Synthesis of α-MnO$_2$ Nanowires *via* Facile Hydrothermal Method and Their Application in Li-O$_2$ Battery

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Abstract: Li-O$_2$ batteries are regarded as a promising energy storage system for their extremely high energy density. MnO$_2$-based materials are recognized as efficient and low-cost catalyst for a Li-O$_2$ battery positive electrode material. In this work, α-MnO$_2$ nanowires were successfully synthesized by a hydrothermal method and their electrocatalytic performance were investigated in Li-O$_2$ batteries. X-ray diffraction and field emission scanning electron microscope confirms the formation of α-MnO$_2$. The Li-O$_2$ battery which consists of α-MnO$_2$ nanowires shows a high discharge capacity up to 12000 mAh·g^{-1} at a restrict voltage of 2.0 V with the current density of 100 mA·g^{-1}. When restricting the discharge capacity at 500 mAh·g^{-1}, it can operate over 40 cycles and exhibit good cycle stability. These results indicate that the α-MnO$_2$ nanowires can be used as positive electrode catalysts for Li-O$_2$ batteries.

Key words: Li-O$_2$ battery; positive electrode; α-MnO$_2$ nanowires; Ketjen Black; discharge capacity

Nowadays, as fossil fuels are depleted and global warming is becoming more and more serious, an energy storage solution is becoming more and more urgent[1]. On the other side, the rapidly increased development of portable electronics and electric vehicles demands a high energy and high power secondary battery technology[2]. For this point, the metal air batteries with remarkably high energy density have attracted the focus of all battery researchers. The metal air batteries became attractive due to their lighter metal passive electrode and the free oxygen in the air as the positive electrode. Theoretically, with an environmental abundant oxygen positive electrode, the metal air battery could be lighter, cheaper and long lasting with high energy density. Among all rechargeable metal air batteries, Li-O$_2$ batteries, which possess discharge capacity as high as 11430 Wh·kg^{-1}, have already aroused widespread concerns. The theoretical energy density of the Li–O$_2$ battery is about 3500 Wh·kg^{-1}, which is 4 to 6 times higher than that of traditional Li-ion batteries[3]. A typical rechargeable Li-O$_2$ battery consists of a Li metal electrode[4], organic electrolyte and an air electrode which is exposed to gaseous O$_2$. During the discharge process, the reaction between Li and oxygen yields Li$_2$O$_2$ or Li$_2$O[5]; during the charge process, these Li$_2$O$_2$ or Li$_2$O products decompose to Li$^+$ and O$_2$. What's more, as the positive reactant, oxygen is obtained directly from the outside. However, there are still many obstacles to overcome, such as large overpotential[6], poor cycle performance, insoluble discharge products aggregation, and electrolyte instability. Among the above obstacles, the insoluble discharge products aggregation is the most serious factor which related to the charge/discharge efficiency. As the positive electrode materials, catalysts help to decompose the reaction products, which affect the charge process and charge/discharge efficiency. Catalysts are the single most important materials for Li–O$_2$ batteries[7]. In previous efforts, many types of catalysts, such as noble metals or their alloys[8], transition metal oxides[9], carbon based materials[10], transition-metal carbide have been used to reduce the overpotential and enhance the cycling performance. Self-supported and porous catalysts are becoming more and more popular, such as 3D hierarchical porous Co$_3$O$_4$ nanotube network[11], self-assembled 3D foam-like NiCo$_2$O$_4$[12] and so on.

