Facile synthesis of porous MnO/C nanotubes as a high capacity anode material for lithium ion batteries†

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Porous MnO/C nanotubes are synthesized by a facile hydrothermal method followed by thermal annealing, and possess excellent cyclability and high rate capability as an anode for lithium ion batteries.

Lithium ion batteries (LIBs) have been considered as one of the most promising power sources for hybrid electric vehicles (HEVs) and portable electronic devices due to their high specific capacity, lack of memory and long cycle life.1,2 The electrode materials play a crucial role on the performance of LIBs, and are therefore the key for improving the cyclability and rate capability in order to meet the increasing demand in high energy and high power LIBs. Tremendous efforts have been made to explore anode and/or cathode materials in the past years. As first reported by Tarascon et al.,3 transition metal oxides are very appealing anode materials due to their higher theoretical capacities than that of commercial graphite (372 mAh g−1). Among them, MnO has attracted more and more attention recently owing to its high theoretical capacity (755.6 mAh g−1), low cost, environmentally benign property and low electrochemical motivation force (emf) (1.032 V vs. Li/Li+).4 In comparison with other metal oxides such as Fe2O3, NiO, CoO, CuO, etc.4,5 The MnO reacts with lithium through a conversion reaction to form manganese nanocrystals that are well dispersed in the Li2O matrix. Such a process usually causes drastic volume change and severe capacity fading. In addition, the low conductivity of the MnO makes it suffer from very poor rate capability. It is well recognized that electrode materials with deliberately designed nanostructures could accommodate the volume change, and the high specific surface area of nanosized materials could offer more active sites for lithium ions. As a consequence the performances of such anode or cathode nanomaterials could be significantly enhanced.6,7 Various nanostructures of MnO have been synthesized and employed as anode materials of LIBs, nanorods,4 nanocubes,5 coaxial nanotubes,7 etc. To the best of our knowledge, Chen et al. have reported so far the best cycle performance of MnO anode materials, which delivered 650 mAh g−1 after 150 cycles at 35.5 mA g−1,8 while the rate capability was not remarkable, for which the capacity at a high current density of 1600 mA g−1 in 3 cycles was only ca. 210 mAh g−1. Therefore, the synthesis of MnO anode materials possessing both superior cyclability and high rate capability presents a great challenge.

One dimensional (1D) nanostructures have attracted a great attention as anode materials for LIBs; since they allow for better accommodation of volume changes during repeated charge/discharge cycles. Moreover, the 1D nanostructure possesses direct one-dimensional electronic pathways for efficient charge transport.12 Furthermore, porous and hollow structures have also attracted lots of attention as electrode materials for LIBs, since they can facilitate the transportation of electrolytes and accommodate volume changes.13,14

In this Communication, MnO/C nanotubes with porous structure are synthesized by a facile hydrothermal method followed by thermal annealing. The as-synthesized materials serving as an anode for LIBs present superior cyclability and rate capability. 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.

