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MOFs-derived Porous Mn$_2$O$_3$ as High-performance Anode Material for Li-ion Battery
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MOFs-derived porous Mn$_2$O$_3$ are synthesized by a high-temperature calcination of a metal-organic framework, [Mn(Br$_2$-bdc)(4,4’-bpy)(H$_2$O)$_3$]$_n$ (Br$_2$-bdc = tetrabromoterephthalate and 4,4’-bpy = 4,4’-bipyridine). The porous Mn$_2$O$_3$ as an anode material for lithium ion batteries displays excellent performances, 705 mAh g$^{-1}$ after 250 cycles at 1 A g$^{-1}$.

Porous transition metal oxides have drawn enormous attention in a wide variety of energy and environmental applications such as sewage treatment, catalysis, sensing, and energy collection, storage and conversion. The common strategies for fabrication of porous transition metal oxides are always involved template (such as soft and hard template). But their stringent experimental conditions and/or complicated post-treatment inevitably introduce impurities and increase the cost, which make them unsuitable for large-scale production. Therefore, novel strategy is still necessary to develop in order to scaleably fabricate porous materials. The recently developed thermal decomposition method is considered to be a practical way to prepare porous materials because it only needs a calcination process.\cite{5,6} Contrasted with the template methods, this strategy is simple, cost effective, and more advantageous for large-scale production.\cite{6} The porous structure has many advantages when used as electrode materials for energy storage, because of its high surface area (offer facile access of the electrolyte to the electrode surface), nanosized feature (permit increased utilization of active material), and sufficient of voids (accommodate volume variation owing to first phase modifications during cycling.). Most recently, the exploration of Metal-Organic Frameworks (MOFs) as templates and/or precursors to fabricate porous transition metal oxides materials presents great potential for applications in energy and environmental fields.\cite{7,9} By a simple calcination at a high temperature, MOFs could completely convert to oxides, yielding many tiny pores inside the product. The prolific chemistry and flexible structure of MOFs offer bountiful opportunities for us to fabricate porous structures, which makes them superior to other precursors.

Manganese oxide (Mn$_2$O$_3$) is of significant importance in technological applications including molecular adsorption, biosensor, catalysis and energy storage, due to their structural flexibility and good physicochemical properties.\cite{10,12} When used as electrode materials for Li-ion batteries, Mn$_2$O$_3$ will give higher energy density (compare to other transition metal oxides) because of the low voltage potential of manganese (average discharge voltage at 0.5 V and charge voltage at 1.2 V). Therefore, it is considered as one of the most promising anode materials. The performance of the Mn$_2$O$_3$ anode, however, has been frustrated by its poor electrochemical reactivity and large volume changes during the lithium intercalation/deintercalation.\cite{12} To solve these issues, various nanostructured Mn$_2$O$_3$ anode materials have been fabricated to achieve improved electrochemical performance.\cite{13-15} Despite remarkable progress, the Mn$_2$O$_3$ electrodes are still far from commercialization. Therefore, new strategies for constructing advanced Mn$_2$O$_3$ electrodes with high power rates and long cyclic stability are still needed. It is well known that electrode materials with appropriate porous structures cannot only increase their energy density, but also ameliorate their rate capabilities. Thus, the porous Mn$_2$O$_3$ may have a bright future as the high performance anode materials for LIBs. To date, only a few Mn$_2$O$_3$ porous structures have been synthesized; however, these compounds have represented enhanced electrochemical performances including high capacity, good cycling stability, and rate capability as anode materials for LIBs.\cite{13-15}

Fig. 1 The XRD patterns of the product obtained after the calcinations.

In this communication, we report a facile strategy to fabricate Mn$_2$O$_3$ porous structures derived from a MOFs. Because of its easy preparation, high yield, and low cost, [Mn(Br$_2$-bdc)(4,4’-bpy)(H$_2$O)$_3$]$_n$ (Mn-LCP, Br$_2$-bdc = tetrabromoterephthalate and 4,4’-bpy = 4,4’-bipyridine) was selected as the precursor to synthesize porous Mn$_2$O$_3$.\cite{18,19} First, Mn-LCP was synthesized...
from manganese (II) nitrate hexahydrate, 2,3,5,6-tetrabromoterephthalic acid, NaOH, and 4,4′-bipyridine at room temperature. Then, the precipitate was collected and calcined at 600 °C for 2 h to obtain the porous Mn$_2$O$_3$. Due to its excellent geometry, the porous Mn$_2$O$_3$ displays improved electrochemical performance including high specific capacity, long cycling stability and good rate property.

