible specific capacity of 700 mAh g^{-1} at 0.05 C after 100 cycles, and 428 mAh g^{-1} at 20 C. These values demonstrate that the sputtering-grown MnO films exhibit excellent cyclability and rate performance in comparison to the MnO powders. They suggested that pure phase with low oxidation state and certain porosity could be favorable factors accounting for such improved electrochemical performance.

In addition to phase-pure MnO, the MnO-based nanocomposites have also been intensively studied as negative electrodes due to their improved electrochemical (Table 2).[46, 55-74] The group of Li[46] synthesized carbon-coated commercial MnO (MnO-L) by ball milling with sugar followed by pyrolysis at 600 °C in Ar atmosphere (C/MnO-L) and found that a reversible capacity of ~650 mAh g^{-1} at 50 mA g^{-1} (0.08C) could be almost stable up to 150 cycles in the voltage range 0.01−3.0 V. Good rate performance with 400 mAh g^{-1} at a rate of 400 mA g^{-1} was also found. They have also demonstrated that the C/MnO-L nanocomposites have a lower voltage hysteresis (<0.7 V with a charging voltage of 1.2 V), during the discharge/charge cycles compared to other metal oxides.
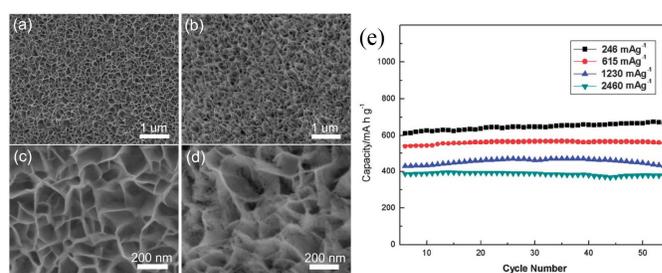
Fig. 1 (a), (b) Low-magnification SEM images of the samples before and after reduction; (c), (d) High-magnification SEM images of the samples before and after reduction; and (e) The discharge capacity at various current densities of MnO nanpflakes. Reproduced with permission.[49] Copyright 2012, RSC.

Inspired by the positive effect of carbon-coating, the MnO/C nanocomposites as anode materials for LIBs have received considerable interests.[55-59] For example, unique amorphous MnO_x–C nanocomposite particles with interspersed carbon are synthesized using aerosol spray pyrolysis.[55] The amorphous MnO_x–C nanoparticles showed a high reversible capacity of approximately 650 mAh g^{-1} under a current density of 200 mA g^{-1}, with exceptional capacity retention of 93% after 130 cycles. The coulombic efficiency of the amorphous MnO_x–C remained stable during the cycling after the first few cycles. They suggested that the 100% coulombic efficiency is attributed to the absence of new SEI formation during cycling, in which the carbon blocks liquid electrolyte penetration into MnO_x–C particles, reducing the contact area between MnO_x and electrolytes. Chae *et al.*[56] obtained a MnO_x/OMC (OMC = ordered mesoporous carbon) nanocomposite by a simple wet-impregnation of $Mn(NO_3)_2$ aqueous solution onto OMC nanorods followed by thermal treatment at 450 °C in an Ar flow (Fig. 2a). The MnO_x/OMC exhibited a high reversible capacity (>950 mAh g^{-1}) after 50 deep charge–discharge cycles with excellent cycling stability (Fig 2b), acceptable coulombic efficiency (97%) and good rate capability (750 mAh g^{-1} at 1000 mA g^{-1}) (Figs. 2b-c). The incorporation of insulating and high density MnO_x into OMC nanorods exhibited synergistic benefits including higher volumetric as well as specific capacities, and smaller redox voltage hysteresis than OMC nanorods.

[Table 2]

Very recently, Luo *et al.*[57] have developed an efficient microwave-polyol process with a subsequent thermal treatment for the synthesis of MnO nanoparticles that are encapsulated uniformly in three-dimensional (3D) mesoporous interconnected carbon networks (MnO-MICN). Sodium citrate plays an important role on the morphology of the Mn-based precursors. An interesting phenomenon was observed for the nanocomposites as anode materials that the specific capacities (~30% of the overall capacity) gradually increase after 100 cycles. They suggested a new electrochemical reaction might occur. For instance, Mn^{2+} may be oxidized to a higher oxidation state. After 200 cycles at 200 mA g^{-1}, the specific discharge capacity reaches 1224 mA h g^{-1} with a coulombic efficiency of ~99%. Moreover, a specific capacity of 731 mA h g^{-1} is

retained after 200 cycles at 1500 mA g^{-1}, indicating good rate performance of the nanocomposites. Inspired by the natural microalgae with its special features (easy availability, biological activity, and carbon sources). Xia et al.[58] developed a green and facile biotemplating method to fabricate monodisperse MnO/C microspheres. Due to the unique hollow porous structure in which MnO nanoparticles were tightly embedded into a porous carbon matrix and form a penetrative shell, the MnO/C microspheres exhibited high reversible specific capacity of 700 mAh g^{-1} at 0.1 A g^{-1}, excellent cycling stability with 94% capacity retention after 50 cycles, and good rate performance of 230 mAh g^{-1} at 3 A g^{-1}. More recently, the nanocomposites of manganese monoxide and multi-walled carbon nanotubes (MnO/MWNTs) have been prepared hydrothermally by MWNTs and KMnO$_4$ followed with a sintering process.[59] The nanocomposites also show improved electrochemical performance as anode materials for LIBs, with a reversible capacity as high as 770.6 mA h g^{-1} at the current density of 7.21 mA g^{-1} and good capacity retention (over 92.4% after 200 cycles at 216.14 mA g^{-1} between 0.01 and 3.0 V).
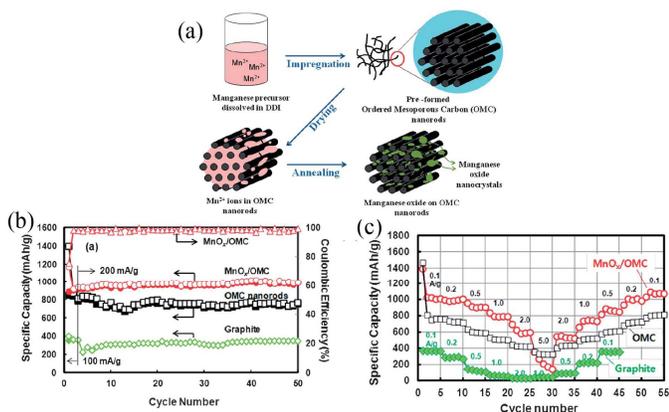
Fig. 2 (a) Schematic diagram for the preparation of MnO$_x$-loaded OMC nanorods; (b) Specific capacities OMC nanorods and MnO$_x$/OMC with cycle number; and (c) Rate performances of MnO$_x$/OMC, OMC nanorods and graphite cycled at different current densities. Reproduced with permission.[56] Copyright 2012, RSC.

It has been demonstrated that the strategy of preparing MnO/graphene composites is an effective route to obtain enhanced lithium-storage properties because graphene has superior conductivity, large surface area, structural flexibility, and chemical stability. In 2011, a composite of graphene nanosheets (GNs) supported by MnO nanocrystals was fabricated through a chemical-wet impregnation followed by the thermal reduction route.[60] The MnO-attached GN anode delivers a reversible capacity of 635 mAh g^{-1} at 0.2 C in the voltage range between 0.01 and 3.5 V, a high coulombic efficiency (92.7%) at the 1st cycle and good rate capability [capacity retention (5 /0.2 C: >70%)]. They also investigated the effect of Mn/C atomic ratio on the functions of the coulombic efficiency and found that the reversibility of Li$^+$ intercalation/deintercalation gradually increases with the Mn atomic ratio. This result may due to two major reasons: i) Mn ions tend to terminate dangling bonds located at the edges of

GNs, forming MnO-terminated edges of graphene fragments and (ii) appropriate amount of MnO spacers tend to stabilize the GN network, offering more active sites for reversible Li-storage. After this work, MnO/graphene nanocomposites with different MnO structures have been synthesized by different route and used as anode materials for LIBs. Qiu et al.[61] prepared a MnO nanoparticle/graphene composite (the diameters of the formed MnO nanoparticles are ranging from 20 to 250 nm) via in-situ carbothermal reduction of Mn$_3$O$_4$ on the surface of graphene nanosheets. The detachment and agglomeration of MnO nanoparticles were effectively prevented due to the tight combination of MnO nanoparticles and graphene. The MnO nanoparticle/graphene composites show a high specific capacity of approximately 700 mAhg^{-1} at 100 mAg^{-1}, excellent cyclic stability, and good rate capability as anode material for LIBs. Zhang et al.[62] synthesized nitrogen-doped MnO/graphene nanosheets (N-MnO/GNS) hybrid material by a hydrothermal method followed by ammonia annealing (Fig. 3a). Because of its unique N-doped nanostructure and efficiently mixed conducting network, this nanostructured hybrid exhibited a reversible electrochemical lithium storage capacity as high as 772 mAh g^{-1} at 100 mA g^{-1} after 90 cycles (Fig. 3b), and an excellent rate capability of 202 mA h g^{-1} at a high current density of 5 A g^{-1} (Fig. 3c).
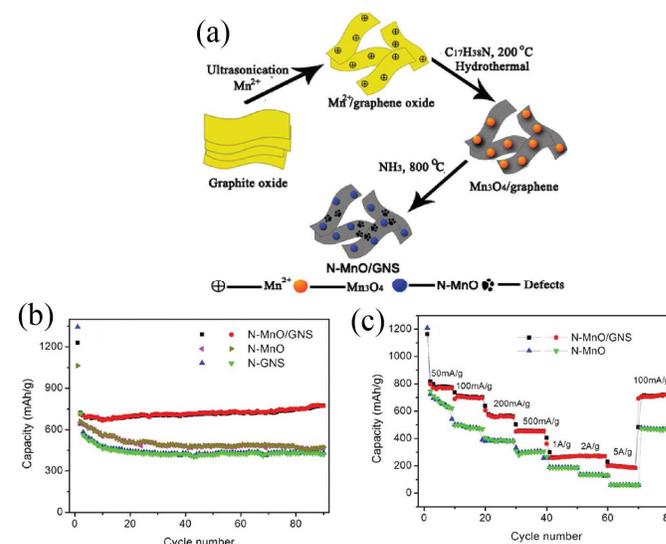
Fig. 3 (a) Schematic illustration for the preparation of N-MnO/GNS hybrid material; (b) Comparison of cycling performance of N-MnO, N-GNS, and N-MnO/GNS hybrid at a current density of 100 mA g^{-1}; and (c) Rate capability of N-MnO and N-MnO/GNS at various current densities. Reproduced with permission.[62] Copyright 2012, ACS.

Mai et al.[63] synthesized a MnO/reduced graphene oxide sheet (MnO/RGOS) hybrid by a two-step electrode design consisting of liquid phase deposition of MnCO$_3$ nanoparticles on the surface of graphene oxide sheets followed by heat treatment in nitrogen flow. The MnO/RGOS hybrid electrode shows a reversible capacity of 665.5 mA h g^{-1} after 50 cycles at a current density of 100 mA g^{-1} and delivers 454.2 mA h g^{-1} at a rate of 400 mA g^{-1}. It is found that the MnO/RGOS hybrid electrode exhibits an enhanced reversible capacity with respect

to that of MnO electrode, which is attributed to the re-oxidation from the Mn/Li_2O nanocomposite to MnO nanoparticles. In addition, they suggested that the corporation of RGOS is not very effective for the decrease of the hysteresis voltage of MnO electrode by galvanostatic intermittent titration technique (GITT) as well as electrochemical impedance spectroscopy (EIS). This remarkable hysteresis has both thermodynamic and kinetic origins. In 2013, Sun et al.[64] reported a facile solution-based method combined with a subsequent reduction process for the large-scale fabrication of a MnO/graphene nanocomposite. The prepared MnO/graphene hybrid anode exhibits an initial reversible capacity of around 890.7 mAh g^{-1} at a current density of 200 mA g^{-1} and a reversible capacity as high as 2014.1 mAh g^{-1} after 150 discharge/charge cycles (Fig. 4). In addition, the composite shows excellent rate capability (625.8 mAh g^{-1} at 3000 mA g^{-1}) and superior cyclability (843.3 mAh g^{-1} even after 400 cycles at 2000 mA g^{-1} with only 0.01% capacity loss per cycle). The specific capacity is much higher than the theoretical capacities of both MnO ($\sim$ 756 mAh g^{-1}) and graphene ($\sim$ 744 mAh g^{-1}). The lithiation and delithiation behaviors suggest that the further oxidation of Mn(II) to Mn(IV) which is similar to the recent report of Luo et al.,[57] and the interfacial lithium storage upon cycling have significant contributions to the specific capacity enhancement.
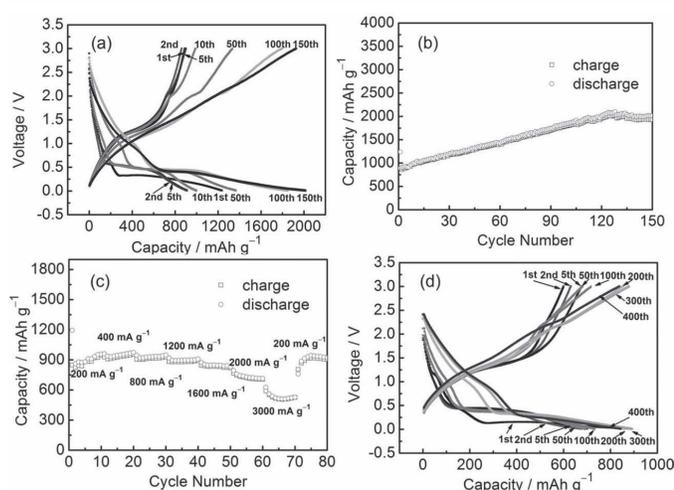
Fig. 4 (a) Discharge and charge voltage profiles of the obtained MnO/graphene product at a current density of 200 mA g^{-1}; (b) Cycling performance of the prepared MnO/graphene hybrid electrode cycled at 200 mA g^{-1} and (c) at various current densities of 200, 400, 800, 1200, 1600, 2000, and 3000 mA g^{-1}; and (d) Discharge and charge curves at a current density of 2000 mA g^{-1}. All carried out in the voltage range 3–0.01 V vs. Li. Reproduced with permission.[64] Copyright 2013, Wiley.

