

Mn₃O₄/CNTs composite as anode materials for lithium-ion batteries

Xiangjun Xu^a, Peng Ding^b, Muyi Yin^c, Wei Li^d, Yulin Chen^e

Department of Air Defense and Fire Control, Wuhan Ordnance Non-Commissioned Officer Academy, Wuhan 430075, P. R. China

Abstract: Transition metal oxides especially manganese oxides are being intensively studied as candidate anode materials for next generation lithium ion batteries in high efficiency energy storage applications. In this paper, Mn₃O₄/CNTs composite is prepared via a facile one-step solvothermal method. The results of XRD and SEM showed that Mn₃O₄ uniformly coated on the surface of CNTs. It could deliver a reversible charge capacity of 809.9 mA h g⁻¹ at the current density of 40 mA g⁻¹, and the specific discharge capacity slightly increased from 644.2 mA h g⁻¹ to 796.1 mA h g⁻¹ after 50 cycles at a current density of 160 mA g⁻¹ demonstrating excellent cycling stability.

1. Introduction

Poizot et al. [1, 2] first reported that lithium can be stored reversibly in nanostructured transition-metal oxides (M_xO_y, M=Fe, Co, Ni, Cu, etc.) through heterogeneous conversion reaction: M_xO_y + 2Li⁺ + 2ye⁻ → xM⁰ + yLi₂O. These nanocompounds have attracted great attention as anode materials, due to their high theoretical capacity, natural abundance and environmental benignity.

The theoretical specific capacity of Mn₃O₄ is about 937 mA h g⁻¹, which is nearly three times higher than that of graphite. But Mn₃O₄ exhibits extremely low electrical conductivity (~10⁻⁷-10⁻⁸ S cm⁻¹), limiting its capacity, cycling stability and rate capability as anode material for LIBs. Some strategies have been proposed to improve its electrochemical performance. Co doped Mn₃O₄ have better cycle stability than undoped Mn₃O₄, with a capacity is only 400 mA h g⁻¹ at a current density of 33-55 mA g⁻¹ [3]; Gao et al. [4] have prepared spongelike nanosized Mn₃O₄ by precipitation method with a stable reversible capacity of 800 mA h g⁻¹ after 40 cycles at a current rate of 0.25 C.

In this paper, we have employed a facile and fast one-step solvothermal method to prepare Mn₃O₄/CNTs composite and evaluated its electrochemical performance as anode for lithium-ion batteries. We also used X-ray diffraction and scanning electron microscopy to characterize the structure and morphology of Mn₃O₄/CNTs composite.

2. Experimental

CNTs was first functionalized by sonicating with a concentrated solution of H₂SO₄/HNO₃ (3/1, volume ratio) in a water bath for 12 h to remove the impurities and to improve their dispersion. The so-obtained CNTs was dissolved in ethanol, followed by sonicating for 2 h. Then KMnO₄ was added into the as-prepared CNTs dispersion under vigorous magnetic stirring for 1 h at room

temperature. The mixture was transferred into a Teflon-lined stainless steel autoclave and was sealed into an oven with a heat treatment of 180 °C for 12 h, and then cooled down to ambient temperature. The black products were filtered for several times and dried at 80 °C for 12 h under vacuum.

The material was characterized by a X'Pert Pro PANalytical X-ray diffractometer, using filtered Cu K α radiation ($\lambda=1.5406$ Å). The general morphology and particle size of the synthesized products were investigated by an FEI Quanta 200 FEG field emission scanning electron microscopy (FESEM).

The electrochemical experiments were performed using 2016 coin-type cells assembled in an argon filled glove box. The working electrodes were fabricated by using mixed slurry of as-prepared samples, carbon black, and polyvinylidene fluoride (PVDF) in a weight ratio of 80:10:10 in N-methyl-2-pyrrolidone (NMP) solvent. The resultant slurry was uniformly pasted onto Cu foil and dried at 120 °C overnight under vacuum. The electrolyte was 1.0 mol L⁻¹ LiPF₆ in 1:1 mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). Pure lithium foil was used as counter electrode. The batteries were discharge/charged at constant currents on a CT2001A Land Battery Testing System to evaluate their electrochemical performance in the galvanostatic mode between 0.01 V and 3.0 V.

