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α-MnO_2 nanoneedle-based hollow microspheres coated with Pd nanoparticles as a novel catalyst for rechargeable lithium−air batteries

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Abstract: The hollow α-MnO_2 nanoneedle-based microspheres coated with Pd nanoparticles were reported as a novel catalyst for rechargeable lithium−air batteries. The hollow microspheres are composed of α-MnO_2 nanoneedles. Pd nanoparticles are deposited on the hollow microspheres through an aqueous-solution reduction of $PdCl_2$ with $NaBH_4$ at room temperature. The results of TEM, XRD, and EDS show that the Pd nanoparticles are coated on the surface of α-MnO_2 nanoneedles uniformly and the mass fraction of Pd in the Pd-coated α-MnO_2 catalyst is about 8.88%. Compared with the counterpart of the hollow α-MnO_2 catalyst, the hollow Pd-coated α-MnO_2 catalyst improves the energy conversion efficiency and the charge−discharge cycling performance of the air electrode. The initial specific discharge capacity of an air electrode composed of Super P carbon and the as-prepared Pd-coated α-MnO_2 catalyst is 1220 mA·h/g (based on the total electrode mass) at a current density of 0.1 mA/cm^2, and the capacity retention rate is about 47.3% after 13 charge−discharge cycles. The results of charge−discharge cycling tests demonstrate that this novel Pd-coated α-MnO_2 catalyst with a hierarchical core−shell structure is a promising catalyst for the lithium−air battery.

Key words: lithium−air battery; composite catalyst; nanoneedle-based hollow microsphere; core−shell structure

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1 Introduction

Traditional cathode materials used in Li-ion batteries, such as $LiCoO_2$ and $LiFePO_4$, have limited capacities ranging from 130 to 150 mA·h/g owing to the nature of their crystal structures and their electrochemical properties [1]. Recently, lithium−air batteries have attracted much attention because of their extreme high specific energy density, so they have the potential to be the power source for the advanced electric vehicles. Unlike conventional lithium and lithium-ion batteries, the cathode material for lithium−air batteries is not stored inside the batteries, and the theoretical specific energy density of the lithium−air battery excluding oxygen is 11140 W·h/kg [2−4]. The lithium−air battery was firstly reported by ABRAHAM and JIANG [5], that it had an open-circuit potential of about 3 V and an energy density of 250−350 W·h/kg. Such a lithium−air battery comprises a Li-containing anode, an organic electrolyte and an air cathode [5−7].

Although the lithium−air battery is a very attractive system, there are still many challenges that need to be overcome before practical applications, such as the blocking of pores within air electrodes, decomposition of the non-aqueous electrolyte, high overpotential and the poor charge−discharge cycling performance [4,8,9]. The foremost challenge that needs to be focused on is how to improve the cycling performance of rechargeable lithium−air batteries in the non-aqueous electrolyte. To improve the energy conversion efficiency and the cycling performance of lithium−air batteries, various electrochemical catalysts for the air electrode have been studied recently, such as the transitional metal oxides [10], the carbon-supported manganese oxide nanocatalysts [11], the MnO_2 nanoflakes coated multi-

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walled carbon nanotubes [12], the bifunctional electrocatalyst of platinum−gold nanoparticles loaded on the XC-72 carbon [13], the nitrogen-doped carbon nanotubes [14] or graphene nanosheets [15], the compound transitional metal oxides ($MnCo_2O_4$ [16] and $Ag_2Mn_8O_6$ [17]) and the platinum nanoparticle−graphene complexes [18].

Recently, a novel MnO_2/Pd composite catalyst of rechargeable lithium−air batteries was prepared by mixing manganese dioxide, Pd and PTFE [19]. Using this MnO_2/Pd composite catalyst, the charging potential of the air electrode may nearly decrease to its theoretical value (3.7 V vs Li/Li^+) and a stable specific capacity of 225 mA·h/g for the air electrode could be obtained during 20 charge−discharge cycles. In addition, another new Pd-coated manganese dioxide composite catalyst with a core−shell structure was synthesized by depositing Pd on the surface of β-MnO_2 nanorod particles, and exhibited a good electrocatalytic performance for the oxygen reduction in alkaline media [20]. The MnO_2/Pd core−shell catalyst composed of MnO_2 cores and less Pd shell may not only reduce the Pd dosage within the catalyst but also improve the electro-catalytic activity for the oxygen reduction reaction (ORR) by a synergetic effect between MnO_2 and Pd [21]. Unfortunately, the electrocatalytic behavior of MnO_2/Pd catalysts with a core−shell structure for rechargeable lithium−air batteries has attracted less attention until now.