Manganese oxide materials because of its rich resources, environment-friendly, toxicity, low cost, and unique electrochemical properties, have become a hot research[13]. It can be used as electrode material for Li-O$_2$ batteries[1-2], supercapacitors[14-15], Li ion batteries[16-17] and alkaline batteries[18-19] (Zn-MnO$_2$). MnO$_2$ is regarded

as one of the hopeful and most suitable catalyst materials for high performance Li-O_2 batteries. Cao, *et al*[2] has studied the mechanism of the oxygen reduction reaction (ORR) in MnO_2 catalyzed air electrodes in alkaline solution. They found that the catalytic activities of MnO_2 with different crystalline structures are in the order of β-MnO_2 < λ-MnO_2 < γ-MnO_2 < α-MnO_2. Bruce, *et al*[20] and a few others have also proved that α-MnO_2 nanowires are the most effective catalysts for Li-air battery due to their crystal structure and high surface area. So, it is clear that the morphology and crystalline structure of MnO_2 nanomaterials play an important role in the catalytic property. However, the inherent poor electrical conductivity of MnO_2 limits its performance in Li-O_2 battery. To enhance the electron conduction, manganese oxides are commonly supported on or mixed with conductive carbon materials[21].

Nanostructured manganese oxides[22] have been the subject of intensive research due to their potential applications as an ideal electrode for energy storage and conversion such as supercapacitors, Li-ion batteries and Li-O_2 batteries. A number of methods have been reported on the preparation of nanosized manganese dioxide materials, such as Sol-Gel method[23], ultrasonic chemical method[24], electrochemical deposition method[25] and hydrothermal method[26]. The hydrothermal method is highly concerned by its simple operation and simple controllability, and is an effective method for preparing nanometer materials. In previous works, various nanostructured MnO_2 materials have been synthesized, such as MnO_2 hollow spheres[27], nanorods[28], nanobelts[29], nanoflakes[25], nanoneedles[20] and nanowires[1].

While Ketjen Black (KB) is known as an excellent conductive carbon material with its ultra-high specific surface area. In this work, α-MnO_2 nanowires were synthesized by a facile hydrothermal method. The as prepared α-MnO_2 nanowires were mixed with KB as positive electrode materials and displayed good performance in Li-O_2 battery.

1 Experimental

1.1 Synthesis of α-MnO_2 nanowires

All chemicals used in this study were analytical grade. In brief, 1 g $KMnO_4$ was dissolved in 30 mL deionized water. Then 50 mL ethanol was added slowly into the above solution. After stirring for 20 min, the resulted solution was transferred into a 100 mL Teflon (PTFE)-lined autoclave, sealed, and then kept at 120℃ for 2 h. After cooling naturally, the products were filtered, washed by distilled water and ethanol for several times, and finally dried at 60℃ in a vacuum oven.

1.2 Characterization

Powder X-ray diffraction (XRD, Rigaku Rint 2500) was used to detect the phase composition of samples with Cu Kα (λ=0.15418 nm) as a source at a wide-angle scanning range of 5°-85° (2θ) with a scan speed of 10°/min. Morphologies and microstructure of α-MnO_2 were examined using a field emission scanning electron microscope (FE-SEM, HITACHI S-4800).