One dimensional (1-D) nanostructures have attracted considerable attention as anode materials for LIBs, since they allow better accommodation of volume changes during repetitive charge/discharge cycles and the 1-D nanostructure possesses direct one-dimensional electronic pathways for efficient charge transport. In 2011, the 1-D coaxial MnO/C nanotubes with an average diameter of about 450 nm, a wall thickness of about 150 nm, a length of 1–5 μm and a 10 nm thick carbon layer were first reported by Ding et al.,[65] using β-

MnO_2 nanotubes as self-templates in acetylene at 600 °C. This sample exhibits a reversible capacity of about 500 mAhg^{-1} at a current density of 188.9 mA g^{-1}, and 83.9% of capacity retention. Although the as-prepared sample shows better lithium storage properties compared to the bare MnO nanotubes (58.2%) and MnO nanoparticles (25.8%), its electrochemical performance is still not satisfactory due to the quick capacity fading. The enhanced reversible capacity and cycling stability for coaxial MnO/C-NTs are attributed to the conductive carbon layer on the MnO nanotubes, which can provide improved electronic transport to MnO nanotube core and be considered as a buffering layer to alleviate the volume changes caused by repetitive cycling. In recent years, the reduction of MnO_x ($x > 1$) with special nanostructure features has been appeared to be more widely practiced. Wang's group[66] synthesized MnO/C core–shell nanorods by an in-situ reduction method using MnO_2 nanowires as precursor and block copolymer F127 as carbon source in a gas flow of 5 vol.% H_2 in Ar. The as-prepared MnO/C core–shell nanorods exhibit a higher specific capacity than MnO microparticles as anode material for lithium ion batteries, with a specific discharge capacity of about 700 mAh g^{-1} after 40 cycles under a current density of 200 mA g^{-1}. Li et al.[67] reported a facile synthetic method for the preparation of MnO@carbon core–shell nanowires with a jointed appearance, based on the reduction of Mn_2O_3 precursors followed by graphitization of C_2H_2. The MnO@carbon core–shell nanostructures could deliver reversible capacities as high as 801 mAh g^{-1} at a high current density of 500 mA g^{-1}, with excellent electrochemical stability over 200 cycles. The remarkable electrochemical performance is mainly attributed to the highly uniform carbon layer around the MnO nanowires, which is not only effective in buffering the structural strain and volume variations of anodes during repeated electrochemical reactions, but also greatly enhances the conductivity of the electrode material. They also suggested that their strategy is simple but very effective, and appears to be sufficiently versatile and extended to other high-capacity electrode materials with large volume variations and low electrical conductivities. More recently, Zhu's group[68] has developed a novel route to synthesize MnO@1-D carbon composites through a pyrolysis process, using $C_4H_4MnO_6$ as the single molecule precursor. The MnO nanoparticles are uniformly dispersed inside or adhered to the surface of the 1-D carbon nanotubes, and these carbon nanotubes overlap each other to form carbon scaffolds. This special structure feature not only improves the electronic conductivity, but also provides a support for loading MnO nanoparticles, resulting in a high specific capacity (1482 mA h g^{-1} at 200 mA g^{-1}), good rate performance (420 mA h g^{-1} at 2.0 A g^{-1}) and excellent capacity retention capability (810 mA h g^{-1} at 1460 mA g^{-1} after 1000 cycles).

The solvo/hydrothermal approach has been proved to be a suitable route for the preparation of 1-D MnO/C nanocomposites. For examples, Sun's group[48] developed a facile hydrothermal method followed by thermal annealing to synthesize porous MnO/C nanotubes (Fig. 5). Electrochemical results demonstrate that the porous MnO/C nanotubes could

deliver a reversible capacity as high as 763.3 mAh g^{-1} after 100 cycles at a charge/discharge current density of 100 mA g^{-1} (0.13 C, 1 C = 755.6 mA g^{-1}), and 618.3 mAh g^{-1} after 200 cycles at a rate of 0.66 C (Fig. 6). They suggested that the superior cyclability and rate capability are attributed to the hollow interior, porous structure, 1D structure and the uniformly dispersed carbon in the porous MnO/C nanotubes. Su *et al.*[69] reported a two-step hydrothermal treatment and subsequent sintering at 600 °C to prepare hierarchical MnO@C nanorods using $KMnO_4$ and citric acid as raw materials. The ultra-small MnO nanocrystals (< 5 nm) were homogeneously dispersed in a carbon matrix and further coated with a well-proportioned carbon shell. This sample exhibited a reversible capacity of 481 mA h g^{-1} after 50 cycles at a current density of 200 mA g^{-1}, which is higher than that of carbon-coated MnO nanoparticles.
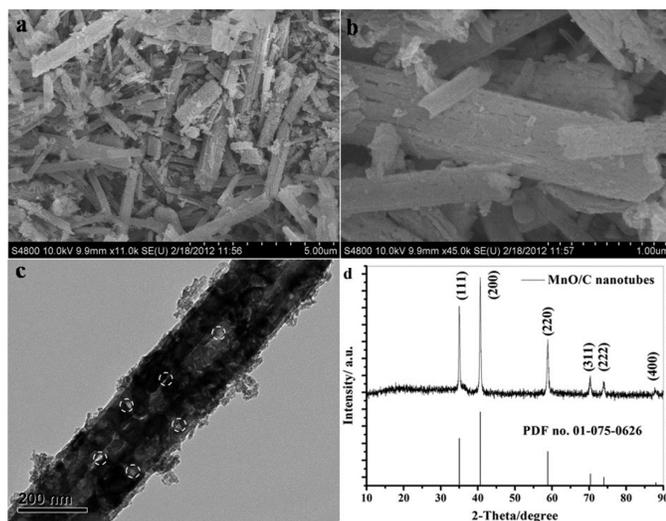
Fig. 5 (a) Low and (b) high magnification SEM images; (c) TEM image and (d) XRD pattern of the porous MnO/C nanotubes. Reproduced with permission.[48] Copyright 2012, RSC.
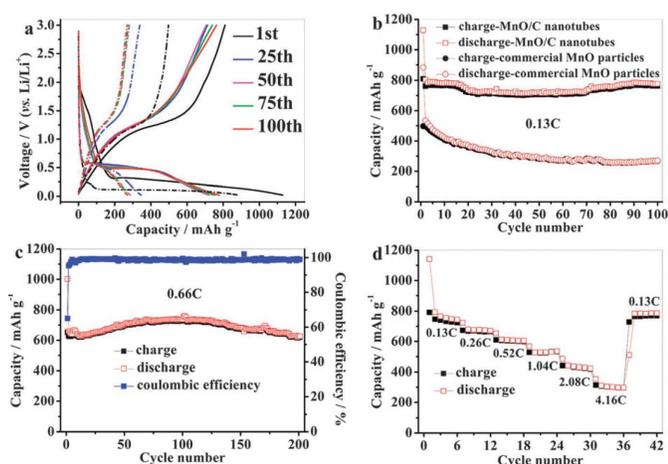
Fig. 6 (a) Charge/discharge curves and (b) cycle performances of commercial MnO particles (short dash dot) and the porous MnO/C nanotubes (solid) at a charge/discharge rate of 0.13 C; (c) cycle performance of the porous MnO/C nanotubes at a charge/discharge rate of 0.66 C; (d) rate performance of the porous MnO/C nanotubes. Reproduced with permission.[48] Copyright 2012, RSC.

The 2-D nanostructures of MnO-based nanocoposites are not as well researched as their 1-D counterparts. The reason probably lies in the difficulty in fabricating well-defined MnO-based nanocomposites. Sun *et al.*[70] prepared porous carbon-modified MnO disks with about 50 nm in average thickness and up to 3 mm in diameter by a microwave-polyol process followed by thermal annealing of the disk-like Mn-complex precursor. In their work, they demonstrated that each C–MnO disk has a single-crystal-like nature and is built up by the assembly of carbon-modified MnO nanocrystals of ~12 nm through the same crystallographic orientation. Because the unique assembled nano-architecture involving three-dimensionally interconnected nanopores and carbon modification as well as small particle sizes of MnO nanocrystals, the as-synthesized C–MnO nanocomposites exhibit high capacity (an initial capacity of 1387.2 mA h g^{-1} with a coulombic efficiency of 71.9% at a current density of 100 mA g^{-1} in the first cycle) and excellent cycling stability (a reversible capacity of 1044.2 mA h g^{-1} after 140 cycles at 100 mA g^{-1}). It is also worthy to note that the capacity first drops then increases upon cycling, which has been observed in the case of MnO/C,[53] MnO/reduced graphene oxide[63] and MnO_x/C.[55] They suggested that the mechanism behind the U-shaped curve of capacity retention is not clear, but may be attributed to the formation of high oxidation state products[49] or mixed effects of Mn cluster aggregation and reversibility improvement of the conversion reaction in manganese oxide due to the formation of defects and deformation.[55] Although the carbon materials (amorphous carbon, carbon nanotube and graphene) have apparent beneficial effects on the electrochemical cycling and rate performance of the MnO-based composites, they have very low electrochemical activity and limited lithium storage capacity. Therefore, the carbon content in the composites needs to be carefully adjusted in order to find a balance between the capacity and the cycle life of the electrode. Chen's group[61] synthesized carbon-coated nano-MnO powders (MnO/C) with different carbon contents by reduction of Mn_3O_4 with a particle size of about 20 nm, using glucose as both carbon source and reducing agent. The electrode fabricated using 10.7wt% carbon-coated MnO/C shows the best cycling stability and rate performance, with a high reversible capacity of 939.3 mAh g^{-1} after 30 cycles at 0.1 C. By controlling the treatment temperature and reaction time, Zhang *et al.*[72] synthesized MnO@C core–shell nanoplates with controllable carbon shell thickness via thermal treatment deposition of acetylene on the $Mn(OH)_2$ nanoplates precursor (Fig. 7a). When controlling the temperature of carbon-decoration and the reaction duration time, the thickness of the carbon shell can be tuned from 3.1 to 13.7 nm. The electrochemical experimental results show that the MnO@C nanoplates with a carbon shell thickness of 8.1 nm display a higher reversible capacity (770 mAh g^{-1} at a current density of 200 mA g^{-1}) and better cyclability than those of nanoplates with carbon shell thicknesses of 3.1, 4.0, 4.2, 10.9 and 13.7 nm (Fig. 7b).
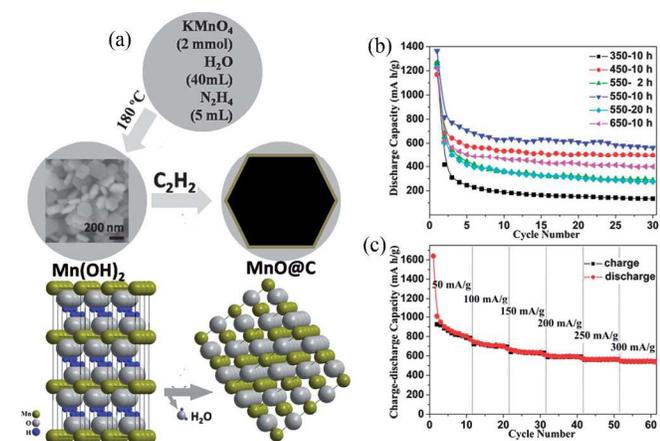
Fig. 7 (a) Schematic illustrating the formation process of the MnO@C; (b) Discharge capacity vs. cycle number for MnO@C products synthesized at different conditions at a current density of 200 mA g^{-1}; and (c) The rate performance of the MnO@C products synthesized at 550 $^{\circ}$C for 10 h. Reproduced with permission.[72] Copyright 2012, RSC.

In summary, results from this series of studies show that, despite the high theoretical capacities of MnO and the improved cyclic and rate performance by many strategies, however, these data were obtained through the Li/MnO half-cells. Up to now, few papers[73,74] have reported the full cells using MnO-based oxides as anode and $LiMn_2O_4$, and $LiNi_{0.5}Mn_{1.5}O_4$ as cathode. A lithium ion battery using $LiMn_2O_4$ as cathode and MnO_x/mesoporous carbon as anode has been reported by Lee et al..[73] The capacity of the MnO_x/C anode decayed gradually from 700 mAh g^{-1} to 500 mAh g^{-1} after 100 cycles, and the MnO_x/mesoporous carbon/$LiMn_2O_4$ full cell operates at an average working voltage of 3.3 V with a capacity of 105 mAh g^{-1} (Fig. 8).
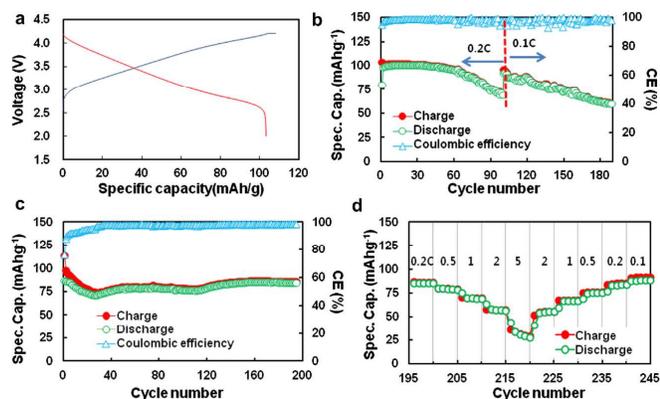
Fig. 8 (a) Voltage profile; (b) Cycling performance of LMO-MnO$_x$/C (A) cell at 0.2 C for 100 cycles and then at 0.1 C for up to 188 cycles; (c) Cycling performance of LMO-MnO$_x$/C (B) cell at 0.2 C for up to 195 cycle; and (d) Rate performance of LMO-MnO$_x$/C (B) cell. Voltage cut-off range is between 2.0 and 4.1 V. Reproduced with permission.[73] Copyright 2013, Elsevier.