In this work, a novel Pd-coated manganese dioxide composite catalyst (MnO_2/Pd) with a core−shell structure was prepared for rechargeable lithium−air batteries. Hollow microspheres composed of α-MnO_2 nanoneedles were synthesized by a hydrothermal method, and Pd nanoparticles were precipitated on the surface of the as-prepared hollow α-MnO_2 microspheres by an electroless deposition method at room temperature. The electrocatalytic performance of the MnO_2/Pd core−shell catalyst was investigated in an air electrode supported by carbon materials (Super P carbon).

2 Experimental

All chemical reagents used in the experiments were of analytical grade and used without further purification.

2.1 Preparation of hollow α-MnO_2 microspheres

The manganese dioxide (α-MnO_2) microspheres with a hollow structure were synthesized by a hydrothermal method reported in Ref. [22]. $KMnO_4$ (0.474 g), $MnSO_4 \cdot H_2O$ (0.845 g), $FeCl_3 \cdot 6H_2O$ (0.054 g) and 1 mL of concentrated sulfuric acid（98%）were mixed in 15 mL of de-ionized water and stirred with a magnetic stirrer at room temperature for 10 min to form a homogeneous solution. Then the obtained solution was transferred into a Teflon (PTFE)-lined autoclave (20 mL) and heated at 150 °C for 20 min. The obtained precipitates were filtered, washed with distilled water and dried at 60 °C for 4 h in air.

2.2 Preparation of hollow α-MnO_2/Pd core−shell microspheres

The Pd-coated manganese dioxide microspheres with a hierarchical core−shell structure were prepared by an electroless deposition of Pd on the surface of the as-prepared hollow α-MnO_2 microspheres. 0.3 g α-MnO_2 microspheres dispersed in an ethanol/water solution (1:1, in volume ratio) were mixed with 100 mL of 3.1 mmol/L $PdCl_2$ solution ultrasonically. Then the $NaBH_4$ was added dropwise to the solution with a continuous magnetic stirring. After the reductive reaction performed at room temperature for 20 min, the obtained product was washed with de-ionized water and dried in a vacuum oven at 70 °C for 12 h.

2.3 Characterization of hollow microsphere catalysts

The surface morphology of the as-prepared catalysts was investigated by a Hitachi S−4800 field emission scanning electron microscope (FE-SEM) and the components were analyzed by a HORIBA 7593-H energy-dispersive spectrometer. The X-ray diffraction (XRD) patterns of the as-prepared catalysts were recorded by a Rigaku D/max−2500 diffractometer with a Cu K_α radiation. The nitrogen adsorption−desorption measurement was conducted by a Quadrasorb SI surface area analyzer at 77 K. The specific surface area of the as-prepared catalysts was calculated by a Brunauer-Emmett-Teller (BET) method and experimental points were obtained at a relative pressure of 0.05−0.25.

2.4 Preparation of air electrode including hollow microsphere catalysts

The catalytic layers of air electrodes were composed of Super P carbon, the as-prepared hollow α-MnO_2/Pd core−shell catalyst, and polyvinylidene fluoride (PVDF) solutions in a mass ratio of 75:15:10. For comparision, the air electrode composed of Super P, the as-prepared α-MnO_2 catalyst and PVDF solutions with the same composition was also prepared. When preparing the air electrode, the catalytic layer was tiled on a foam nickel current collector, and then dried at 60 °C in a vacuum oven for 24 h. The loading content of the catalytic layer in an air electrode is about 5 mg/cm^2.