1.3 Electrocatalytic performance of α-MnO_2 nanowires

The electrocatalytic performance of α-MnO_2 nanowires/ KB was performed by coin cells, which consisted of a Li metal disc, a piece of glass fiber that was soaked with electrolyte containing 1 mol·L^{-1} LiTFSI in tetraethylene glycol dimethylether (TEGDME) and a working electrode. For preparing the working electrode, α-MnO_2 nanowires, KB and PVDF (polyvinylidene fluoride) were mixed in NMP (*N*-methyl-2-pyrrolidone) solution with a weight ratio of 3∶6∶1. The resulting mixture was pressed onto a carbon fiber (15 mm in diameter) current collector and the cell was airtight, except for the stainless steel mesh window exposing the porous positive electrode to 1×10^5 pressure of oxygen atmosphere. The positive electrode was dried at 80℃ for 24 h under vacuum. The mass loading of each coin cell was fixed to about 1.0 mg·cm^{-2}. For comparison, pure KB mixed PVDF with a weight ratio of 9∶1 was also prepared. All the Li-O_2 batteries were assembled in an argon filled glove-box with both the value of water and O_2 are below 0.1×10^{-6}. The batteries were let set for 24 h in glovebox before testing. Galvanostatic discharge-charge tests were conducted on a battery tester (LAND CT2001A) in a voltage range of 2−4.5 V (*versus* Li^+/Li) at room temperature in an O_2 atmosphere under various current densities.
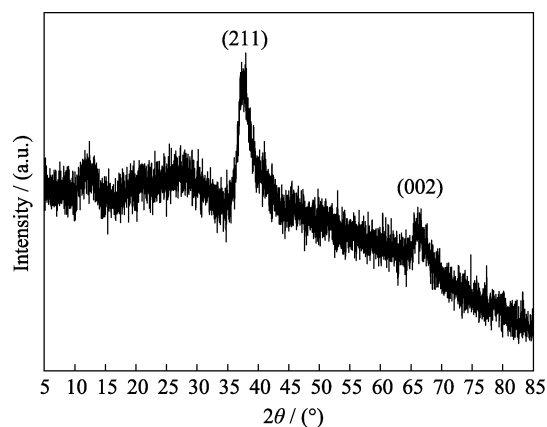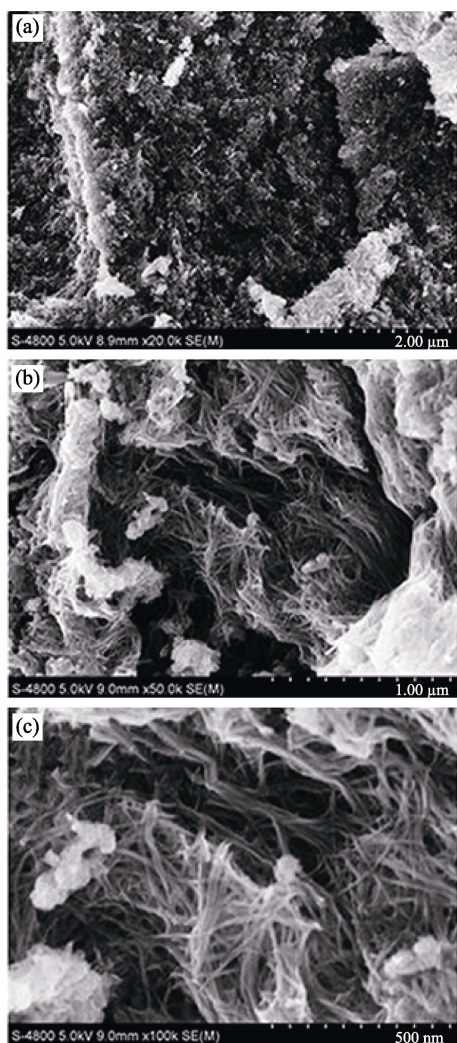
2 Results and discussion

2.1 Morphology, structural characterization

As shown in Fig. 1, there are two obvious broaden peaks at 2θ of about 37° and 66°, which are corresponded to the α-MnO_2 (JCPDS No.44-0141). There are no other impurity peaks in the figure, it clarified that pure α-MnO_2 nanowires were synthesized. Fig. 2(a)-(c) show SEM images of the α-MnO_2 nanowires with different magnification. It can be concluded that α-MnO_2 nanowire is about 12 nm in diameter and hundreds of nanometer in length.

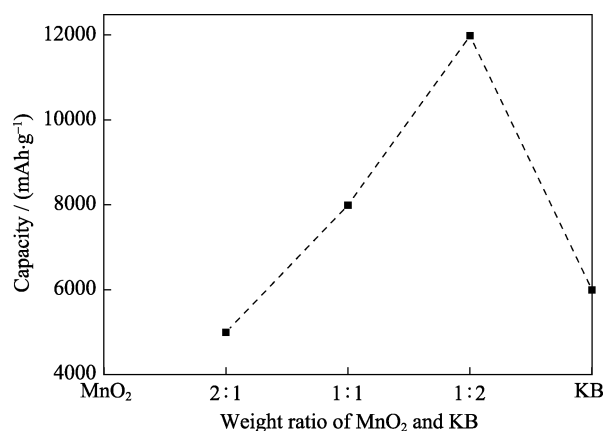## 2.2 Electrocatalytic performance

In order to investigate the effect of weight ratio of α-MnO_2 nanowires and KB on the electrocatalytic performance