In a recent paper, Sun's group[74] successfully developed a facile rout to synthesize hierarchical micro/nanostructured MnO anode and spinel $LiNi_{0.5}Mn_{1.5}O_{4-\delta}$ cathode materials by using hierarchical micro/nanostructured $MnCO_3$ with olive shape as precursor. Both the MnO and $LiNi_{0.5}Mn_{1.5}O_{4-\delta}$ materials

possess excellent lithium storage properties owing to their unique hierarchical micro/nanostructures. The MnO in a MnO/Li half-cell can deliver a reversible capacity of 782.8 mAh g^{-1} after 200 cycles at a rate of 0.13 C, and a stable reversible capacity of 350 mAh g^{-1} at a high rate of 2.08 C. A full lithium ion battery using the MnO as anode and the $LiNi_{0.5}Mn_{1.5}O_{4-\delta}$ as cathode demonstrates a high discharge specific energy ca. 350 Wh kg^{-1} after 30 cycles at 0.1 C with an average working voltage at 3.5 V and a long cycle stability. The $MnO/LiNi_{0.5}Mn_{1.5}O_{4-\delta}$ full cell can maintain a discharge specific energy of 227 Wh kg^{-1} after 300 cycles at a higher rate of 0.5 C (Fig. 9). Considering these two successful examples, the full cells assembled by MnO-based nanocomposites anode may present a promising potential application for next generation of LIBs.
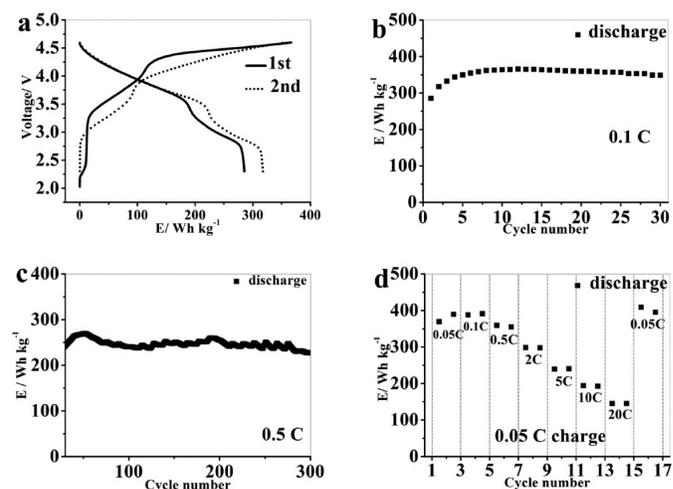
Fig. 9 (a) Charge/discharge profiles and (b) cycling performance of the MnO/LNMO full cell at a rate of 0.1 C; (c) cycling performance of the MnO/LNMO full cell at a rate of 0.5 C; and (d) the discharge specific energies of MnO/LNMO full cell at different rates (0.05 C charge). Reproduced with permission.[74] Copyright 2013, ACS.

2.2 Mn$_3$O$_4$ and its nanocomposites

In 1983, the group of Goodenough[75] reported the electrochemical insertion of Li into Mn_3O_4. However, few literatures[75-78] have reported on this material as anode material for LIBs partially due to its extremely low electrical conductivity ($\sim 10^{-7}$-10^{-8} S cm^{-1}), limiting its capacity to $\sim$400 mAh g^{-1} even with Co doping. The optimization of synthesis conditions is therefore necessary to obtain single-phase Mn_3O_4 material. In 2010, Li's group[79] reported a facile solvothermal process for the controllable synthesis of the Mn_3O_4 nanocrystals with different sizes and shapes, which includes dots, rods, and wires with the presence of the surfactants of dodecanol and oleylamine. The as-prepared monodisperse nanocrystals, acting as ideal building blocks, can be rationally assembled into three-dimensional (3D) Mn_3O_4 colloidal spheres, using a facile ultrasonication strategy. This paper gave a good example for the preparation of pure Mn_3O_4 nanomaterials. After that, this mixed-valent oxide (Mn_3O_4) and its nanocomposites have been

extensively investigated as anode material by "conversion reaction" of lithium and continue to be studied (Table 3).[80-89] Shen et al.[80] synthesized Mn_3O_4 nanorods with diameters of 50–150 nm and lengths of about 1–2 μm via the heat-treatment of the $MnCO_3$ nanorods, which were obtained from a facile hydrothermal method, in nitrogen atmosphere. When applied as anode materials for lithium ion batteries, the Mn_3O_4 nanorods exhibited a reversible lithium storage capacity of 1050 mAh g^{-1} in the first a few cycles. However, the pure Mn_3O_4 nanorods show a rapid capacity loss with the increase of the cycle number and the capacity decreased to 108 mAh g^{-1} at the 100th cycle. Engineering the morphology of Mn_3O_4 nanomaterials has been an effective strategy to enhance their electrochemical performance. Therefore, other pure Mn_3O_4 with different morphologies and microstructures, including octahedral Mn_3O_4 crystals with exposed high-energy facets[81], spongelike Mn_3O_4 nanostructures,[43] mesoporous stacked Mn_3O_4 nanosheets,[82] foamlike porous Mn_3O_4,[83] mesoporous Mn_3O_4 nanotubes,[84] order-aligned Mn_3O_4 nanostructures[85] and Mn_3O_4 octahedrons with a typical diameter around 300–400 nm,[86] have been synthesized and intensively investigated as anode materials for LIBs. In these Mn_3O_4 nanomaterials, the mesoporous Mn_3O_4 nanotubes[84] and Mn_3O_4 octahedra[86] show high specific capacities and excellent cycling performance. Specifically, the mesoporous Mn_3O_4 nanotubes[84] with a high surface area of 42.18 m^2 g^{-1} and an average pore size of 3.72 nm, obtain from the hydrogen reduction of β-MnO_2 nanotubes under a H_2/Ar atmosphere at 280 ^{o}C for 3 h, exhibit a high specific capacity of 641 mA h g^{-1} after 100 cycles at a high current density of 500 mA g^{-1} (Fig. 10). The Mn_3O_4 octahedra,[86] which was straightforwardly prepared at room temperature using a one-step dealloying method (Fig. 11a), have an ultra- long cycle life with capacity retentions of 81.3% and 77.8% after 500 cycles at 100 and 300 mA g^{-1}, respectively (Fig. 11b and 11c).

[Table 3]
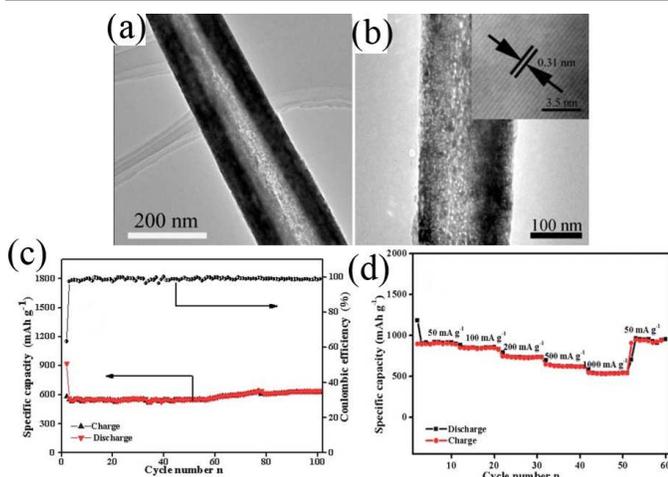
Fig. 10 (a) TEM and (b) HRTEM images of mesoporous Mn_3O_4 nanotubes; (c) Cycle performance and coulombic efficiency versus cycle number of Mn_3O_4 nanotubes at a current density of 500 mA g^{-1} and (d) Rate capabilities with increasing current density. Reproduced with permission.[84] Copyright 2013, RSC.
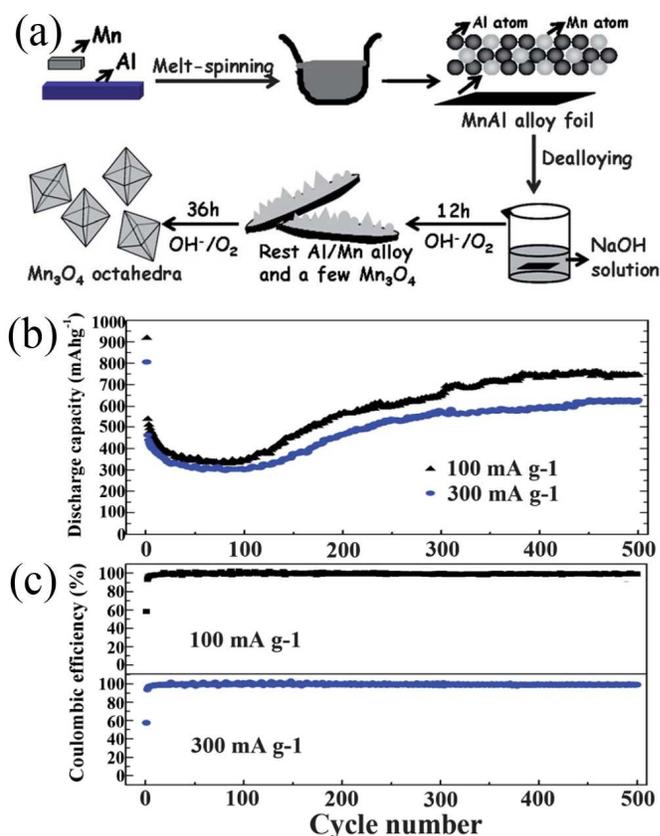
Fig. 11 (a) The schematic fabrication of the Mn_3O_4 octahedra; (b) Cycling behavior; and (c) Coulombic efficiency of the Mn_3O_4 anode at different current densities. Reproduced with permission.[86] Copyright 2014, RSC.

In order to tackle the problem of low capacity retention capability of the pure Mn_3O_4 material, researchers have designed M-doped Mn_3O_4 (M = Co, Fe and Cu) samples.[76,87-89] In 2005, Shen et al.[76] synthesized Co-doped Mn_3O_4 sample to improve the cycling performance of pure Mn_3O_4 phase. The Co-doped Mn_3O_4 sample delivers a specific capacity of 400 mA h g^{-1}, which is much higher than the specific capacity of pure Mn_3O_4 (~ 200 mA h g^{-1}). More recently, Ma et al.[87] prepared Fe-doped Mn_xO_y with connected macropores and mesopores to provide a hierarchical porosity by a facile and scalable nanocasting technique followed by controlled calcination, using a novel macroporous amine-functionalized bromomethylated poly (2,6-dimethyl-1,4-phenylene oxide) (BPPO) membrane as the sacrificial template (Fig. 12). The macropores in the final product were mainly formed by the reversible replication of the membrane porous structure, and interconnected branches in the pore system. The macropores cushioned the volume change in the conversion reaction of lithium during cycling, and also acted as reservoirs and thoroughfares to improve Li$^+$ transport in the electrolyte phase. The mesopores between primary nanocrystalline particles were formed upon heat treatment, and provided the large interfacial contact between electrolyte and electrode active material to support a high Li$^+$ flux across the solid/liquid interface. The selection of iron as a dopant was intentional: the redox potential

of iron (1.0 V for discharge/1.7 V for charge) is higher than that of manganese (0.5 V for discharge/1.2 V for charge)[90]. Therefore, the evenly distributed iron could remain in the zero valent state during a large part of Mn_xO_y conversion reaction, serving conceptually the dual function of (1) electrical wiring of the electro-active material to lower the resistance for electron transport and (2) promoting ionic conduction by creating narrowly spaced interfaces at the oxide grain boundary. As anticipated, the Fe-doped Mn_xO_y composites show good capacity retention and high rate capabilities, delivering a capacity of ~ 400 mAh g^{-1} at 1500 mA g^{-1} after 900 cycles (Fig. 13). In the work, they synthesized manganese oxides doped with different amounts of iron and investigated the effect of Fe content on the phase structures and electrochemical performance of the as-synthesized samples. These results indicate the importance of a moderate level of iron doping to balance its effects on interfacial charge transfer and the structural integrity of the mesopores. Further studies are required to explore the effect of metal dopants on the rate and long-term cycling performance as well as the columbic efficiency of Mn_3O_4 composites.

Fig. 13 (a) The 1st and 2nd discharge-charge curves of Fe-doped Mn_xO_y-2 electrode; (b) Cycle stability of Fe-doped Mn_xO_y-0, Fe-doped Mn_xO_y-1, Fe-doped Mn_xO_y-2, Fe-doped Mn_xO_y-3 and Fe-doped Mn_xO_y-4 measured at 200 mA g^{-1}; (c) Cycling stability of Fe-doped Mn_xO_y-2 at different current densities; and (d) Cycling performance of Fe-doped Mn_xO_y-2 at 1500 mA g^{-1}. Reproduced with permission.[87] Copyright 2013, Wiley.