2.5 Electrochemical measurements of air electrode containing hollow microsphere catalysts

The electrochemical behavior of the as-prepared air electrodes was tested by a lithium−air coin battery which had four 3 mm-diameter holes on the side of shells of battery. This lithium−air coin battery was assembled from the as-prepared air electrode and a lithium foil (0.5 mm in thickness) used as the counter electrode in a 2032-type coin cell. The electrolyte was 1 mol/L $LiClO_4$/PC+DEC (1:1 in volume ratio) and a Celgard 2300 membrane was used as the cell separator. The assembling process of the lithium−air coin battery was performed in an argon filled glove box (MIKROUNA Advanced 2440/750) with water and oxygen level less than 1×10^{-6}.

To avoid some side effects produced by the humidity and CO_2 in air, all electrochemical measurements of the lithium−air coin battery were conducted in a homemade cylinder which was filled with dry and pure oxygen gas at a pressure of 1×10^5 Pa. The charge−discharge behavior of the lithium−air coin battery was measured by a Solartron analytical system (1400/1470E) at different current densities in a voltage range of 2.0−4.5 V. The air electrode capacity was calculated according to the total mass of the air electrode (carbon + catalyst + binder).

3 Results and discussion

Figure 1 shows the XRD patterns of the as-prepared MnO_2 and the as-prepared Pd-coated MnO_2 catalysts. As shown in Fig. 1(a), it is seen that the XRD diffraction peaks of the as-prepared MnO_2 catalyst are assigned to a pure α-MnO_2 tetragonal phase (Joint Committee on Powder Diffraction Standards (JCPDS) Card No. 44−0141). Compared with the XRD pattern of the as-prepared MnO_2 catalyst (Fig. 1(a)), there are four new peaks located at about 40.1°, 46.7°, 68.1° and 82.1° in the XRD pattern of the Pd-coated MnO_2 catalyst (Fig. 1(b)). These four peaks are well attributed to the lattice faces of Pd (111), Pd (200), Pd (220) and Pd (311) (JCPDS Card No. 65−2867), respectively. This indicates that the as-prepared α-MnO_2 catalyst is coated by Pd.

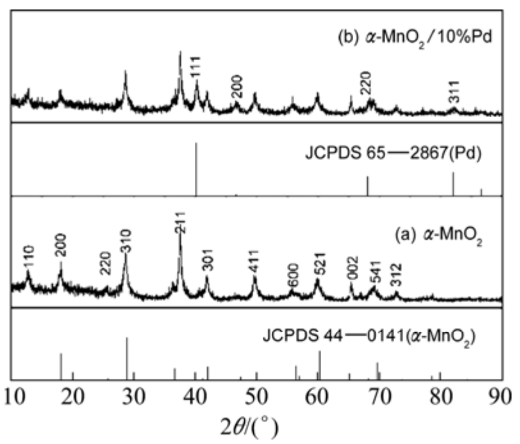


Fig. 1 XRD patterns of as-prepared catalysts

Figure 2 shows the curves of N_2 adsorption−desorption isotherm measurements of the as-prepared α-MnO_2 catalyst. The N_2 adsorption/desorption curves exhibit a typical IV shape, indicating that the as-prepared α-MnO_2 catalyst has a characteristic of the mesoporous [18]. The specific surface area of the as-prepared α-MnO_2 catalyst is estimated to be about 145 m^2/g.