The morphology and structure features of the produced porous Mn$_2$O$_3$ are characterized by SEM and TEM techniques. The panoramic view of the product is presented in Figure 2a, where one can see that the sample is made up of microcrystals with size of ~5 µm. Close-up observations reveal that the microcrystals composed of many tiny particles which assembled up to 3D porous structure (Figure 2b and c). A typical cross-section of the porous Mn$_2$O$_3$ is presented in Figure 2c, in which the porous structure can be further fixed by the evident holes. Besides, the nanosized building blocks can be also clearly disclosed. Such a fascinating porous structure is thought advantageous in accommodating the strain derived from the Li$^+$ insertion/extraction, and accessing of the electrolyte to the electrode surface. Therefore, the improved electrochemical performances including cycling performance and rate performance might be obtained. The porous feature is also supported by distinct contrast in the TEM image (Figure 2d) though the particle size is big. The magnified TEM image disclosed that the second particle size of the sample is about 10 nm and they interconnected each other to produce 3D porous structure. A representative HRTEM image of porous Mn$_2$O$_3$ is shown in Fig. 2f. The interplanar distance is 0.34 nm, which agrees with (220) plane of cubic Mn$_2$O$_3$. The selected-area electron diffraction (SAED) pattern (inset Figure 2f) taken from the entire porous Mn$_2$O$_3$ clearly shows a single-crystalline structure.

The porous feature of the prepared porous Mn$_2$O$_3$ was further investigated by nitrogen adsorption-desorption instruments and displayed in Fig. 3. The sample demonstrates isotherm of type I which (Fig. 3) indicates it has large porosity.
sample shows a high surface area of 15.34 m² g⁻¹ and total pore volume of 0.118 cm³ g⁻¹. The pore size distribution evaluated from adsorption isotherms is represented in Fig. 3 (the inserted curve). The large surface area and porous framework of the as-synthesized Mn₂O₃ make it potentially favorable for applications

![Cyclic voltammograms of the obtained Mn₂O₃](image)

**Fig. 4** (a) Cyclic voltammograms of the obtained Mn₂O₃ in the voltage range of 0.01-3.0 V at a scan rate 0.1 mV s⁻¹; (b) The 1st, 2nd, 10th and 30th voltage profiles of the porous Mn₂O₃ electrode between 0.01 and 3 V at the current density of 1000 mA g⁻¹. Galvanostatic discharge-charge cycling was performed in the voltage range from 0.01 to 3.0 V. (b) Compared cycling performance and coulombic efficiency versus cycle number of porous Mn₂O₃ and microsized Mn₂O₃ electrode at a current density of 1000 mA g⁻¹. (c) Rate capabilities with increasing current density of the porous Mn₂O₃ and microsized Mn₂O₃ electrode.

such as electrochemical supercapacitor and high performance LIBs, since they can favor the ion transfer at the electrode/electrolyte interface.

When used as an anode material for LIBs, the porous Mn₂O₃ exhibits outstanding lithium storage performance. The good cycling stability of the porous Mn₂O₃ is affirmed by cyclic voltammetric examinations, and displayed in Fig. 4a. In the first cathodic scan, three reduction peaks are observed. The first one centers at 1.25 V, which can be ascribed to the lithiation of Mn³⁺ to Mn²⁺. The second one (0.95 V) may come from the formation of a solid electrolyte interphase (SEI) layer on the electrode surface. The insensitve peak at low voltage (0.2 V) is attributable to the reduction of Mn²⁺ into metallic Mn nanoparticles along with the formation of Li₂O matrix. In the subsequent anodic process, one peak locating at around 1.28 V is detected, which is derived from the oxidation of metal Mn⁰ to MnO and the decomposition of Li₂O. In the second cycle, the initial two reduction peaks (1.25 and 0.95 V) in the first cycle disappears, while the last one shifts to 0.36 V. This circumstance is common in transition metal oxides because some side reactions and structure arrangements only occurred in the first cycle. The anode process of the second cycle is very similar to the first cycle except for a decrease in the intensity, which implies irreversible capacity of the porous Mn₂O₃ electrode. In the following cycles, the CV curves are similar to the second cycle and almost overlapped, indicating the good electrochemical reversibility of the porous Mn₂O₃ electrode.

The voltage is dropped to a plateau ca. 0.26 V from the open circuit potential followed by decreased slowly to 0.01 V, accounting for the reduction of Mn⁷⁺ to Mn⁵⁺ (in the first cycle). The initial discharge and charge capacities of the porous Mn₂O₃ is 1158 mAh g⁻¹ and 852 mAh g⁻¹, respectively, corresponding to an initial coulombic efficiency of 74%. The low initial coulombic efficiency may be mainly attributed to the irreversible processes such as the formation of a SEI layer and electrolyte decomposition. In the second discharge process, the plateau changes to about 0.5 V due to the drastic lithium driven and activation of the electrode. After then, the profiles do not change much. This result is agreement well with the CV examination.