Fig. 12 (a) Schematic illustration of the preparation of hierarchical macro/mesoporous metal oxide structures; (b) FESEM images at low and high magnifications (inset) of Fe-doped Mn_xO_y-2; (c) TEM images at low and high magnifications (inset) of Fe-doped Mn_xO_y-2; (d) SEM image of Fe-doped Mn_xO_y-2 and EDX element maps of Mn, Fe, and O; and (e) Nitrogen adsorption-desorption isotherms of Fe-doped Mn_xO_y-2 and corresponding pore size distribution (inset). Reproduced with permission.[87] Copyright 2013, Wiley.

Mn_3O_4-graphene hybrid as a high capacity anode material for LIBs was first investigated by Cui's group.[91] They developed

two-step solution-phase synthesis route to to form hybrid materials of Mn_3O_4 nanoparticles with diameters around 10-20 nm on 10wt% reduced graphene oxide (RGO) sheets (Fig. 14). A stable capacity of ~900 mA·h g^{-1} (~810 mA h g^{-1} based on the total mass of the composite) was obtained for the first five cycles when cycled at a current of 40 mA g^{-1} in the voltage range of 0.1−3.0 V vs Li/Li$^+$. Very good rate capability and cycling stability waere observed. For example, a capacity of ~720 mA·h g^{-1} at 400 mA g^{-1} was retained after 40 cycles of charge/discharge at various C-rates. However, the bare Mn_3O_4 nanoparticles exhibit very inferior electrochemical performance, with an initial reversible specific capacity of 300 mA·h g^{-1} at 40 mA g^{-1}. The high capacity, good rate capability and cycling stability of this Mn_3O_4/RGO hybrid material are attributed to the intimate synthesized nanocomposites of Mn_3O_4 (20 nm in diameter) wrapped in graphene sheets (GSs) via a facile, effective, energy-saving, and scalable microwave hydrothermal technique. The composite shows a high specific capacity of more than 900 mAh g^{-1} at 40 mA g^{-1}, and excellent cycling stability with nearly no capacity decay can be observed up to 50 cycles. They firstly give evidence that there is charge transfer between the graphene and the Mn_3O_4 nanoparticles by theoretical calculations. Li et al.[95] developed a facile one-step route to provide interactions between the graphene substrates and the Mn_3O_4 nanoparticles which directly grow on them, which making Mn_3O_4 electrochemically active since charge carriers can be effectively and rapidly conducted back and forth from the Mn_3O_4 nanoparticles to the current collector through the highly conducting three-dimensional graphene network. In addition, the graphene-nanoparticle interactions afford good dispersion of Mn_3O_4 nanoparticles on the RGO sheets which could avoid aggregations of Mn_3O_4 nanoparticles, leading to
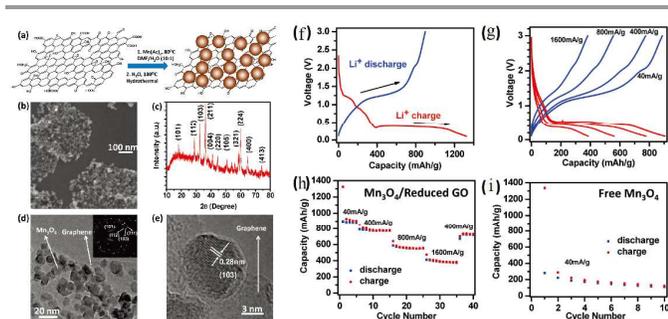
Fig. 14 (a) Schematic two-step synthesis of Mn₃O₄/RGO; (b) SEM image of Mn₃O₄/RGO hybrid; (c) XRD spectrum of a packed thick film of Mn₃O₄/RGO; (d) TEM image of Mn₃O₄/RGO; inset shows the electron diffraction pattern of the Mn₃O₄ nanoparticles on RGO; (e) High-resolution TEM image of an individual Mn₃O₄ nanoparticle on RGO; (f) Charge (red) and discharge (blue) curves of Mn₃O₄/RGO for the first cycle at a current density of 40 mA g^{-1}; (g) Representative charge (red) and discharge (blue) curves of Mn₃O₄/RGO at various current densities; (h) Capacity retention of Mn₃O₄/RGO at various current densities and (i) Capacity retention of free Mn₃O₄ nanoparticles without graphene at a current density of 40 mA g^{-1}. Reproduced with permission.[91] Copyright 2010, ACS.

better cycle stability. This growth-on-graphene approach offers a new technique for the design and synthesis of high performance anode materials based on highly insulating Mn₃O₄ material. After this work, Mn₃O₄/carbon-based hybrid materials have been intensively studied because of their potential for improving their cycle stability and rate performance as anode materials for LIBs. The specific capacity value and cycling performance were listed in Table 3.[92-101] For example, Li et al.[93] successfully synthesized three-dimensional hybrids with Mn₃O₄ nanoparticles homogeneously embedded in the ordered mesoporous carbon (OMC). The Mn₃O₄/OMC hybrids display a high specific capacity up to 802 mA h g^{-1}, and a high coulombic efficiency of up to 99.2% even after 50 cycles at a high current density of 100 mA g^{-1}, revealing its good rate capability and cycling stability. This value is 1.6 times higher than the discharge capacity of 512 mA h g^{-1} for pure ordered OMC materials, and more than 5.4 times higher than the discharge value of 148 mA h g^{-1} for pure Mn₃O₄ nanoparticles. They suggested that the enhanced capacity and cycling performance of the Mn₃O₄/OMC hybrids can be attributed to their unique robust three-dimensional composite structure and the synergistic effects between the Mn₃O₄ nanoparticles and OMC. The ordered mesostructured channels of Mn₃O₄/OMC hybrids are expected to buffer well against the local volume change during the Li uptake/removal reactions and thus to enhance the structural stability. The OMC matrix wall with a thickness of <10 nm greatly reduces the solid-state transport length for Li diffusion. Moreover, the hierarchical ordered mesoporosity facilitates the liquid electrolyte diffusion into the bulk of the electrode material and hence provides fast conductive ion transport channels for the conductive Li$^+$ ions. The improved cycling performance can also be mainly attributed to good electrical contact between the Mn₃O₄ and OMC in the three-dimensional nanocomposites during phase transformation of Mn₃O₄ upon lithiation/delithiation that usually leads to capacity fading. Wang et al.[97] developed a

facile one-step solvothermal reaction route for large-scale synthesis of carbon homogeneously wrapped manganese oxide (Mn₃O₄@C) nanocomposites for anode materials, using manganese acetate monohydrate and polyvinylpyrrolidone as precursors and reactants. The synthesized tetragonal structure Mn₃O₄ (space group I41/amd) samples display nanorod-like morphology, with a width of 200−300 nm and a thickness of 15−20 nm. The Mn₃O₄@C nanocomposites display enhanced capacity retention on charge/discharge cycling, with a stable specific capacity of 473 mA h g^{-1} after 50 cycles (as much 3.05 times as that of pure Mn₃O₄ sample). Wang et al.[99] fabricated colloidal Mn₃O₄ nanocrystals supported by graphene oxide (GO) and reduced graphene oxide (RGO) (Mn₃O₄/GO and Mn₃O₄/RGO nanocomposites) through a facile ultrasonic-assisted synthetic route in ethanol amine (ETA)-water system (Fig. 15a). The integration of GO with abundant O-containing groups and the colloidal Mn₃O₄ crystals enable such composite to possess excellent electrochemical performances including high reversible capacity, good cycle stability, and high rate performance that are more suitable to use as the electrode material for electrochemical capacitors (ECs). Comparing with Mn₃O₄/GO nanocomposite, Mn₃O₄/RGO exhibits excellent electrochemical performance in rechargeable LIBs due to the high electrical conductivity of RGOs and the structure of Mn₃O₄ nanocrystals enwrapped in RGOs (Fig. 15b). In addition, they firstly explain how the synergetic compositing structure of Mn₃O₄/GO and Mn₃O₄/RGO nanocomposites plays a very important role in their properties for ECs or LIBs (Fig. 15c). Luo et al.[100] recently reported the Li cycling behavior of Mn₃O₄−cabon nanotubes hybrid material, which is a composite of Mn₃O₄ nanoparticles anchored on continuous super-aligned carbon nanotube (SACNT) films. They reported that the electrochemical performance of the Mn₃O₄/SACNT composite electrode is significantly affected by the content and particle
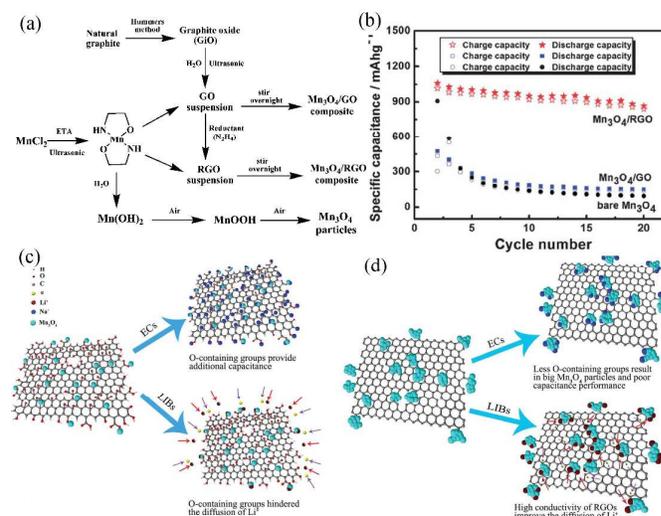
Fig. 15 (a) Preparation routes of Mn₃O₄ nanoparticles, Mn₃O₄ /GO and Mn₃O₄ /RGO nanocomposites. (b) Cycling performance of these samples at 40 mA $^{-1}$; (c) The charge mechanism of Mn₃O₄/GO; and (d) Mn₃O₄/RGO for ECs and LIBs. Reproduced with permission.[99] Copyright 2013, RSC.

size of Mn_3O_4. It was found that the Mn_3O_4/SACNT composites with size of Mn_3O_4 less than 10 nm demonstrated higher capacity, less extent of polarization, and better cycle stability than the Mn_3O_4/SACNT composite with size of Mn_3O_4 at 165 nm. The optimized Mn_3O_4/SACNT composite displays a capacity of more than 700 mAh g^{-1} at 0.1 C (based on the total mass of the electrode). A large capacity of 342 mAh g^{-1} can still be obtained at a high rate of 10 C, and a capacity retention of 95% was achieved for 100 cycles at 1 C. Despite improvements on the anodic properties of Mn_3O_4 by conductive coating/composites, further studies on the effect of conductive coating on the cycling stability and rate performance still needed to be conducted in the future.

2.3 Mn_2O_3 and its nanocomposites

There were only few reports on Mn_2O_3 nanomaterial based anodes for LIBs before 2010.[102,103] Liu et al.[102] reported preliminary studies of Li cycling behaviors on Mn_2O_3 and found a first discharge and charge capacity of 1080 and 480 mAh g^{-1}, respectively, in the voltage range of 0.2–3.0 V vs. Li/Li$^+$ at 0.25 mA cm^{-2}. Lavela et al.[103] prepared Mn_2O_3 by sol−gel method followed by heat treatment at different temperatures. They reported that Mn_2O_3 showed a discharge potential (1st cycle) at ~ 0.25 V vs. Li/Li$^+$. The Mn_2O_3 delivered reversible capacities of 500−700 mA h g^{-1} depending on the synthesis temperature, when cycled in the voltage range of 0.005−3.0 V Li/Li$^+$. However, capacity fading was noted in all cases with capacities ranging from 250 to 400 mAh g^{-1} after 20 cycles. Porous one-dimensional Mn_2O_3 nanostructures, containing nanofibers, nanowires and nanorods, were successfully fabricated via a facile hydrothermal treatment and sequential thermal decomposition without any template or surfactant.[104] The as-prepared porous Mn_2O_3 nanofibers, nanorods and nanowires manifested high initial capacities. However, capacity fading was also observed in all cases with capacities of ~250 mA h g^{-1} after 30 cycles. Similar phenomenon was also found by Shen' group[105] By means of morphology-conserved transformation, Qiu et al.[106] synthesized hierarchically structured Mn_2O_3 nanomaterials with different morphologies (oval-shaped and strawsheaf-shaped) and pore structures by hydrothermal method followed by heating of the products in air at 600 °C. Both of the as-prepared mesoporous Mn_2O_3 nanomaterials deliver high reversible capacities and excellent cycling stabilities compared to the commercial Mn_2O_3 nanoparticles. They observed a reversible capacity of 380 and 320 mA·h g^{-1}, respectively, at the end of the 150th cycle for straw-sheaf- and oval-shaped nanostructured Mn_2O_3 at a current of 200 mA g^{-1} when cycled in the voltage range of 0.01−2.5 V vs. Li/Li$^+$. Moreover, they suggested that the good capacity retention capability of the straw-sheaf-shaped Mn_2O_3 is due to the relatively high surface area and the peculiar nanostrip structure, resulting in the reduced length for lithium ion diffusion. Recently, our group[107] have synthesized porous Mn_2O_3 microspheres by morphology-controlled decomposition of spherical $MnCO_3$ precursors at 600 °C. The porous Mn_2O_3

microspheres show a specific capacity as high as 796 mAh g^{-1} at a current density of 100 mA g^{-1} after 50 cycles. In addition, a high rate performance (~ 600 mA h g^{-1} at 1200 mA g^{-1}) was also observed. Based on the CV curves, the discharge–charge curves and the ex-situ XRD analysis, a novel lithium storage mechanism of the synthesized porous Mn_2O_3 material after the first discharge process was suggested as follows:

$$Mn + xLi_2O \leftrightarrow 2xLi^+ + MnO_x + 2xe^- \ (1.0 < x < 1.5)$$
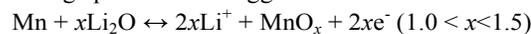
After our work, porous Mn_2O_3 hierarchical microspheres[108, 109] Mn_2O_3 nanocones,[110] polyhedrons,[111] porous sheets,[112] cubic and spindle[113] have been synthesized and investigated as anode materials by other groups. All of these results were listed in Table 4. Although some advance have been made in Mn_2O_3 anode materials via the morphology optimization, further studies on the improvement of the cycling stability and rate performance are still required.