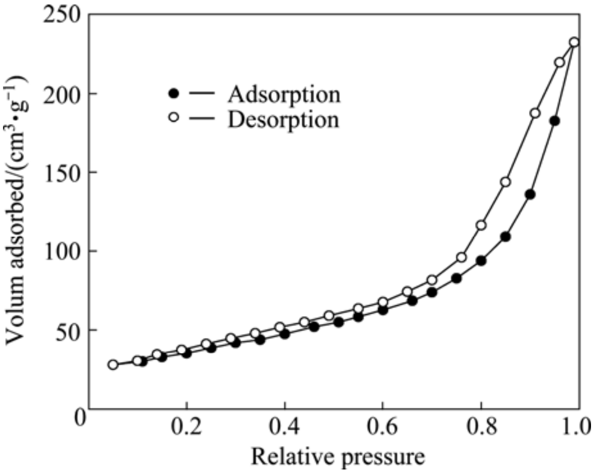


Fig. 2 N_2 adsorption−desorption isotherms of as-prepared α-MnO_2 catalyst

Figure 3 shows the SEM and TEM images of the as-prepared α-MnO_2 catalyst. As shown in Fig. 3(a), the as-prepared α-MnO_2 catalyst has a typical microspherical morphology which is composed of many hollow microspheres with the oriented nanoneedles arranged on the surface. The diameter of these microspheres is 1−2 μm. Furthermore, it is seen from the surface ruptures that the α-MnO_2 microspheres are hollow. The TEM image further indicates that the nanoneedles with a length of 100−200 nm form a hollow α-MnO_2 microsphere structure. This hierarchical microstructure results in a large specific surface area of the α-MnO_2 catalyst.

Figure 4 shows the SEM, TEM and HRTEM images of the as-prepared Pd-coated α-MnO_2 catalyst. As shown in Fig. 4(a), the surface morphology of the composite catalyst is similar to that of the above-mentioned hollow α-MnO_2 catalyst in Fig. 3(a). Namely, the original morphology has been retained after the deposition of Pd. From Fig. 4(b), it is clear that Pd nanoparticles with a diameter of about 5 nm are distributed on the surface of α-MnO_2 nanoneedles evenly. Furthermore, no obvious agglomeration of Pd nanoparticles appears on the surface of the α-MnO_2 catalysts. In addition, the HRTEM image of the Pd-coated α-MnO_2 catalyst is shown in Fig. 4(c). The (110) lattice spacing of the as-prepared α-MnO_2 catalyst is about 0.67 nm and the (111) lattice spacing of Pd deposited on the surface of the α-MnO_2 catalyst is 0.24 nm, which match well with the standard lattice