The synthesis process of the porous MnO/C nanotubes is illustrated in Scheme S1 (ESI†). In our previous study,15 we found that hydroxyls can function as a structure-directing agent to form different nanostructures based on the organic molecules' structure. Therefore, when the hydrothermal reaction started, ethanol molecules may be self-assembled into a rod-like aggregating entity due to the chain structure of the ethanol molecule. Since primary alcohols are easy to oxidize into an acid using a strong oxidant such as potassium permanganate under heat treatment, the ethanol rod-like aggregating entity was oxidized to acetic acid with rising temperature, which resulted in the formation of a MnO2 precipitate outside the acetic acid rod-like aggregating entity (eqn (S1, ESI†)). They were further gradually aggregated...
and coarsened to MnO2@acetic acid nanorods through an Ostwald ripening process. These are confirmed by the SEM images (Fig. S1, ESI†) of the products at different hydrothermal reaction times. Along with the progress of the hydrothermal reaction, MnO2 was decomposed to MnO(OH) and oxygen accompanying the decomposition of acetic acid into carbon dioxide and water (eqn (S2) and (S3), ESI†), leading to the formation of MnO(OH) nanotubes with hollow interiors, as adequately demonstrated in Fig. S2 (ESI†). The MnO(OH) nanotubes were then annealed under 300 °C for 2 h in Ar atmosphere to generate Mn3O4 nanotubes (eqn (S4, ESI†)). The structure and composition of the Mn3O4 nanotubes are confirmed by XRD pattern in Fig. 1a. The diffraction peaks are in good agreement with the standard values for the tetragonal phase of Mn3O4 (JCPDF no. 01-075-1560) with space group I41/amd. The sharp intensities of the diffraction peaks indicate its good crystallinity. The SEM images (Fig. 1b and the inset) and TEM image in Fig. 1c indicate that the tubular morphology is well maintained after thermal annealing. The SAED pattern in Fig. 1d demonstrates the single-crystalline property of Mn3O4 nanotubes and the d-spacing is measured at 0.249 nm and 0.330 nm, which are in accordance with the d-spacing of the (211) and (112) crystal planes of Mn3O4, respectively. After hydrothermal reaction of the Mn3O4 nanotubes with glucose solutions, a thin carbon shell was coated on the surface of Mn3O4 nanotubes to form Mn3O4@C nanotubes. Finally, porous MnO/C nanotubes were yielded after sintering at 500 °C for 3 h in argon. The formation of the porous structure was ascribed to the release of gases when Mn3O4 was reduced to form MnO by carbon (eqn (S5, ESI†)). The overall synthesis procedure for the MnO/C nanotubes may be described by the equations presented in ESI†.

The morphology and microstructure of the porous MnO/C nanotubes are clarified by the SEM and TEM images in Fig. 2. The tubular morphology is also conserved after carbon coating. However, as clearly seen in Fig. 2a and 2b, numerous pores appeared on the surface of nanotubes. The TEM image of an individual MnO/C nanotube in Fig. 2c further confirms the porous structure. We observe cavities as evidenced by the sharp contrast between bright cavity part and darker edges. The N2 adsorption/desorption measurement indicates that the porous MnO/C nanotubes have a Brunauer–Emmett–Teller (BET) surface area of 40 m2 g−1, and the average pore size is at ca. 7.7 nm (Fig. S3, ESI†). The content of carbon in the porous MnO/C nanotubes is measured as 3.2 wt% by elemental analysis conducted on the instrument of Vario Elemental III (Table S1, ESI†). The carbon layer is very thin, and is confirmed as being in an amorphous state (Fig. S4, ESI†). As demonstrated in the SEM elemental mapping images (Fig. S5, ESI†), carbon is uniformly dispersed in the MnO/C nanotubes. Fig. 2d illustrates the XRD pattern of the porous MnO/C nanotubes, which coincides well with the standard XRD pattern of MnO (JCPDF no. 01-075-0626), implying that the Mn3O4 nanotubes had been completely reduced into MnO.