Fig. 1　XRD pattern of α-MnO$_2$ sample

Fig. 2　FE-SEM images of the α-MnO$_2$ nanowires with different magnification

for a Li-O$_2$ battery, some experiments for different weight ratio of α-MnO$_2$ nanowires and KB as the positive electrode catalysts for Li-O$_2$ batteries have been carried out. From Fig. 3, it can be seen easily that the positive electrode with the weight ratio of 1 : 2 delivered a highest discharge capacity which was close to 12000 mAh·g^{-1} at

a restrict voltage of 2.0 V with a current density of 100 mA·g^{-1}. Followed by the weight ratio of 1 : 1 whose discharge capacity can get to nearly 8000 mAh·g^{-1}, next is the pure KB which achieved a discharge capacity of 6000 mAh·g^{-1}, the lowest discharge capacity is about 5000 mAh·g^{-1}, corresponding to the weight ratio of 2 : 1. In summary, the intrinsic low electrical conductivity of MnO$_2$ limits its performance in Li-O$_2$ batteries, with addition of conductive carbon materials KB, the migration of electrons was sped up. In addition, KB has an ultrahigh specific surface area to provide a stacking place for the discharge products. Above all, the α-MnO$_2$ nanowires which mixed with moderate amount of KB show good discharge capacity for the Li-O$_2$ battery. However, the capacity of KB itself is limited, and excessive KB will result in reduced capacity. Thus it can be concluded that the best weight ratio between α-MnO$_2$ nanowires and KB is 1 : 2.

The capacity-limited approach is usually used to avoid larger capacity depth so that the batteries performance could be evaluated. The catalytic activities of KB and α-MnO$_2$/KB (1 : 2) were examined and compared at a constant current density of 100 mA·g^{-1} in the potential range 2.0–4.5 V at room temperature and 1×10^5 Pa O$_2$ atmosphere. From Fig. 4(a), it can be clearly seen that the pure KB positive electrode only ran 25 cycles then followed by severely polarization with a fixed capacity of 500 mAh·g^{-1} at 100 mA·g^{-1}, which indicates the poor cycle stability of KB. While from Fig. 4(b), it can be seen that the Li-O$_2$ batteries with α-MnO$_2$/KB (1 : 2) as positive electrode catalyst can ran 40 cycles at a fixed capacity of 500 mAh·g^{-1} with stable discharge-charge voltage platforms, demonstrating good stability. For the comparison of discharge capacity, it can be seen that the electrode with KB reached a maximum capacity of nearly 6000 mAh·g^{-1} at 2.0 V with a current density of