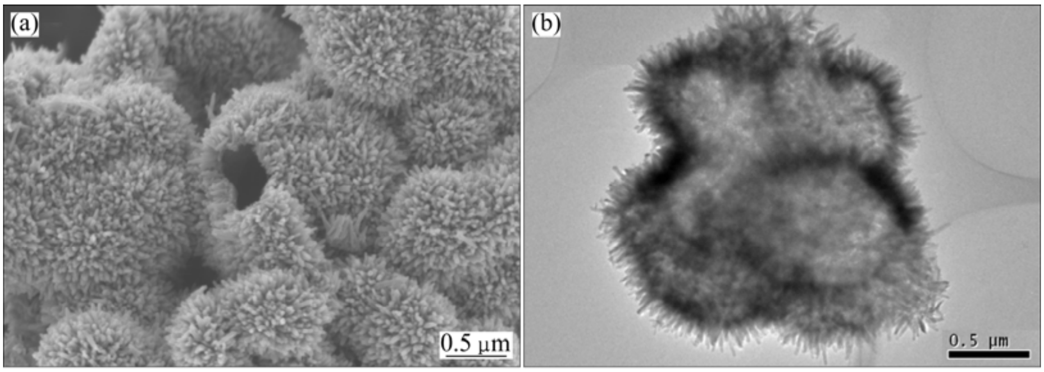


Fig. 3 SEM (a) and TEM (b) images of as-prepared α-MnO_2 catalyst

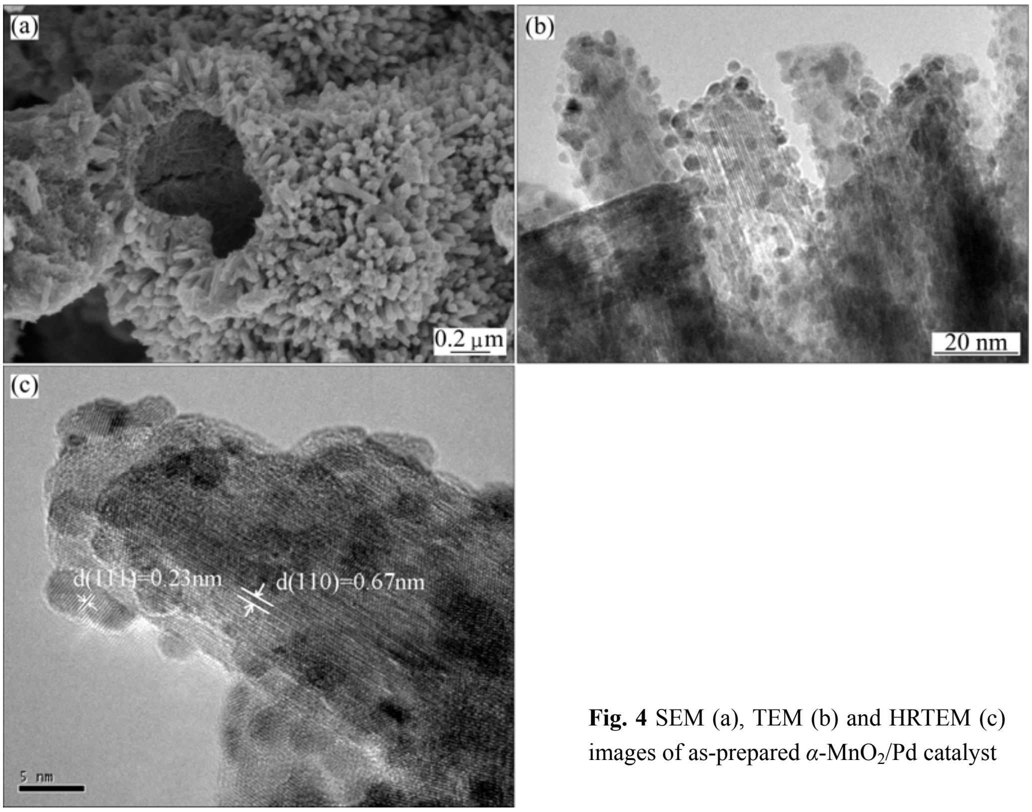
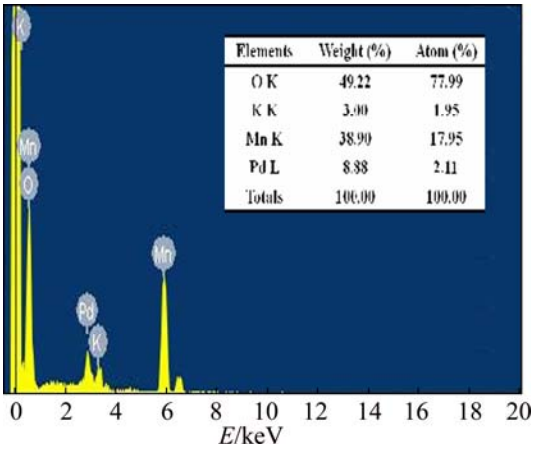


Fig. 4 SEM (a), TEM (b) and HRTEM (c) images of as-prepared α-MnO_2/Pd catalyst

spacing of the α-MnO_2 (d_{110}=0.6919 nm) and Pd (d_{111}=0.2246 nm), respectively. These results also demonstrate that the composite MnO_2/Pd catalysts with a core−shell structure have been prepared successfully by an electroless deposition of Pd on the surface of the α-MnO_2 catalyst.

Figure 5 shows the EDS analytical result of the as-prepared Pd-coated α-MnO_2 catalyst. It shows the existence of palladium, manganese and oxygen in the composite α-MnO_2/Pd catalyst. The mass fraction of Pd approximates 8.88 %, which is close to the feed ratio of 10 %.