[Table 4]

A recent good report of Cu-doped hollow spherical Mn_2O_3 sample by Li et al.[113] showed a higher specific capacity of 642 mAhg^{-1} at a current density of 100 mA g^{-1} after 100 cycles. They suggested that the significant enhancement of the electrochemical lithium storage performance can be attributed to the improvements of the electronic conductivity and lithium diffusivity of electrodes.

Xia's group[114] prepared Mn_2O_3 nanowires by thermal annealing of MnOOH nanowires precursor, which was transformed from hydrothermally grown MnO_2 nanoflakes and directly attached on Ti foils via reaction with poly(vinyl pyrrolidone) (Fig. 16a). The Mn_2O_3 nanowires (Fig. 16b) show an initial discharge capacity of 815.9 mA h g^{-1} at 100 mA g^{-1} and maintains a capacity of 502.3 mA h g^{-1} after 100 cycles (Fig. 16c), and good rate performance of 220 mAh g^{-1} at 1000 mA g^{-1} (Fig. 16d). Furthermore, they firstly fabricated a flexible Mn_2O_3//$LiMn_2O_4$ lithium ion full cell using the Mn_2O_3 nanowires as anode and $LiMn_2O_4$ nanowires as cathode, respectively (Fig. 17). The full cell has an output voltage of >3
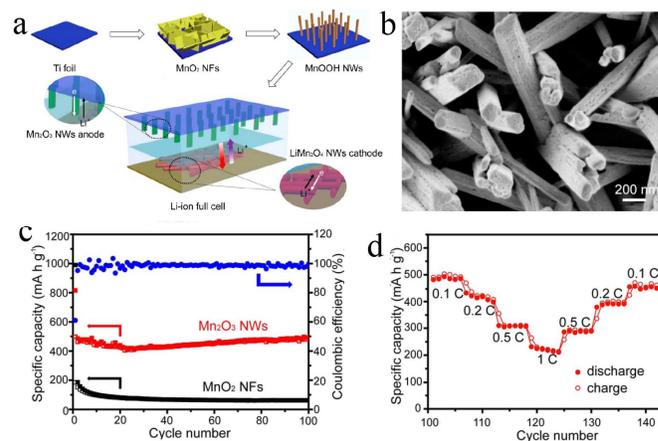
Fig. 16 (a) Schematic of the synthesis of the Mn_2O_3 nanowires (NMs) and fabrication the Mn_2O_3/$LiMn_2O_4$ LIB full cell; (b) SEM images of Mn_2O_3 NWs grown on Ti foils; (c) Cycling performance of Mn_2O_3 NWs (red curve) for the first 100 cycles; and (d) Rate performance of Mn_2O_3 NWs (1C = 1000 mA g^{-1}). Reproduced with permission.[114] Copyright 2013, ACS.

V, low thickness of 0.3 mm, high flexibility, and a specific capacity of 99 mA h g^{-1} based on the total weight of the cathode material. It also exhibits good cycling stability with a capacity of ~80 mA h g^{-1} after 40 charge/discharge cycles. This successful example of the Mn_2O_3//$LiMn_2O_4$ full cell and further optimization and development of the nanowire design and fabrication will lead to new opportunities of high power-density energy storage devices.
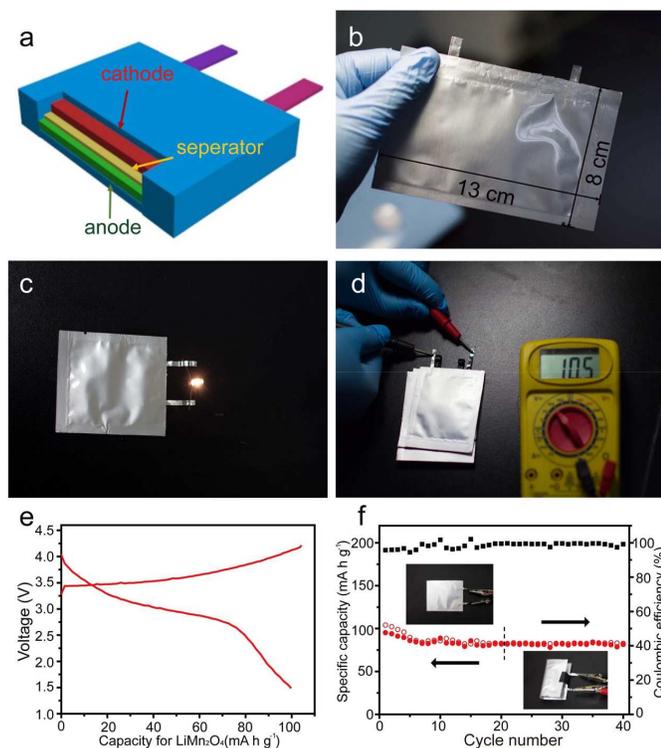
Fig. 17 Flexible Mn_2O_3//$LiMn_2O_4$ full cells. (a) 3D structure scheme and (b) optical image of a flexible Mn_2O_3//$LiMn_2O_4$ full cell;(c) Optical images showing a light emitting diode (3 V, 10 mW) powered by a flexible Mn_2O_3//$LiMn_2O_4$ full cell; (d) Optical image of the voltage output of a three-cell battery in tandem; (e) Charge/discharge curves of a flexible Mn_2O_3//$LiMn_2O_4$ full cell at the first cycle and (f) Cycling performance (red curve) and Coulombic efficiency (black curve) of a representative flexible Mn_2O_3//$LiMn_2O_4$full cell. Reproduced with permission.[114] Copyright 2013, ACS.

2.4 MnO$_2$ and its nanocomposites

Manganese dioxide (MnO_2) possesses a high theoretical capacity of 1233 mAh g^{-1} based on the conversion mechanism.[44, 115] Moreover, it is of environmental benignity and natural abundance. This makes it a promising material for applications in lithium ion batteries. However, due to the low conductivity of MnO_2 and large volume expansion during battery operation, rather low coulombic efficiencies in the first cycle and rapid capacity decays with cycling were obtained.[116-119] For example, Li et al.[117] synthesized novel α-MnO_2 hollow urchins on a large scale by a facile and efficient low-temperature (60 °C) mild reduction route. The α-MnO_2 hollow urchins show a high capacity of 746.0 mAh g^{-1} in the first discharge process, but the capacity of the 40th cycle is only 481 mAh g^{-1}, about 64.4% of the initial capacity. As reported by Reddy et al.,[119] a coaxial MnO_2/CNT array material can give an initial capacity of

around 2000 mAh g^{-1} at a rate of 50 mA g^{-1}. However, the capacity is sharply decayed to 500 mA h g^{-1} after only 15 cycles. They suggested the initial high capacity and enhanced lithium storage capacity can be attributed to in-situ deposition of MnO_2 on CNTs, while the fast capacity decay might result from a structural deterioration of a thick layer of MnO_2 with a compact structure deposited on the outside surface of CNTs. One of the best results showing a capacity of 600 mAh g^{-1} after 100 cycles for a γ -MnO_2 film deposited on nickel metal was reported before 2010.[118] Notwithstanding these results, systematic efforts have been dedicated to optimize the MnO_2 electrodes by combining materials synthesis, processing and engineering techniques, so as to improve the electrochemical performance.

Attempts have also been made recently to fabricate MnO_2 composites with unique nanostructures,[120-122] MnO_2-based nanocomposites consisting of MnO_2 nanostructures and electrically conductive carbon such as carbon nanotubes[123-125] amorphous carbon[126] or graphene,[127-131] its nanocomposites including MnO_2 and other transition metal oxides,[132-134] and MnO_2@polymers.[135] All of these relative results are listed in Table 5. Kundu et al.[132] report the direct growth of mesoporous MnO_2 nanosheet (NS) arrays on a nickel (Ni) foam current collector by electro-deposition followed by a low temperature thermal annealing process (170 °C) in a nitrogen atmosphere. When using the Ni foam supported mesoporous MnO_2 NS arrays as an anode in LIBs, they found that the electrode can deliver a reversible capacity as high as 1690 mA h g^{-1} even after 100 cycles at a charge–discharge current density of 100 mA g^{-1}. Two anodic peaks located at 1.3 and 2.4 V vs Li/Li$^+$ are observed, and they suggested that the re-oxidation of manganese may take place in two steps. It is also interesting to note that the capacity gradually increases with the increasing cycle numbers, which is opposite to the previous literatures.[116-120,135] It is assumed that the increase in capacity might originate from the increased number of vacancies and grain boundaries due to the pulverization of the MnO_2 NSs upon cycling, where Li ions could be stored. This example suggests the electrochemical performance of MnO_2 may be optimized by nanostructure tuning. Guo et al.[127] reported a novel approach to fabricate a hierarchically nanostructured composite comprising one-dimensional (1-D) rod-like layered birnessite-type manganese oxide (LMO), 2-D graphene nanosheets, and a 3-D porous structure (LMO/PEDOT/graphene). As shown in Fig. 18a, the 3-D graphene material is used as a supporting matrix, on which in situ polymerized poly(3,4-ethylenedioxythiophene) (PEDOT) is assembled for the direct growth of uniformly distributed 1-D rod-like LMOs. The composites exhibit a large first discharge capacity of 1835 mAh g^{-1}, a reversible discharge capacity of 1105 mA h g^{-1} and 948 mA h g^{-1} after 15 cycles at a rate of 50 mA g^{-1} (Fig. 18b and 18c). They suggested that the performance enhancement of the LMO/PEDOT/graphene in lithium ion batteries can be explained as follows: (1) the LMO in LMO/PEDOT/graphene has characteristics of an open structure with an interlayer space of approximately 7.2 Å to promote efficient lithium intercalation/deintercalation for high specific capacity; (2) the use of highly conductive 3-D graphene material is favorable in electron transport to enable a fast charge/discharge rate and (3) the PEDOT coating directs the growth of relatively ordered textured LMO and prevents its aggregation for

uniform distribution, which can accommodate large volume expansion during battery operation.

[Table 5]
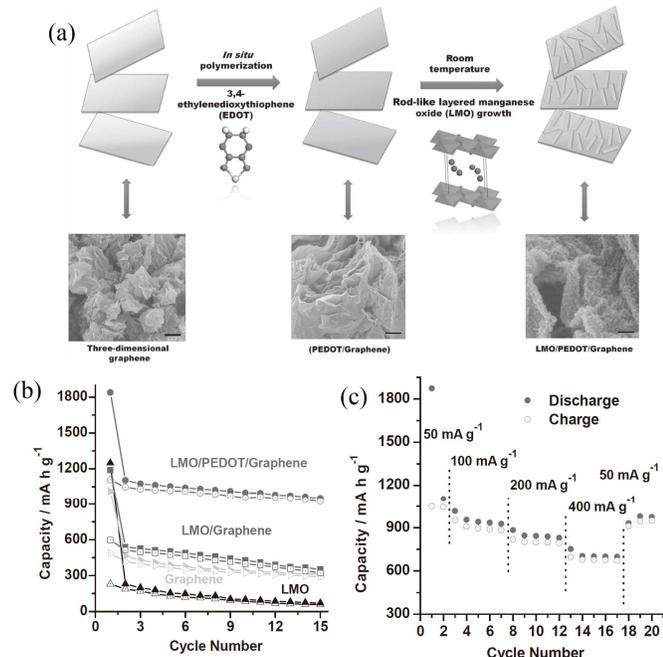
Fig. 18 (a) Schematic representation of the hierarchically nanostructured composite fabrication; (b) Cycling variation in charge/discharge capacity vs. cycle number for different lithium ion batteries; and (c) Capacity of LMO/PEDOT/graphene batteries under various current densities. Reproduced with permission.[127] Copyright 2011, Wiley.

Fig. 19 (a) Schematic illustration of the synthesis of the GMG composite; (b) Rate performance of GMG at various current rates from 0.1 to 1.0 A g^{-1}; and (c) Cycling performance of MnO_2, MG, and GMG at the 0.1 A g^{-1} for the first five cycles and the 0.4 A g^{-1} for the following cycles. Reproduced with permission.[129] Copyright 2013, Wiley.

Li *et al.*[129] designed a unique hierarchical sandwiched structured graphene–MnO_2–GNRs (GMG) composite in which the graphene wraps the porous MnO_2 that directly grows from graphene nanoribbons (GNRs). Fig. 19a depicted the synthesis procedures of the GMG composites. In the composites, graphene and GNRs are in good contact with MnO_2, improving the electrical conductivity of the GMG composites. More importantly, graphene and GNRs can buffer the volume changes and prevent the loss of MnO_2 during Li ion conversion reaction with Li, improving the composite's electrochemical stability performance. As an anode material, the GMG composites demonstrate a reversible specific discharge capacity of 890 mAh g^{-1} at 0.1 A g^{-1} after 180 cycles with various current rates ranging from 0.1 to 1.0 A g^{-1} and shows about 24% improvement compared to the initial capacity after 245 cycles at a current density of 0.4 A g^{-1} (Fig. 19b).