Fig. 3　First discharge capacity of the positive electrode with different weight ratio of α-MnO$_2$ nanowires and KB at a constant current density of 100 mA·g^{-1}
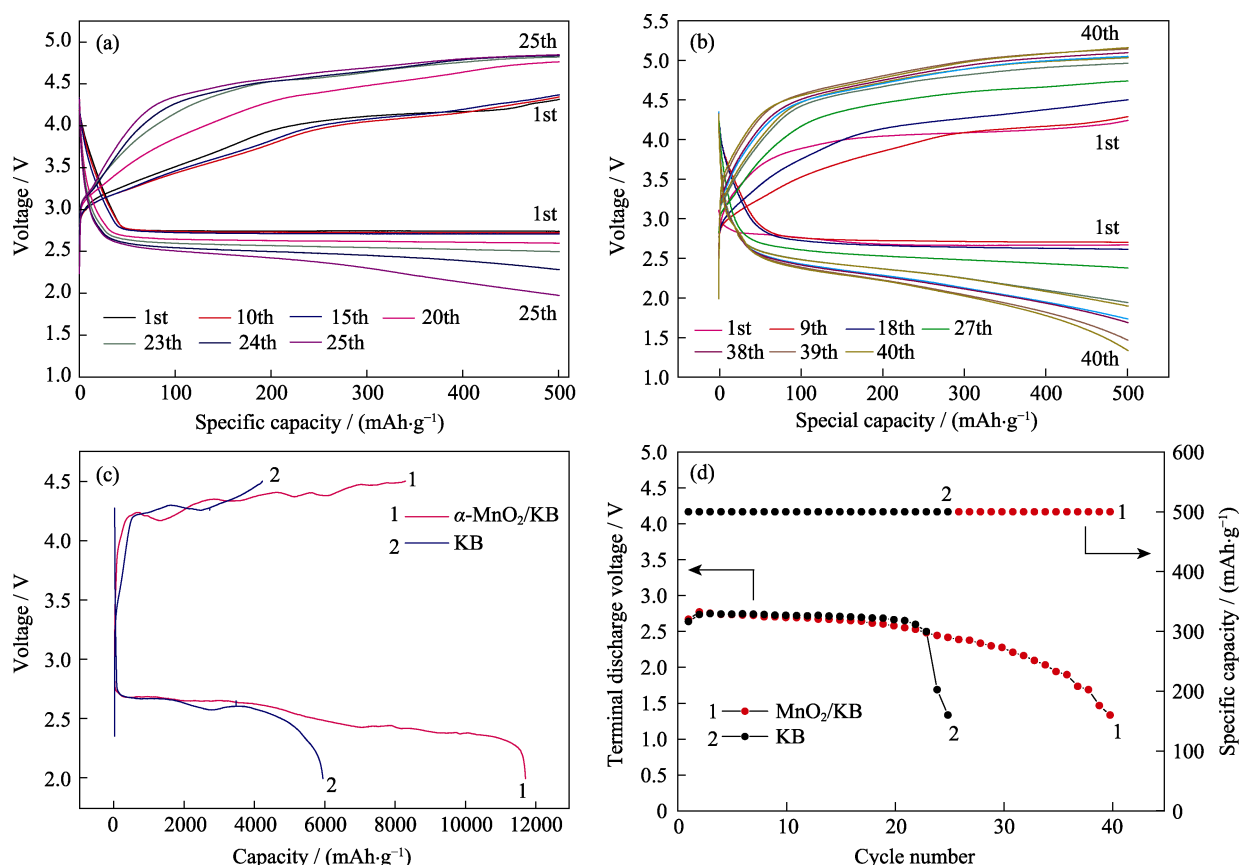
Fig. 4　Charge-discharge curves of Li-O_2 batteries with (a) KB, (b) α-MnO$_2$/KB (1 : 2), with (c) the comparison of the first discharge curves of pure KB and α-MnO$_2$/KB (1 : 2) and (d) the comparison of cyclic performance

100 mA·g^{-1} from Fig. 4(c). While the electrode with α-MnO$_2$/KB (1 : 2) reached a maximum capacity of about 12000 mAh·g^{-1} which was 2 times of that of pure KB. This discharge capacity is comparable to the previous works which consist of manganese dioxides as the positive electrode catalysts[2-3, 5, 7]. Fig. 4(d) shows the comparison of cycle performance, remarkably, the Li-O_2 batteries with α-MnO$_2$/KB (1 : 2) displayed longer cycle life and better cycle stability than those with pure KB. These results suggest that the α-MnO$_2$ nanowires can be used as positive electrode catalysts for Li-O_2 batteries.