The initial charge−discharge curves of the α-MnO_2/Super P air electrode and the α-MnO_2/Pd/Super



Elements	Weight (%)	Atom (%)
O K	49.22	77.99
K K	3.00	1.95
Mn K	38.90	17.95
Pd L	8.88	2.11
Totals	100.00	100.00

Fig. 5 EDS analysis result of as-prepared α-MnO_2/Pd catalyst

P air electrode at different current densities are shown in Fig. 6. The specific discharge capacity of the α-MnO_2/Pd/Super P air electrode is 1220 mA·h/g at a current density of 0.1 mA/cm^2, while 1089.6 mA·h/g is obtained from the α-MnO_2/Super P air electrode at the same current density. Furthermore, the specific discharge capacities of the α-MnO_2/Pd/Super P air electrode are 921.4 and 419.3 mA·h/g at the current densities of 0.2 and 0.5 mA/cm^2, respectively. Under the same conditions, 700.0 and 203.9 mA·h/g are obtained from the α-MnO_2/Super P air electrode, respectively. These results show that the specific discharge capacities of above two air electrodes decrease with the increase of current densities owing to the polarization of air electrodes. The reasons may be that both the blocking of insoluble discharge products within pores of the air electrode and the decrease of the oxygen concentration in the electrolyte become more and more serious with the increase of current densities [7,23].

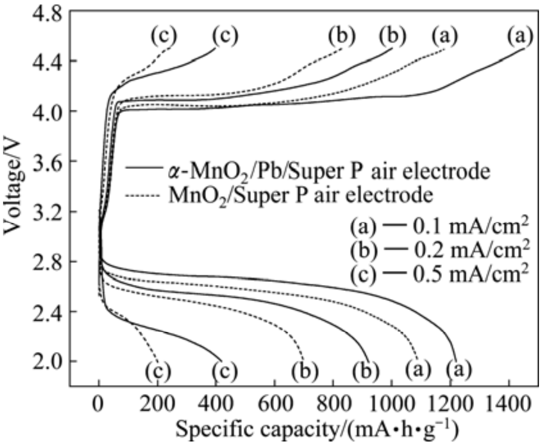


Fig. 6 Charge−discharge curves of both α-MnO_2/Pd/Super P air electrode and MnO_2/Super P air electrode in 1×10^5 Pa O_2 atmosphere between 2.0−4.5 V at different current densities

From Fig. 6, we could also find that every charge−discharge voltage difference of the α-MnO_2/Pd/Super P air electrode at different current densities is lower than that of the α-MnO_2/Super P air electrode at the same current density. This means that the composite α-MnO_2/Pd catalyst has higher electrocatalytic activity than the α-MnO_2 catalyst for the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) [13], which is ascribed to the high catalytic activity of Pd nanoparticles anchored on the surface of the α-MnO_2 catalysts [19]. Furthermore, the polarization of both the α-MnO_2/Pd/Super P air electrode and the MnO_2/Super P air electrode is significant in the initial stage of charge−discharge. This is due to the decomposition of the carbonate-based electrolyte [24].

Figure 7 shows the charge−discharge curves of the above two air electrodes at a current density of 0.1 mA/cm^2 during different charge−discharge cycles. As shown in Fig. 7(a), the initial specific discharge capacity of the α-MnO_2/Super P air electrode is 1089.6 mA·h/g, and then steadily declines to 262.8 mA·h/g after 13 charge−discharge cycles. This indicates that the capacity retention rate of the α-MnO_2/Super P air electrode is only 24.1%. By comparison, the α-MnO_2/Pd/Super P air electrode exhibits a better charge−discharge cycling performance. The initial specific discharge capacity of the α-MnO_2/Pd/Super P air electrode is 1220 mA·h/g, and then steadily decreases to 567.6 mA·h/g after 13 charge−discharge cycles. Namely, its capacity retention rate is about 47.3%. These results show that the composite α-MnO_2/Pd catalyst not only improves the electrocatalytic activity of the oxygen reduction in the discharge process, but also facilitates decomposition of the discharge products in the charge process [13].