Fig. 4c shows the cyclic performance and coulombic efficiency versus cycle number of porous Mn₂O₃ at a current density of 1000 mA g⁻¹. Fast capacity decay in the first cycles is observed, due to the complicated side-reactions and irreversible structure transformation. Afterward, the capacity was generally maintained because the electrochemically reversible structures for Li-ion insertion reaction have been established. After 250 cycles, the porous Mn₂O₃ still maintains a high discharge specific capacity of 705 mAh g⁻¹. For comparison, the microsized Mn₂O₃ were synthesized and its electrochemical properties were tested in the same situation (Fig. S2). Only after a few cycles, the specific capacity dropped to about 200 mAh g⁻¹ (Fig. 4c). The main reason for this result may be that the porous structure provides large surface area for the effective contact of the electrode and electrolyte, and plenty of void spaces for accommodating the huge volume variations during lithium uptake/release. In the microsized Mn₂O₃, the large volume variations lead to pulverization of the electrode and then bad cyclic stability. Furthermore, the electrochemical property is also better than most of the former reports of the Mn₂O₃ materials, such as mesoporous straw-sheaf-shaped and oval-shaped Mn₂O₃ delivered capacities of 380 mAh g⁻¹ and 320 mAh g⁻¹ in the 150th cycle at the current density of 200 mA g⁻¹, respectively. Mn₂O₃ sheets exhibited 521 mAh g⁻¹ at the current density of 300 mA g⁻¹. Porous Mn₂O₃ nanofibers, nanorods and nanowires are maintained at 404, 384 and 374 mAh g⁻¹ after 10 cycles at the current density of 100 mA g⁻¹. Porous Mn₂O₃ microsphere displayed 600 mAh g⁻¹ at the current density of 1200 mA g⁻¹. The coulombic efficiency of the porous Mn₂O₃ is calculated about 73.7% in the first cycle, while it increases to about 99% in the second cycle and retains at this value for the whole test process.

The compared rate performance for the prepared microsized and porous Mn₂O₃ are displayed in Fig. 3d. As the current densities changes from 200 to 4000 mA g⁻¹, the specific capacities of 917, 880, 756, 572 and 450 mAh g⁻¹ are correspondingly obtained for porous Mn₂O₃. More significantly, when current density restores to 200 mA g⁻¹, the capacity of the electrode also recovers to 950 mAh g⁻¹. This result indicates that the porous Mn₂O₃ structure is stable in various current densities. Accordingly, the contrasted microsized Mn₂O₃ exhibits average capacities of 450, 147, 105, 62 and 33 mAh g⁻¹. With the current density increasing, the capacity of microsized Mn₂O₃ sharply declines because at the high current density, the polarization of the electrode is become more severely. The porous structure has many voids which is similar to reducing the particle size, decreasing the polarization and leading to better electrochemical performance. This result is confirmed by electrochemical impedance spectra of the samples (Fig. S4). Both of curves
comprise a depressed semicircle in the region of high-to-medium frequencies and a sloping line in the region of low frequencies. The semicircle incarnates the charge-transfer resistance ($R_{ct}$) between the electrolyte and the electrode. The sloping line is associated with the diffusion of lithium inside the electrode ($R_w$). Apparently, the porous $\text{Mn}_2\text{O}_3$ gives smaller $R_{ct}$ than microsized $\text{Mn}_2\text{O}_3$, implying better charge transfer kinetics. This result well explains the superior rate property and cycling stability of the porous $\text{Mn}_2\text{O}_3$ to the microsized $\text{Mn}_2\text{O}_3$.

In summary, hierarchically porous $\text{Mn}_2\text{O}_3$ are successfully synthesized using [Mn(Br$_2$-bdc)(4,4’-bpy)H$_2$O$_2$] as a precursor. The resultant $\text{Mn}_2\text{O}_3$ displays the hierarchical porosity, which plays a significant role in the improvement of electrochemical properties. After 250 cycles at 1 A g$^{-1}$, the reversible capacity could be maintained at 705 mA h g$^{-1}$. To the best of our knowledge, this is one of the best performances of $\text{Mn}_2\text{O}_3$ based materials for LIBs. In the rate performance, hierarchically porous $\text{Mn}_2\text{O}_3$ exhibits a specific capacity of 450 mA h g$^{-1}$ at 4 A g$^{-1}$, still higher than the theoretical capacity of commercial graphite. All the results suggest the promising potential of hierarchically porous $\text{Mn}_2\text{O}_3$ as advanced anode materials.

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Notes and references