In a recent paper, Li *et al.*[131] prepared MnO_2/3D porous graphene-like (PG) (3D PG–xMn) composites via a simple and cost-effective redox process. Typically, the self-controlled reaction between 3D PG and $KMnO_4$ under neutral pH conditions led to the homogeneous deposition of MnO_2 on the 3D PG networks. They suggested that the porosities of the 3D PG–xMn composites can adjusted by the initial concentration of $KMnO_4$. The surface area and total pore volume of 3D PG–MnO_2 on 3D PG, there was no obvious decrease in powder conductivity of the 3D PG–xMn (x = 0.5 and 1.0) composites,

while the 3D PG–1.5Mn composite shows an obvious decrease. Among the three 3D PG–xMn composites, the 3D PG–1Mn composite displayed the best electrochemical performance. It delivered a discharge capacity of 988 mAh g^{-1} at the second cycle and the discharge capacity could be retained as high as 836 mAh g^{-1} after 200th cycle (~ 84.6% capacity retention). The excellent electrochemical performances of the as-prepared 3D PG–1Mn composites can be attributed to the synergistic effects that stem from its reasonable MnO_2 content (62.7wt% MnO_2) and high conductivity. The branched nanocomposites with β-MnO_2 nanorods as the back-bone and porous α-Fe_2O_3 nanorods as the branches were synthesized by Gu *et al.*.[132] They used a high-temperature annealing process to achieve epitaxial grown of FeOOH on the β-MnO_2 nanorods. The branched nanorods of β-MnO_2/α-Fe_2O_3 exhibit a reversible specific capacity of 1028 mAh g^{-1} at a current density of 1000 mA g^{-1} up to 200 cycles and 881 mAh g^{-1} at 4000 mA g^{-1}. The presence of α-Fe_2O_3 in the branched nanorods greatly promotes the charge transfer at the electrode/electrolyte interface, which is beneficial to the electrochemical performance. These results indicate the importance of the selection of proper chemical xMn composites gradually decrease with the increase of the concentration of $KMnO_4$. The combination of the advantages in structure and components would effectively improve the performance of electrode materials in LIBs.

3. Ternary Mn-based Oxides as anode materials

Ternary Mn-based oxides containing AMn_2O_4 (A = Co and and Zn) with a spinel or spinel-like crystal structure have been investigated as anode materials for LIBs. The Li cycling mechanism involves the "alloying and conversion reaction" for $ZnMn_2O_4$ and the "conversion reaction" for $CoMn_2O_4$.[8] Depending on the structure, morphology, particle size and composition, large and stable reversible capacities have been reported.

3.1 ZnMn₂O₄-based anodes

$ZnMn_2O_4$ has been proposed as a practical alternative anode material for LIBs because of its high theoretical capacity of 1008 mAh g^{-1} (the Zn metal can form an alloy with Li and participate in the conversion reaction along with manganese), low oxidation potentials (*i.e.*, delithiation potential) of zinc and manganese at 1.2 and 1.5 V vs. Li/Li$^+$, respectively. These low oxidation potentials could eventually increase the battery output voltage compared to $ZnFe_2O_4$, and $ZnCo_2O_4$, allowing higher energy density delivery. Furthermore, zinc and manganese are abundant, environmentally friendly, and relatively inexpensive compared to cobalt.[45, 136]

Yang *et al.*[45] synthesized $ZnMn_2O_4$ nanocrystals by a polymer pyrolysis method and fist used the obtained nanocrystals as lithium storage anode materials. The nanocrystalline $ZnMn_2O_4$ electrode delivers an initial reversible capacity of 766 mAh g^{-1} when cycled at 100 mA g^{-1} in the voltage range of 0.01–3.0 V vs. Li/Li$^+$. Cycling studies up to 50 cycles show almost stable cycling performance between 10 and 50 cycles with only an average capacity fading of 0.20% per cycle and the electrode still maintains a capacity of 569 mAh g^{-1} after 50 cycles. After that, $ZnMn_2O_4$ with different particle size and morphologies including flower-like $ZnMn_2O_4$ superstructures,[136] $ZnMn_2O_4$ nanoparticles,[44,137,138] $ZnMn_2O_4$ nanowires,[139] $ZnMn_2O_4$ nanoplates,[140] $ZnMn_2O_4$ hollow microspheres,[141-143] ball-in-ball $ZnMn_2O_4$ hollow microspheres,[144] loaf-like $ZnMn_2O_4$ nanorods,[145] $ZnMn_2O_4$ nanofibers[146] and $ZnMn_2O_4$ mesoscale tubular arrays[147] have been studied and applied as anode materials for LIBs. All of the corresponding results are listed in Table 6. Specifically, the ball-in-ball $ZnMn_2O_4$ hollow microspheres[143] were prepared by a novel template-free method (Fig. 20a-d). The hollow microspheres typically consist of small nanoparticles with an average size of 30 nm, and exhibit a mesoporous feature. When used as an anode material for LIBs, the $ZnMn_2O_4$ hollow microspheres show a high specific capacity of 750 mAh g^{-1} after 120 cycles at 400 mA g^{-1} (Fig. 20e and f). Despite the improved cyclic and rate performance of the $ZnMn_2O_4$ nanomaterials obtained by different strategies, further studies are still required to achieve the long cycling stability and the high rate performance of these materials.

[Table 6]

Recently, in an attempt to improve the electrochemical properties of $ZnMn_2O_4$, Zheng *et al.*[148] prepared thermally reduced graphene oxide (rGO)-wrapped $ZnMn_2O_4$ nanorods via a facile bottom-up approach. They suggested that this unique architecture can provide 1D interconnected $ZnMn_2O_4$ nanoparticle networks to facilitate rapid diffusion of lithium ions within the electrode material. Meanwhile, the rGO sheets could act as a conductive layer for electron transfer and an efficient buffer layer to enable the structural stabilization of $ZnMn_2O_4$ crystals. As the results, a high and stable reversible capacity (707 mA h g^{-1} at 100 mA g^{-1} over 50 cycles) and an excellent rate capability (440 mA h g^{-1} at 2000 mA g^{-1}) are achieved with this composite.
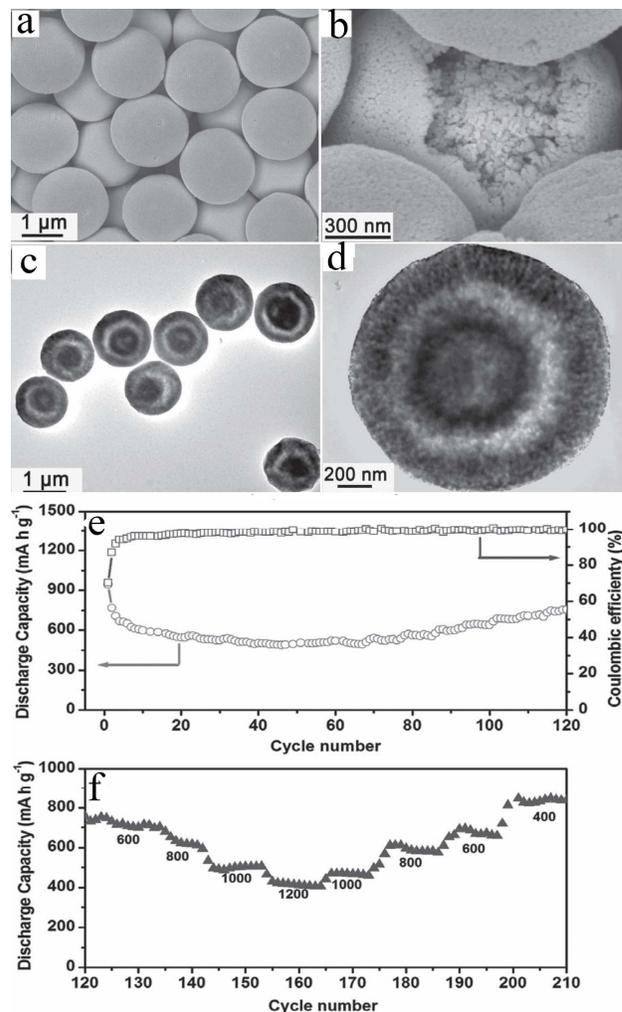
Fig. 20 Typical (a), (b) FESEM and (c), (d) TEM images of $ZnMn_2O_4$ ball-in-ball hollow microspheres; (e) Cycling performance of the $ZnMn_2O_4$ hollow microcubes in the voltage range of 0.01–3.0 V vs. Li/Li$^+$ at current densities of 400 mA g^{-1} and rate performance at different current densities for the same cell after 120 cycles. Reproduced with permission.[143] Copyright 2012, Wiley.

As mentioned in the introduction section, the reasonable selections of binders and electrolyte are beneficial to the improvement of the rate and cyclic performance of metal oxides-based electrodes. Courtel *et al.*[44] have studied the effects of the binder and electrolyte on the cycling performance of $ZnMn_2O_4$ in a recently published paper. The electrochemical performance of $ZnMn_2O_4$ electrodes using five binders (PVDF dissolved in NMP, and four other water-soluble binders such as NaCMC, LiCMC, XG and Baytron; CMC = carboxymethylcellulose) show that the LiCMC and NaCMC are

the best binders (Fig. 21). Specifically, the electrode fabricated by $ZnMn_2O_4$ nanoparticles (<150 nm) sintered at 800 °C and LiCMC binder exhibit a capacity of 690 mA h g^{-1} after 70 cycles at C/10 and good rate capability (450 mA h g^{-1} for 0.5C, 340 mA h g^{-1} for 1 C, 230 mA h g^{-1} for 2C, and 150 mA h g^{-1} for 3C rate, respectively). In addition, studies on the effect of the electrolyte on the cycling performance of $ZnMn_2O_4$ electrode showed that carbonate (EC) : dimethyl carbonate (DEC) mixture (3:7 by vol.) is the best electrolyte and the PC (propylene carbonate) is the worst one (Fig. 22). These results could be explained by the fact that PC does not form the polymeric organic layer or that the layer formed with PC is
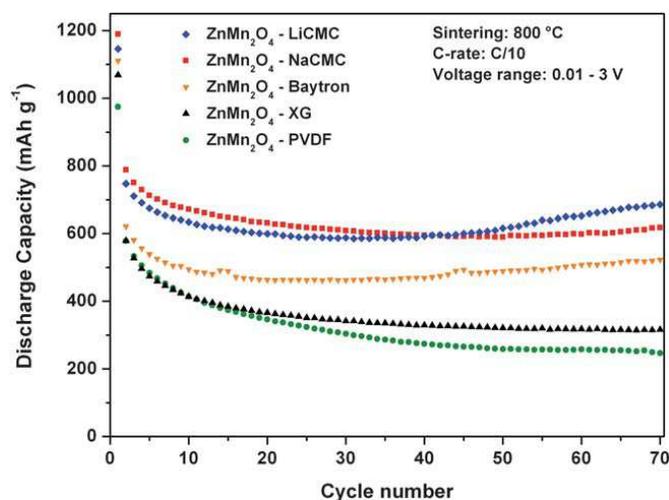
Fig. 21 Discharge capacities of ZnMn2O4 electrodes made using five different binders: PVDF, NaCMC, LiCMC, XG, and Baytron. Reproduced with permission.[44] Copyright 2011, RSC.
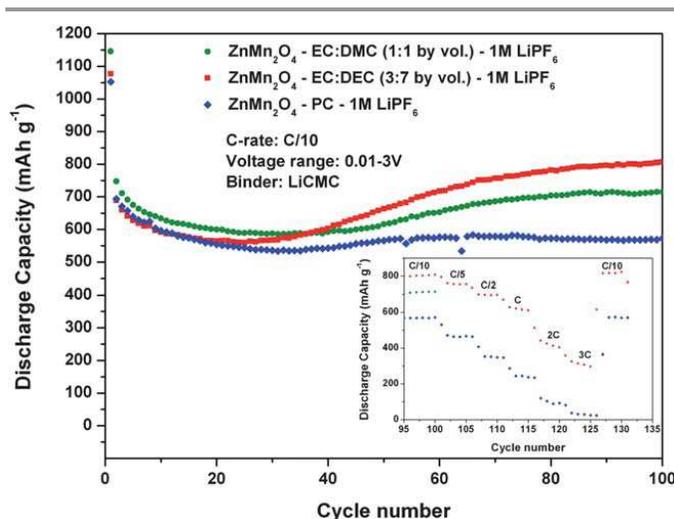
Fig. 22 Discharge capacities of $ZnMn_2O_4$ electrodes. The cells were cycled at room temperature using the same lithium salt, 1 M $LiPF_6$ in three different electrolytes: EC : DMC (1 : 1 by vol.), EC : DEC (3 : 7 by vol.), and PC. Reproduced with permission.[21] Copyright 2011, RSC.

inactive to lithium storage. Furthermore, the authors assembled a full cell for the first time, using $ZnMn_2O_4$ as an anode material, $LiMn_{1.5}Ni_{0.5}O_4$ as cathode material, and 1 M $LiPF_6$ in

EC : DEC (3:7 by vol.) as electrolyte. The full cell was cycled between 1.5 V and 4.7 V at 0.1 C and the capacity was reported versus the limiting electrode (cathode). The initial capacity at a cycling rate of 0.1 C is 108 mAh g^{-1}. During the first charge there is a plateau at 4.1 V. However, in the subsequent discharge and charge cycles, the charge vs. voltage curve exhibits a sloping voltage between 3.5 V and 3 V and 3.5 and 4.1 V, respectively. Unfortunately, after 20 cycles, the battery only exhibits a capacity of 75 mAh g^{-1}.