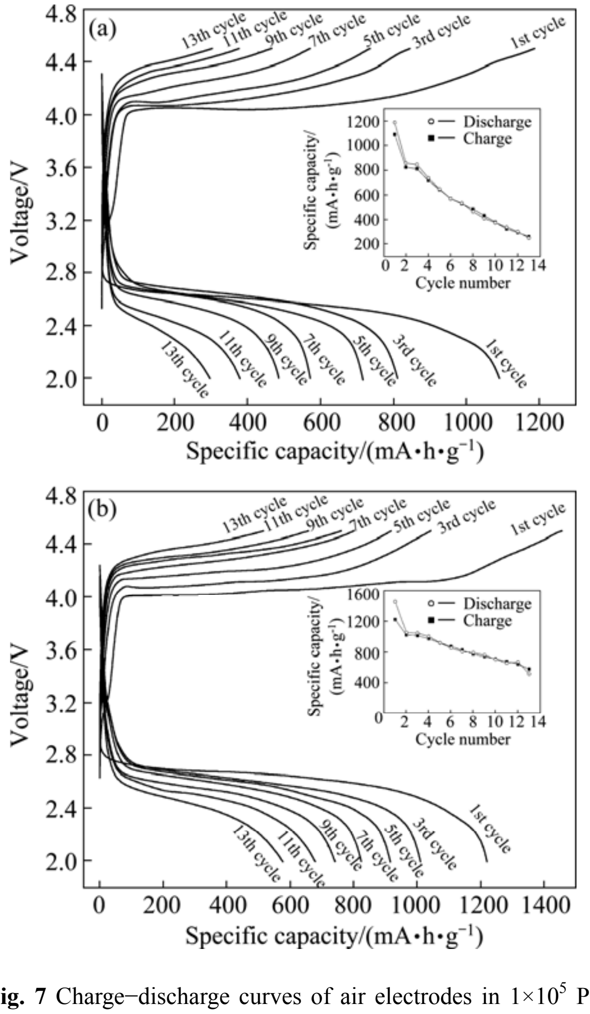


Fig. 7 Charge−discharge curves of air electrodes in 1×10^5 Pa O_2 atmosphere between 2.0−4.5V at current density of 0.1 mA/cm^2: (a) MnO_2/Super P air electrode; (b) α-MnO_2/Pd/Super P air electrode (The insets are the cycling performance curves)

4 Conclusions

A novel Pd-coated α-MnO_2 catalyst with a hierarchical core−shell structure was prepared by an electroless deposition method. The results of SEM and TEM confirm that the as-prepared composite MnO_2/Pd catalyst has a microspherical structure with Pd nanoparticles deposited on the surface of the oriented α-MnO_2 nanoneedles. These α-MnO_2 nanoneedles form a hollow α-MnO_2 microsphere structure. The initial specific discharge capacity of the α-MnO_2/Pd/Super P air electrode is 1220 mA·h/g and the capacity retention rate is about 47.3% after 13 charge−discharge cycles. Compared with the α-MnO_2/Super P air electrode, both the energy conversion efficiency and the charge−discharge cycling performance are improved. Obviously, this kind of hollow α-MnO_2/Pd catalysts with a complicated core−shell structure is a promising catalyst for the rechargeable lithium−air battery.

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新型可充锂−空气电池的纳米刺状 α-MnO$_2$/Pd 空心微球催化剂

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摘 要：利用 NaBH$_4$ 溶液还原 PdCl$_2$ 的方法在具有纳米刺状表面的 α-MnO$_2$ 中空微球上沉积 Pd，制备一种 α-MnO$_2$/Pd 核壳型复合催化剂作为新一代可充锂−空气电池的催化剂。TEM、XRD 和 EDS 等方法的分析结果表明，在催化剂中纳米 Pd 颗粒均匀地分布在刺状 α-MnO$_2$ 中空微球表面，Pd 在催化剂中的质量分数约为 8.88%。充放电测试结果表明，与纳米刺状的 α-MnO$_2$ 中空微球催化剂相比，α-MnO$_2$/Pd 复合催化剂提高了空气电极的能量转化效率和充放电循环性能。由 Super P 碳材料和所制备的 α-MnO$_2$/Pd 复合催化剂所构成的空气电极在 0.1 mA/cm^2 电流密度下的首次放电比容量可以达 1220 mA·h/g，经 13 次充放电循环后的容量保持率为 47.3%。该纳米刺状 α-MnO$_2$/Pd 核壳型复合催化剂是一种有前途的空气电池催化剂。

关键词：锂−空气电池；复合催化剂；刺状中空微球；核壳结构

(Edited by Xiang-qun LI)