The composite sphere of manganese oxide and carbon nanotubes as a prospective anode material for lithium-ion batteries

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HIGHLIGHTS

- Microsphere MnO is prepared by simple decomposition of $MnCO_3$.
- MnO shows better electrochemical performance than $MnCO_3$.
- Both the performances of $MnCO_3$ and MnO could be improved by supporting with CNTs.
- The MWNTs/MnO composite shows superior capacitive, rate and cycling performances.

GRAPHICAL ABSTRACT
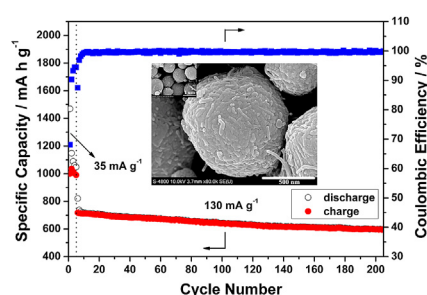
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ABSTRACT

Transition metal oxides and carbonates are emerging anode materials for lithium-ion batteries based on conversion reactions. In this paper, MnO sphere is simply prepared by decomposition of the spherical $MnCO_3$ precursor, and multi-walled carbon nanotubes (MWNTs) are employed to modify their lithium storage capabilities. It is found that the MnO system has superior battery performance over $MnCO_3$ although both of their performances could be significantly improved by carbon nanotube backbones. In particular, the MWNTs/MnO composite sphere shows an outstanding electrochemical performance with a comparatively lower lithium extraction potential. The reversible specific capacity at 35 mA g^{-1} is ~1005 mA h g^{-1} with an initial coulombic efficiency of ~68%. After 200 cycles at 130 mA g^{-1}, the capacity is slowly decreased from ~722 mA h g^{-1} to ~597 mA h g^{-1} indicating a retention of ~83%. Under a high current rate of 715 mA g^{-1} (~1.6 C), it could still deliver ~447 mA h g^{-1}. The high conductivity of MWNTs, unique spherical morphology of the composite, facile electron and Li$^+$ transportations in the electrode/electrolyte interface, self-accommodation of the large volume change during discharge/charge and synergetic lithium storage from each component are ascribed for the advanced performance.

1. Introduction

Due to the high specific capacity, long cycling life and fast charge/discharge rate, lithium-ion battery has been widely used in portable electronic devices, and is being intensively explored in high efficiency energy storage applications such as electric vehicles (EVs) to meet the increasing global energy and environmental crisis

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[1,2]. The current anode material for commercial lithium-ion battery is mostly still graphite-based carbon as was invented. However, the low volumetric capacity and potential safety issue constrain the broad application of carbon anode in next generation high energy/power lithium-ion batteries [3]. A large number of novel materials such as $Li_4Ti_5O_{12}$ [4], Sn [5], Si [6] and transition metal oxides MO_x (M = Fe, Co, Ni, Cu, Mn, etc.) [7] have emerged in recent years as alternative anode candidates. Poizot [8] et al. first reported the attractive lithium storage capability of MO_x via conversion reactions [9] during Li^+ insertion/extraction. When used in lithium-ion batteries, such metal oxides exhibit high theoretical capacities but sluggish reaction kinetics during discharge/charge, therefore, a large potential hysteresis (~ 1.0 V) is usually generated. In addition, the low electric conductivity and large volume change during Li^+ incorporation/extraction make them far away from large scale commercialization.

Among various transition metal oxides MO_x, manganese monoxide MnO has a relatively small potential hysteresis (~ 0.7 V) [10], high specific capacity (theoretically 755.6 mA h g^{-1}), low electromotive force (1.032 V vs. Li/Li$^+$ hereafter) [11] and high density (5.43 g cm^{-3}) [12], therefore, is a perspective anode material for lithium-ion batteries [13]. However, like other MO_x, the capacitive, rate and cycling performances are severely deteriorated by the low electric conductivity and large volume change during Li^+ incorporation/extraction [14]. Particle down-sizing and carbon coating are introduced as common routes to improve the electrochemical performance of MnO [10]. For example, Ding [15] et al. prepared pure nano-MnO by a simple solid state reaction method which shows a reversible capacity of 679.7 mA h g^{-1}, 584.5 mA h g^{-1} and 290 mA h g^{-1} between 0.01 V and 3.0 V at the current density of 46.3 mA g^{-1}, 141.1 mA g^{-1} and 494.7 mA g^{-1}, respectively. Liu [16] et al. further coated a carbon layer on the surface of nano-sized MnO, and increased the reversible capacity to $\sim$700 mA h g^{-1}, 320 mA h g^{-1} and 235 mA h g^{-1} between 0.01 V and 2.0 V (note the narrower potential window) at the current density of 75 mA g^{-1}, 375 mA g^{-1} and 755 mA g^{-1}, respectively. Moreover, nano-structure design [17,18], e.g., nanoplate [19], nanotube [20,21], nanoflake [22], nanosheet [23,24], nanofiber [25], hollow sphere [26] and nanocrystalline thin film [27,28], shows great potential in modification of the physicochemical properties thus the battery performance of MnO.