When serving as an anode material for lithium ion batteries, the porous MnO/C nanotubes demonstrate superior lithium storage performance. The good cycle performance of the porous MnO/C nanotubes is confirmed by cyclic voltammetric studies, and has been demonstrated by voltammograms displayed in Fig. S6 (ESI†). Fig. 3a compares the charge/discharge curves of the porous MnO/C nanotubes and commercial MnO nanoparticles at a charge/discharge current density of 100 mA g−1 (0.13 C). For the anode of the porous MnO/C nanotubes, the voltage is dropped to a plateau ca. 0.26 V from the open circuit potential and then is decreased slowly to 0.02 V, corresponding to the reduction of Mn2+ to Mn0. In the initial charge process, the average charge plateau is ca. 1.2 V, which is much lower than that of other metal CoO (1.8 V), Co3O4 (2.0 V), Fe2O3 (1.6 V), Fe3O4 (1.7 V), NiO (1.9 V), and CuO (2.1 V). This feature will result in a higher working voltage when serving as an anode in a full cell, which can therefore offer a higher energy density. The initial discharge and charge capacity of the porous MnO/C nanotubes is measured at 1129 mAh g−1 and 810 mAh g−1, respectively, accounting for an initial coulombic efficiency of 71.7% that is common for most of the metal oxide anode materials. The initial capacity loss may be mainly attributed to the irreversible processes such as inevitable formation of a solid
The stability that has been confirmed by the SEM and TEM images results indicate the excellent rate capability and a good structure, 1D structure and the uniformly dispersed carbon in the porous MnO/C nanotubes. Such poor lithium storage performance of the commercial MnO particles may be attributed to their large particle size (Fig. S7, ESI†), which will cause a huge volume change and pulverization of the electrode during repeated charge/discharge. The electrochemical results demonstrate that the porous MnO/C nanotubes could deliver a reversible charge capacity of 763.3 mAh g\(^{-1}\) after 100 cycles at a 0.13 C rate, and 618.3 mAh g\(^{-1}\) after 200 cycles at a 0.66 C rate. Moreover, it can still release a capacity of 431.4 mAh g\(^{-1}\) and 302.5 mAh g\(^{-1}\) at 2.18 C and 4.16 C, respectively. 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.

Fig. 3 (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.

After 100 cycles of charge/discharge, the porous MnO/C nanotubes could still maintain a high reversible charge capacity of 763.3 mAh g\(^{-1}\), i.e. a capacity retention of 94.2%, presenting an excellent cyclability (Fig. 3b). In contrast, the commercial MnO particles show a very poor lithium storage performance, for which the initial discharge and charge capacities are only 883.4 and 497.6 mAh g\(^{-1}\), respectively, and the capacity quickly fades to 267.8 mAh g\(^{-1}\) after 100 cycles of charge/discharge. Such poor lithium storage performance of the commercial MnO particles may be attributed to their large particle size (Fig. S7, ESI†), which will cause a huge volume change and pulverization of the electrode during repeated charge/discharge. The cycle performance of the porous MnO/C nanotubes at a higher rate of 0.66 C is shown in Fig. 3c. It is interesting to see that a reversible capacity of 618.3 mAh g\(^{-1}\) could be delivered after 200 cycles, i.e. a capacity fading rate of only 0.026% per cycle, which demonstrates an excellent long cyclability at a high charge/discharge rate. It is interesting to see that the capacity of the porous MnO/C nanotubes starts to increase after tens of cycles, which is also reported in other MnO-based anode materials. Chen has ascribed this phenomenon as relating to either the formation of the SEI film or the forming high oxidation state products. Such structural stability should be responsible for its excellent electrochemical performance.

The superior lithium storage performance of the porous MnO/C nanotubes could be attributed to the following aspects. First, the hollow interior and the porous structure could make a good contact between the porous MnO/C nanotubes and the electrolyte, and further facilitate the transportation of lithium ions. Moreover, the porous MnO/C nanotubes could accommodate the volume changes during repeated lithiation/de-lithiation process. Second, the 1D structure could ensure efficient electron transport. Third, the carbon that is uniformly dispersed in the MnO nanotubes could further increase the conductivity of MnO/C nanotubes. All of these contribute to the excellent cyclability and rate capability of the porous MnO/C nanotubes.

In summary, porous MnO/C nanotubes are synthesized by a facile hydrothermal method followed by thermal annealing and served as anode materials of lithium ion batteries. The electrochemical results demonstrate that the porous MnO/C nanotubes could deliver a reversible charge capacity of 763.3 mAh g\(^{-1}\) after 100 cycles at a 0.13 C rate, and 618.3 mAh g\(^{-1}\) after 200 cycles at a 0.66 C rate. Moreover, it can still release a capacity of 431.4 mAh g\(^{-1}\) and 302.5 mAh g\(^{-1}\) at 2.18 C and 4.16 C, respectively. 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.

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Notes and references