3.2 $CoMn_2O_4$ anodes

$CoMn_2O_4$ has an incomplete normal-type spinel with a tetragonal structure (c/a = 1.14) because of the Jahn–Teller effect of Mn^{3+} ($3d^4$). Co^{2+} mainly occupies the A sites and Mn^{3+} mainly occupies the B sites. It can store Li^+ through the oxidation of metallic Co and Mn to CoO and MnO respectively, leading to a high initial discharge capacity of 921 mA h g^{-1} and a reversible capacity of 691 mAh g^{-1}.[44, 149] Courtel et al.[44] first reported sub-micrometer sized $CoMn_2O_4$ particles with a reversible capacity of about 515 mAh g^{-1} at a current density of 69 mA g^{-1}. However, a capacity of only 330 mAh g^{-1} after 50 cycles was obtained for this material.

Investigation conducted by Zhou et al.[150] on double-shelled $CoMn_2O_4$ hollow microcubes prepared via a facile co-precipitation and annealing method (600 °C with a ramping rate of 2 °C min^{-1}) using $Co_{0.33}Mn_{0.67}CO_3$ as precursor, showed an initial discharge and charge capacities of 1282 and 806 mA h g^{-1} and a reversible capacity of 624 mAh g^{-1} after 50 cycles at 200 mA g^{-1}, respectively (Fig. 23). It is interesting that the initial charge capacity is much higher than the theoretical value (691 mAh g^{-1}) based on the oxidation reactions of metallic Co and Mn nanoparticles to CoO and MnO: $3Li_2O + Co + 2Mn \leftrightarrow 2MnO + CoO + 6Li+ + 6e^-$. They suggested that the extra reversible capacity in their studies is attributed to the reversible formation/dissolution of polymeric gel-like film. Single-crystalline $CoMn_2O_4$ nano/submicrorods with diameters of about 100 nm and lengths up to tens of micrometers were synthesized[151] by using hydrothermally synthesized β-MnO_2 nanorods as the templates and cobalt hydroxide as cobalt source followed by annealing at 650 °C in air for 10 h with a heating rate of 5 °C min^{-1}. The reversible capacities of 512 and 400 mAh g^{-1} at the current densities of 200 and 1000 mA g^{-1} after 100 cycles were obtained, respectively, in their report. Recently, Kim et al.[152] synthesized yolk–shell and hollow $CoMn_2O_4$ powders by spray pyrolysis from aqueous spray solutions of the cobalt and manganese components with different concentrations of sucrose. The single and double-shelled yolk–shell powders prepared from spray solutions with 0.4 and 0.7 M sucrose have high discharge capacities of 519 and 573 mAh g^{-1} in the voltage range of 0.01–3 V vs. Li/Li^+, respectively, after 40 cycles at a high discharge rate of 800 mA g^{-1}. The group of Lou[153] obtained hierarchical $CoMn_2O_4$ array micro-/nanostructures with tunable morphology on conductive stainless steel by a facile solvothermal route and a subsequent annealing treatment. The $CoMn_2O_4$ nanowires show reversible

capacities of 530–215 mA h g^{-1} when cycled at 1–10 C (1 C = 700 mA g^{-1}). Additional recent studies on CoMn$_2$O$_4$ as anode materials are multiporous CoMn$_2$O$_4$ spinel quasi-hollow spheres reported by Li *et al.*[154] and hierarchical nanosheets reported by Hu *et al.*[155]
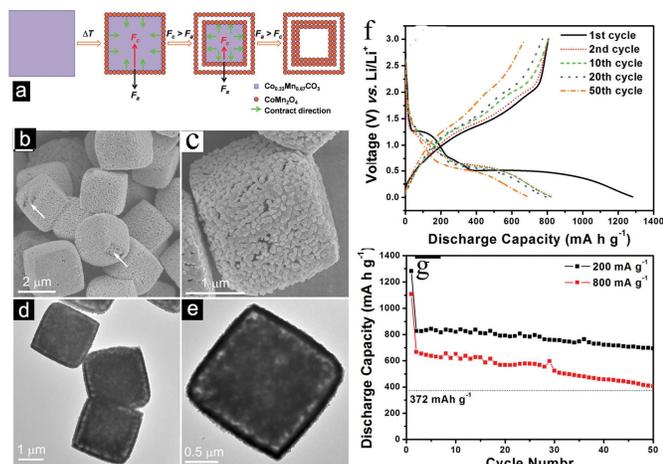
Fig. 23 (a) llustration of the fabrication of double-shell CoMn$_2$O$_4$ hollow microcubes; Typical (b), (c) FESEM and (d), (e) TEM images; (f) discharge/charge profiles; and (g) cycling performance of the double-shelled CoMn$_2$O$_4$ hollow microcubes in the voltage range of 0.01–3.0 V vs. Li/Li$^+$ at current densities of 200 and 800 mA g^{-1}. Reproduced with permission.[150] Copyright 2013, Wiley.

4. Conclusion and Outlook

The progress of design, synthesis and electrochemical evaluation of Li storage and cycling properties of binary, ternary, and complex Mn-based metal oxides in recent years have been reviewed. The motivations of the reviewed studies of these oxides as anode materials came from the eager to replace the graphite anode and increase the energy density, decrease the cost, and improve the safety operation of the existing LIBs.

There are two mechanisms, the "conversion reaction" mechanism for binary Mn-based oxides (MnO, Mn$_3$O$_4$, Mn$_2$O$_3$ and MnO$_2$) and some ternary oxides (CoMn$_2$O$_4$) as well "conversion reaction involving alloying" mechanism for ZnMn$_2$O$_4$. As discussed previously, many strategies including morphology control of the micro-/nanostructures, carbon-coating, composition optimization of the Mn-based oxides have been extensively developed, with the aim to improve the rate and cycling performance and to promote the practical application of these oxides in LIBs. Despite some important advances have been made on the cycling and rate performance of the Mn-based oxides as anode materials, the majority of the literatures regarding the applications of these oxides in LIBs with promising enhancement are mainly experimental results. Furthermore, different experimental results were obtained even if the same synthetic methods were used to prepare Mn-based anode materials with the same morphologies. A comprehensive and in-depth insight into the relationship among the composition, micro/nano-structures and the electrochemical Li storage performance of these oxides are therefore still in imminent demand. This requires *in-situ* characterizations,

including *in-situ* X-ray diffraction (XRD), *in-situ* X-ray absorption spectroscopy (XAS) and *in-situ* high-resolution transmission electron microscopy (HTEM), to verify the fine structure and the reaction pathway of the obtained materials, and to assign electrochemical features with specific reactions.

Because of the large electrode polarization and solid electrolyte interphase (SEI) film formation, the Mn-based oxides suffer from large irreversible capacity loss (ICL) during the first cycle. Moreover, the mechanical and chemical properties of SEI film have significant impacts on the columbic efficiency, the cycling performance and the safety operation of LIBs. Great efforts should be paid to modify the mechanical properties of SEI films by electrolyte additive addition and/or electrode surface modification, aiming at the formation of elastic and flexible SEI films to accommodate large volume variation during charging/discharging cycles and achieve excellent cycling performance and high columbic efficiencies.

The fabrication of full cells using Mn-based oxides as anode materials has been rarely investigated, although several examples have been reported in recent years. The Mn-based oxides are suitable to assemble full cells by combining with 4 V and 5 V cathodes. To obtained full cells with high cycling and rate performance as well as good safety, significant developments need to be made on the optimization the preparation parameters of the anodes, cathodes and electrolytes as well their matching. It will boost the development of full cells based on the Mn-based oxides as anode materials in the coming years.

In spite of the challenges aforementioned, the field for the research of Mn-based oxide anodes, especially for MnO, Mn$_3$O$_4$ and ZnMn$_2$O$_4$, for LIBs has a very bright future due to the extensive applications of nanotechnology and *in-situ* characterization techniques.

Acknowledgements

Notes and references

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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Table 1. Experimental values of potential for the plateaus and theoretical specific capacities associated with conversion reactions in Mn-based oxides.

Mn-based oxides	Potential (Li^+/Li)	Theoretical specific capacity (mA h g^{-1})	Ref.
MnO	0.2	756	41
Mn_3O_4	0.37	937	42
Mn_2O_3	0.3	1019	43
MnO_2	0.4	1223	43
$CoMn_2O_4$	0.3	921	44
$ZnMn_2O_4$	0.3	1008	45

Table 2.A summary of recent studies on MnO-based anodes for LIBs.

Materials	Preparation method	1st discharge/charge capacity (mAh g^{-1})	Capacity retention	Rate performance (mAh g^{-1})	Ref.
MnO powder	Commercial + ball milling	~ 1266/766 at 50 mAg^{-1}	550(10 cycles)	400 at 400mAg^{-1}	46
MnO microspheres	Precipitation + annealing	1126/800 at 50 mAg^{-1}	704(50cycles)	600 at 400mAg^{-1}	53
Porous MnO nanoflakes	Hydrothermal method	781/570 at 246 mAg^{-1}	648 (100cycles)	376 at 2460 mAg^{-1}	49
Crystalline MnO films	Radio-frequency (RF) sputtering + annealing	550/413 at 0.05C	350(100cycles)	150 at 20C	54
Amorphous MnO$_x$/C	Aerosol spray pyrolysis	1083/650 at 200 mAg^{-1}	601 (130cycles)	500 at 800 mAg^{-1}	55
MnO$_x$/OMC nanocomposite	Wet-impregnation + annealing	1390/860 at 100 mAg^{-1}	950(50cycles)	500 at 2000 mAg^{-1}	56
MesoporousMnO/ C	Microwave-polyol process + annealing	1456/1000 at 200 mAg^{-1}	1224(200cycles)	731 at 1500 mAg^{-1}	57
MonodisperseMnO /C hollow microspheres	A facile biotemplating technique	1021.9/755.6 mAg^{-1}	702.2(50cycles)	230 at 3000 mAg^{-1}	58
(MnO/MWNTs)	Hydrothermal + annealing	1050/686 at 14.4 mAg^{-1}	484 (200 cycles) at 144.1 mA g^{-1}	455 at 310 mAg^{-1}	59
MnO-attached graphene	Impregnation + annealing	685/635 at 0.2C	490 (30 cycles) at 1 C	410 at 5C	60
MnO nanoparticles/graph -ene composite	*In-itu*carbothermal reduction	1080/700 at 100 mAg^{-1}	782(60cycles)	402 at 1000 mAg^{-1}	61
Nitrogen-doped MnO/graphenenan osheets	Hydrothermal method +ammonia annealing	1193/829 at 50 mAg^{-1}	772(90cycles)at100 mAg^{-1}	202 at 5000 mAg^{-1}	62
(MnO/RGOS)	Liquid phase deposition + annealing	1001/648 at 100 mAg^{-1}	666 (50cycles)	454 at 400 mAg^{-1}	63
MnO/graphene	Liquid phase deposition + annealing	900/891 at 200 mAg^{-1}	2014 (150cycles)	843 at 2000 mAg^{-1}	64
Coaxial MnO/C nanotubes	Self-templates method	1014/678 at 75.5 mAg^{-1}	600(10cycles)	500 at 188.9 mAg^{-1}	65
MnO/C core–shell nanorods	*In-situ* reduction method	1090/780 at 200 mAg^{-1}	600(40cycles)		66
MnO@carbon core–shell nanowires	Solvothermal+ annealing	1196/840 at 100 mAg^{-1}	801(200cycles)at 500 mAg^{-1}	462 at 2000 mAg^{-1}	66
MnO@1-D carbon	Annealing of C$_4$H$_4$MnO$_6$	1249/738 at 500 mAg^{-1}	660(1000 cycles)	250 at 6Ag^{-1}	67

composites					
Porous MnO/C nanotubes	Hydrothermal method+ annealing	1129/810 at 100 mAg^{-1}	763(100cycles)	303 at 3200 mAg^{-1}	68
MnO/C nanorods	Hydrothermal method+ annealing	1408/707 at 200 mAg^{-1}	481(50cycles)	252 at 1000mA/g	69
Porous carbon-modified MnO disks	Microwave-polyol process + annealing	1387/997 at 100 mAg^{-1}	1044 (140cycles)	535 at 1000 mAg^{-1}	70
Nano-MnO/C composites	An alcoholysis process + annealing	1650/900 at 75.5mA/g	939 (30cycles)	589 at 7550 mAg^{-1}	71
MnO@C core–shell nanoplates	Hydrothermal method+ annealing	1365/770 at 200 mAg^{-1}	563(30cycles)	550 at 300 mAg^{-1}	72
MnO$_x$/C nanocomposite	Sol-gel method + annealing	1055/700 at 200 mAg^{-1}	500(100cycles)	320-345 at 2000 mAg^{-1}	73
Hierarchical micro/nanostructured MnO	hydrothermal method	1051/750 at 98 mAg^{-1}	783 (200cycles)	350 at 1572 mAg^{-1}	74

Table 3.A summary of recent studies on Mn_3O_4-based anodes for LIBs.