Fig. 5 shows the first full discharge curves of Li-O_2 batteries with α-MnO$_2$/KB (1 : 2) at different current densities. The initial discharge capacity is 11000 mAh·g^{-1} at 100 mA·g^{-1}, the discharge capacity only gradually decreased at higher current densities, which were 8600 mAh·g^{-1} (78%) at 200 mA·g^{-1}, 5100 mAh·g^{-1} (46%) at 400 mA·g^{-1}, and 4500 mAh·g^{-1} (41%) at 800 mA·g^{-1}. For the reason of capacity fading, it may account for the follow reasons: i) with the discharging process goes on, the discharge products accumulate on the surface of the α-MnO$_2$ nanowires which blocks the further intake of oxygen; ii) the inadequate Li ion conductivity of organic electrolyte. In addition, it should be noted that, when the
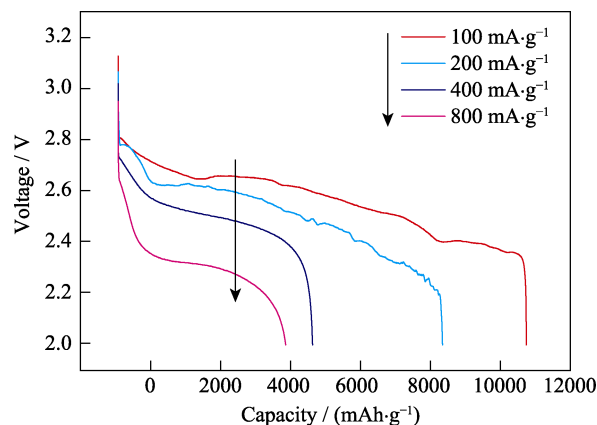

Fig. 5　First full discharge curves of Li-O_2 batteries with α-MnO$_2$/KB (1 : 2) at current densities of 100 mA·g^{-1}, 200 mA·g^{-1}, 400 mA·g^{-1} and 800 mA·g^{-1}

current density increased from 100 mA·g^{-1} to 200 mA·g^{-1}, the discharge capacity degradation is only as low as 22%, which showed high rate property for the batteries with α-MnO$_2$ nanowires/KB. During the discharge process, as it was well known metal Li loses electrons to become Li$^+$ at negative electrode, and then migrate to the active sites of catalysts to react with O_2 coming from outside to form Li$_2$O$_2$ on the positive electrode. Therefore this phenomenon might be associated with the morphology and

size of the particles, and their crystal structures with 2×2 tunnels. With its 2×2 tunnels, it can facilitate the intercalation and adsorption of ions, and provide more active sites for the accumulation of discharge products.

3   Conclusions

α-MnO₂ nanowires about 12 nm in diameter and hundreds of nanometer in length were successfully prepared by a facile hydrothermal method. The Li-O₂ battery with α-MnO₂ nanowires delivered a high discharge capacity of 12000 mAh·g⁻¹ at the current density of 100 mA·g⁻¹ in the first cycle. Besides, the Li-O₂ battery could run 40 cycles with a fixed special capacity of 500 mAh·g⁻¹ under the same current density. This report indicated that α-MnO₂ nanowires can be used as positive electrode catalysts for Li-O₂ batteries.

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α-MnO₂ 纳米线的制备及其在锂氧气电池中的应用

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摘 要: 锂氧气电池由于其极高的能量密度被认为是一种很有前途的储能系统。二氧化锰基材料被认为是锂空气电池阴极的低成本且高效的催化剂。在本研究中, 通过水热法合成了不同长度的 α-MnO₂ 纳米线并对其在锂氧气电池中的电化学性能进行了研究。X 射线衍射和场发射扫描电镜证实了 α-MnO₂ 的形成。由 α-MnO₂ 纳米线组装的锂氧气电池在电流密度为 100 mA/g、放电截止电压为 2 V 时, 以正极总质量为计算标准, 放电容量高达 12000 mAh/g。当限定放电容量为 500 mAh/g 时, 电池能够有效循环超过 40 次, 显现出良好的循环稳定性。这些结果表明, α-MnO₂ 纳米线可以作为锂氧气电池的催化剂。

关 键 词: 锂氧气电池; 正极; α-MnO₂ 纳米线; 科琴黑; 放电容量

中图分类号: TQ174 **文献标识码:** A