In the previous work, we demonstrated the remarkable performance advancement of MnO rods by introducing carbon nanotubes (CNTs) [29], and the electrochemical performance was further improved by forming a CNTs/MnO/C hybrid matrix [30]. Comparing with graphene anchored MnO that exhibits similar performance, CNTs are much more cost-effective. In this paper, the composite spheres of multi-walled carbon nanotubes and manganese monoxide (MWNTs/MnO) are prepared by thermal decomposition of the MWNTs/MnCO$_3$ precursor. The battery performances of MnO spheres with/without MWNTs are comparatively studied, and that of the MnCO$_3$ and MWNTs/MnCO$_3$ precursors are discussed as well.

2. Experimental

The multi-walled carbon nanotubes were purchased from Shenzhen Nanotech Port Co., Ltd, and were pretreated in a mixed solution of H$_2$SO$_4$/HNO$_3$ (3/1, volume ratio) before usage [31,32]. 0.12 g so-functionalized MWNTs were dispersed in 100 mL deionized water by ultrasonicating for 2 h. A little ethanol and OP-10 (polyoxyethylene octylphenol ether) surfactant were added to enhance the solubility of MWNTs. 0.845 g reagent grade MnSO$_4$·H$_2$O was added at 4 °C followed by vigorous stirring for 12 h. 100 mL 0.4 mol L^{-1} NH$_4$HCO$_3$ aqueous solution, which was

also prepared at 4 °C by magnetic stirring, was added with continuous stirring at 4 °C for 2 h. The precipitated MWNTs/MnCO$_3$ was collected by repeated filtration and washing, and was dried at 80 °C for 12 h under vacuum. The MWNTs/MnCO$_3$ composite was sintered at 700 °C for 3 h under argon (Ar) protection to synthesize MWNTs/MnO. Pure MnCO$_3$ was prepared by simply precipitating MnSO$_4$·H$_2$O and NH$_4$HCO$_3$ without adding MWNTs, and the corresponding bare MnO was obtained by the same calcination process as described above.

Powder X-ray diffraction (XRD) was performed on an X'Pert Pro (PANalytical) with Cu Kα radiation. Field emission scanning electron microscopy (FESEM, Hitachi S-4800) was used to observe the particle size and morphology. A thin platinum (Pt) layer was deposited for better freezing of the FESEM images. The chemical elements were detected by the energy dispersive X-ray spectroscopy (EDX) attached to the FESEM. The tap density was measured by a JZ-7 Powder Tap Density Analyzer (Chengdu Jingxin Instruments Co. Ltd.).

CR2016 coin cells were fabricated to study the electrochemical performances. Lithium metal was used as the counter electrode, and the electrolyte was 1 mol L^{-1} LiPF$_6$ in ethylene carbonate/dimethyl carbonate (EC/DMC, 1/1). The working electrode was consisted of 70 wt.% active material (MnCO$_3$, MnO, MWNTs/MnCO$_3$, MWNTs/MnO), 20 wt.% acetylene black and 10 wt.% polyvinylidene fluorine (PVDF). The prototype batteries were made in an Ar-filled glove box under rigid water and oxygen monitoring, and were galvanostatically discharged/charged at room temperature between 0.01 V and 3 V on a CT2001A Land Battery Testing System. The specific capacities of MWNTs/MnCO$_3$ and MWNTs/MnO are calculated by the total weights of the composites throughout this paper, i.e. the weights of MWNTs are not excluded. The electrochemical impedance spectroscopy (EIS) was carried out by a Versatile Multichannel Galvanostat 2/Z (VMP2, Princeton Applied Research) in the frequency range from 10^5 Hz to 10^{-2} Hz.

3. Results and discussion

As shown by powder X-ray diffraction (Fig. 1), well crystallized MnCO$_3$ and MnO are prepared, respectively, after precipitation and calcination. The peak at $\sim 2\theta = 26.6°$ corresponding to carbon nanotubes (CNTs) is also indexed for the composites. It is appreciably broadened possibly due to the defects created by functionalization of MWNTs. In addition, no other impurity is detected for all the samples. Moreover, the FESEM image in Fig. 2(a) shows that MnCO$_3$ has a homogeneous spherical morphology with diameters
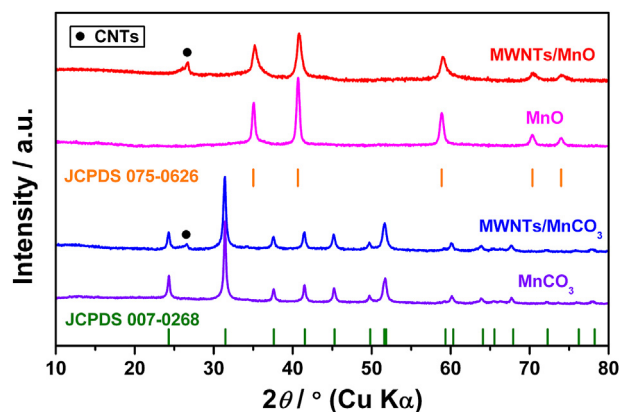

Fig. 1. XRD patterns of MnCO$_3$, MnO, MWNTs/MnCO$_3$ and MWNTs/MnO. The vertical lines indicate the reference patterns of MnCO$_3$ (JCPDS 007-0268) and MnO (JCPDS 075-0626).