Materials	Preparation method	1st discharge/charge capacity (mAh g^{-1})	Capacity retention	Rate performance (mAh g^{-1})	Ref.
SpongelikeNanosized Mn_3O_4	Precipitationmethod	1327/869 at 40 mA g^{-1}	800 (40 cycles)	500 at 10 C	43
Mn_3O_4 nanorods	hydrothermal + annealing method	1050/555 at 0.1C	108(100cycles)		80
Mn_3O_4 octahedral	Hydrothermal method	1009/700 at 50 mAg^{-1}	404 (20cycles)	269 at 500 mAg^{-1}	81
Mesoporous stacked Mn_3O_4nanosheets	Chemical bath deposition (CBD) route	824/300 at 0.1C	400(60cycles)	298 at 1.5C	82
Porous $Mn_xCo_{3-x}O_4$nanocubes	A new facile strategy	discharege1395 at 200 mAg^{-1}	733(30cycles)	473 at 1600mAg^{-1}	83
Mesoporous Mn_3O_4 nanotubes	Hydrothermal +hydrogen reduction	1065/641.5 at 100 mAg^{-1}	641(100cycles) at 500 mAg^{-1}	525 at 1000 mAg^{-1}	84
Order-aligned Mn_3O_4nanostructures	Electrochemically depositing method	919/622 at 936 mAg^{-1}	882(85cycles)	500 at 40Ag^{-1}	85
Mn_3O_4octahedrons	Dealloying of MnAl alloy	918.3/536.8 at 100 mAg^{-1}	746 (500 cycles)	240 at 1500 mAg^{-1}	96
Fe-doped Mn_xO_y	Nanocasting technique+controlled calcination	1358/800 at 200 mAg^{-1}	620(100cycles)	409 at 1600 mAg^{-1}	87
Fe_2O_3–Mn_3O_4 nanocomposite	electrostatically-derived selfassembly method	1050/919.8 at 90 mAg^{-1}	230(25cycles)		88
Mn_3O_4/graphene hybrid	Two-step solution-phase reactions	1350/950 at 40 mAg^{-1}	730 (40 cycles)	390 at 1600 mAg^{-1}	91
Mn_3O_4/graphene composite	Ultra-sonication + annealing	1375/750 at 75 mAg^{-1}	720(100cycles)		92
Mn_3O_4–graphenenanoc omposite	Microwave hydrothermal technique	1354/901 at 40 mAg^{-1}	900 (50cycles)	400 at 1000 mAg^{-1}	93
Mn_3O_4/Graphite nanosheet	Solvothermal route	1079/762 at 50 mAg^{-1}	~ 600 (50cycles)	~ 250 at 600 mAg^{-1}	94
Mn_3O_4/ordered mesoporous carbons	Precipitation + annealing method	1843/773 at 100 mAg^{-1}	802(50cycles)		95
Mn_3O_4 /(MWCNTs)nanocomp osite	Solvothermal route	1380/750 at 100 mAg^{-1}	592(50cycles)	387 at 1000 mAg^{-1}	96
Mn_3O_4/Cnanorod	Solvothermal route	1246/723 at 40 mAg^{-1}	473(50cycles)		97
Mn_3O_4nanoparticles/gr aphene	An *in-situ* transformation method	1600/700 at 60 mAg^{-1}	500(40cycles)	200 at 1500 mAg^{-1}	98
Mn_3O_4nanocrystals/(R GO)	Ultra-sonication-assisted method	1630/1050 at 40 mAg^{-1}	900(20cycles)	200 at 1600 mAg^{-1}	99

| Mn$_3$O$_4$/SACNT | Thermal decomposition | ≈1900/1108.4 at 1C | 390(100cycles) | 342 at 10C | 100 |
| Mesoporous Mn$_3$O$_4$nanosheet/graphene | Precipitation | 1553/973 at 400 mAg^{-1} | 910(230cycles) | 360 at 8Ag^{-1} | 101 |

Table 4 A summary of recent investigations on Mn_2O_3-based anodes for LIBs.

Materials	Pereparation method	1st discharge/charge capacity (mAh g^{-1})	Capacity retention	Rate performance (mAh g^{-1})	Ref.
Mn_2O_3 nanorods	Hydrothermal +	1509/689 at 100 mA g^{-1}	374 (30 cycles)		104
Mn_2O_3 nanofibers	annealing	1694/795 at 100 mA g^{-1}	404 (30 cycles)		
Mn_2O_3 nanowires		1611/707 at 100 mA g^{-1}	384 (30 cycles)		
Mn_2O_3 nanorods	Hydrothermal +	998/349 at 100 mA g^{-1}	~50 (100 cycles)		105
	annealing				
Straw-sheaf-shaped	Solvothermal +	1179/680 at 200 mA	400 (150 cycles)	270 at 800 mA g^{-1}	106
Mn_2O_3	annealing	g^{-1}(0.01-2.5 V)	at 400 mA g^{-1}		
Oval-shaped		1159/~650 at 200 mA g^{-1}	320 (150 cycles)		
Mn_2O_3		(0.01-2.5 V)	at 400 mA g^{-1}		
Porous Mn_2O_3	Solvothermal +	1310/882 at 100 mA g^{-1}	796 (50 cycles)	470 at 2400 mA g^{-1}	107
microsphere	annealing		at 100 mA g^{-1}		
Porous Mn_2O_3	Solvothermal +	2134/1400 at 50 mA g^{-1}	748 (45 cycles)	423 at 1600 mA g^{-1}	108
microspheres	annealing				
Mesoporous Mn_2O_3	Hydrothermal +	668/~630 at 200 mA g^{-1}	524 (200 cycles)	~ 150 at 50 mA g^{-1}	109
microspheres	annealing				
Hollow Mn_2O_3	Hydrothermal +	1875/909 at 50 mA g^{-1}	280 (200cycles)	380 at 400 mA g^{-1}	110
nanocones	annealing		at 200 mA g^{-1}		
Porors Mn_2O_3	Solvothermal +	1518/987 at 300 mA g^{-1}	521 (100cycles)	500 at 500 mA g^{-1}	111
nanosheets	annealing				
Cubic Mn_2O_3	Hydrothermal +	1680/780 at 100 mA g^{-1}	~300 (55 cycles)	240 at 600 mA g^{-1}	113
spindle Mn_2O_3	annealing	1530/620 at 400 mA g^{-1}	~200 (50 cycles)		
Fusiform Mn_2O_3		1402/400 at 100 mA g^{-1}	155 (40 cycles)		
Cu-doped hollow	Hydrothermal +	1998/1190 at 100 mA g^{-1}	642 (100 cycles)	308 at 815 mA g^{-1}	89
Mn_2O_3 spheres	annealing				

Table 5.A summary of recent studies on MnO_2-based anodes for LIBs.

Materials	Preparation method	1st discharge/charge capacity (mAh g^{-1})	Capacity retention	Rate performance (mAh g^{-1})	Ref.
Phase-pure β-MnO_2nanorods	Hydrothermal + annealing	1728/488 at 0.1 mA cm^{-2}			43
Interconnected MnO_2nanowires	Hydrothermal + annealing	1650/800 at 85 mA g^{-1}	~580(100 cycles)		116
Hollowα-MnO_2urchin	low-temperature (60 °C) mild reduction route	746/650 at 270 mA g^{-1}	481 (40 cycles)		117
Nanoporous γ-MnO_2 hollow microspheres	Hydrothermal + annealing	1289/1071at 100mA g^{-1}	657 (20 cycles)		118
Nanoporousγ-MnO_2nanocubes		1992/1042 at 100 mA g^{-1}	602 (20 cycles)		
Coaxial MnO_2/Carbon Nanotube	Templates + infiltration + annealing	2500/880 at 50 mA g^{-1}	500 (16 cycles)		119
α-MnO_2nanotubes	Exfoliation and scrolling approach	~1200/1000 at 200 mA g^{-1}	512 (300 cycles) at 800 mA g^{-1}		120
Hierarchical hollowmicrospheres constructed with MnO_2nanotubes	A bubble template-based self-scrolling method	983/830 at 300 mA g^{-1}	700 (30 cycles)		121
Mesoporous MnO_2 nanosheet	Electrodeposition + annealing	1643/1225 at 50 mA g^{-1}	1690 (100 cycles) at 100 mA g^{-1}	900 at 1000 mA g^{-1}	122
Nanoflaky MnO_2/carbon nanotube	Hydrothermal method	1402/816 at 200 mA g^{-1}	620 (50 cycles)	320 at 4000 mA g^{-1}	123
Mesoporous γ-MnO_2 particles/ carbon nanotube	Ultrasound irradiation	1278/741 at 50 mA g^{-1}	934 (150 cycles)	~380 at 1000 mA g^{-1}	124
Coaxial MWNTs@MnO_2@PPy	Immersing + *in-situ* polymerization	1250/730 at 100 mA g^{-1}	820 (120 cycles)	530 at 1000 mA g^{-1}	125
MnO_2 nanosheets/Core-leaf onion-like carbon	Hydrothermal method	1278/854 at 50 mA g^{-1}	541 (100 cycles)	102 at 2000 mA g^{-1}	126
MnO_2/Conjugated polymer/Graphene	*In-situ* polymerization + Immersing	1835/1050 at 50 mA g^{-1}	948 (15 cycles)	698 at 400 mA g^{-1}	127
MnO_2 Nanotube/Graphene	Ultra-filtration technique	1250/686 at 100 mA g^{-1}	495 (40 cycles)	208 at 1600 mA g^{-1}	128
Graphene-Wrapped MnO_2–Graphene Nanoribbons	Hydrothermal + electrostatic interaction	880/600 at 100 mA g^{-1}	612 (250 cycles) at 400 mA g^{-1}	580 at 1000 mA g^{-1}	129

α-MnO$_2$/grapheme 3D network	Hydrothermal approach	1875/1150 at 60 mA g^{-1}	998 (30 cycles)	590 at 12 A g^{-1}	130
Porous MnO$_2$/3D graphene nanocoposites	A redox process + annealing	1554/917 at 100 mA g^{-1}	836 (200 cycles)	358 at 1600 mA g^{-1}	131
Porous α-Fe$_2$O$_3$ branches on β-MnO$_2$ nanorods	Hydrothermal + annealing	1480/1147 at 100 mA g^{-1}	1028 (200 cycles) at 1000 mA g^{-1}	881 at 4000 mA g^{-1}	132
TiO$_2$−C/MnO$_2$ core−double-shell nanowire	*In-situ* chemical redox	865/500 at 33.5 mA g^{-1}	218 (150 cycles) at 3350 mA g^{-1}	230 at 3350 mA g^{-1}	133
ZnO/MnO$_2$ sea urchin-like sleeve array	Electro-deposition	2023/878 at 200 mA g^{-1}	1259 (100 cycles)	150 at 5000 mA g^{-1}	134
Polythiophene (PTh)-Coated Ultrathin MnO$_2$ Nanosheets	A redox process + *in-situ* polymerization	700 at 500 mA g^{-1}	500 (100 cycles)		135

Table 6 A summary of recent studies on $ZnMn_2O_4$-based anodes for LIBs.

Materials	Preparation method	1st discharge/charge capacity (mAh g^{-1})	Capacity retention	Rate performance (mAh g^{-1})	Ref.
Nanocrystalline $ZnMn_2O_4$	Polymer pyrolysis route	1302/766 at 100 mA g^{-1}	569 (50 cycles)		45
Flower-like $ZnMn_2O_4$	Solvothermal method	1350/763 at 100 mA g^{-1}	626 (50 cycles)		136
Nanocrystalline $ZnMn_2O_4$	Coprecipitation method	1145/800 at 100 mA g^{-1}	690 (70cycles)	365 at 1000 mA g^{-1}	44
Nanocrystalline $ZnMn_2O_4$	A single-source precursor route	1088/680 at 100 mA g^{-1}	650 (200 cycles)	405 at 600 mA g^{-1}	137
Nanocrystalline $ZnMn_2O_4$	Hydrothermal method	1200/680 at 100 mA g^{-1}	430 (50cycles)	75 at 2000 mA g^{-1}	138
$ZnMn_2O_4$ nanowires	solid-state reaction	1400/891 at 60 mA g^{-1}	650 (40cycles)	350 at 1000 mA g^{-1}	139
$ZnMn_2O_4$Nanoplates	An "escape-by-crafty-scheme" method	1277/730 at 100 mA g^{-1}	502 (30 cycles)	324 at 1800 mA g^{-1}	140
$ZnMn_2O_4$ hollow microspheres	Coprecipitation + annealing method	1325/772 at 400 mA g^{-1}	607 (100 cycles)	361 at 1600 mA g^{-1}	141
$ZnMn_2O_4$ hollow microspheres	solvothermal method	1335/750 at 100 mA g^{-1}	433 (50 cycles)	245 at 400 mA g^{-1}	142
$ZnMn_2O_4$ hollow microspheres	Coprecipitation + annealing method	1260/830 at 100 mA g^{-1}	599 (50 cycles)	450 at 1000 mA g^{-1}	143
Ball-in-ball $ZnMn_2O_4$ hollow microspheres	solvothermal + annealing method	945/6622 at 400 mA g^{-1}	790 (120 cycles)	396 at 1200 mA g^{-1}	144
Loaf-like $ZnMn_2O_4$	Hydrothermal + annealing	1357/839 at 100 mA g^{-1}	517 (100cycles) at 500 mA g^{-1}	457 at 1000 mA g^{-1}	145
$ZnMn_2O_4$nanorods	Electrospinning	1257/680 at 60 mA g^{-1}	318 (50 cycles)		146
$ZnMn_2O_4$nanofibers		1469/716 at 60 mA g^{-1}	705 (50 cycles)		
$ZnMn_2O_4$ nanowires		1526/891 at 60 mA g^{-1}	530 (50 cycles)		
$ZnMn_2O_4$mesoscale tubular arrays	A reactive template route + annealing	1198/784 at 100 mA g^{-1}	784 (100 cycles)	364 at 1600 mA g^{-1}	147
rGO–$ZnMn_2O_4$ composite	A bottom-up wrapping route	1412/960 at 100 mA g^{-1}	707 (100 cycles)	450 at 2000 mA g^{-1}	148