3. Result and discussion

Fig. 1 shows the X-ray diffraction (XRD) pattern of the as-prepared Mn₃O₄/CNTs composite powder. The crystal structure of Mn₃O₄/CNTs composite can be indexed to the tetragonal phase of Mn₃O₄ (JCPDS No. 24-0734). The diffraction peaks at 28.9°, 32.3°, 36.1°, 38.0°, 44.4°, 50.7°, 58.5° and 59.8° positions can be well-assigned to (112), (103), (211), (004), (220), (105), (321) and (224) planes of the hausmannite Mn₃O₄ with tetragonal structure. The

Peng Ding: jxsgdp@126.com

weak peak at 26.3° can be assigned to the hexagonal carbon in CNTs (JCPDS No. 01-075-1621), and no other impurity phases was observed in the synthesized products, indicating high purity and crystallinity of the as prepared product.

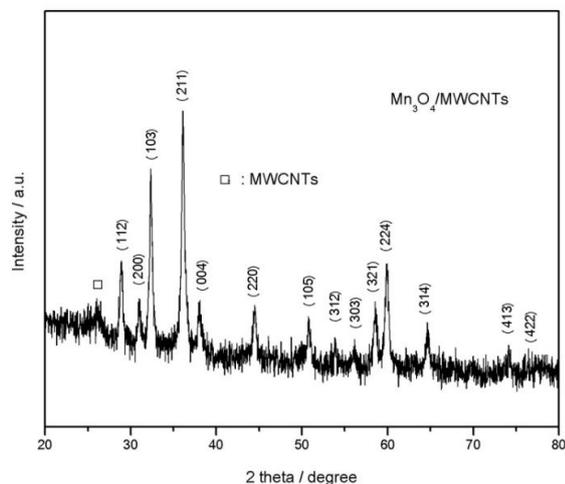


Fig. 1 X-ray diffraction pattern of $\text{Mn}_3\text{O}_4/\text{CNTs}$ composite

To investigate the morphology of the products, field emission scanning electron microscope (FESEM) images were collected for the $\text{Mn}_3\text{O}_4/\text{CNTs}$ composite, as shown in Fig. 2. Fig. 2(a) presents the overall FESEM images of the as prepared $\text{Mn}_3\text{O}_4/\text{CNTs}$ composite sample. It exhibits homogeneous nanotube architecture. At high magnification (Fig. 2(b)), it can be easily seen that Mn_3O_4 are uniformly coated on the surface of CNTs. The average diameter of the nanotube is about 50 nm. So the coating thickness of Mn_3O_4 is about 10 nm, and Mn_3O_4 particle that coated on CNTs is very small.

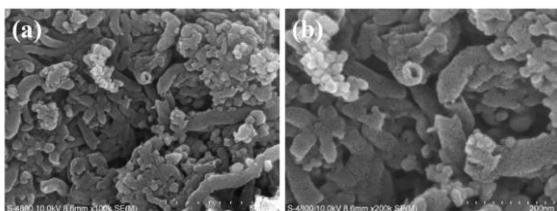


Fig. 2 FESEM images of (a) low magnification and (b) high magnification of the $\text{Mn}_3\text{O}_4/\text{CNTs}$ composite

Fig. 3 shows the typical voltage profiles of the first five cycles for the $\text{Mn}_3\text{O}_4/\text{CNTs}$ composite at a current density of 40 mA g^{-1} between 0.01 and 3 V vs. Li/Li^+ . In the first discharge curve, there is an obvious sloping voltage from 1.5 V to 0.38 V, which can be ascribed to formation of the solid-electrolyte interphase (SEI) and initial reduction of Mn_3O_4 . A well-defined voltage plateau at around 0.38 V can be attributed to the Li^+ charge reaction: $\text{Mn}_3\text{O}_4 + 8\text{Li}^+ + 8\text{e}^- \rightarrow 3\text{Mn}(0) + 4\text{Li}_2\text{O}$ [5]. The initial specific discharge capacity extends to $1528.7 \text{ mA h g}^{-1}$, slightly higher than the theoretical capacity of 937 mA h g^{-1} for the conversion reaction to Mn and Li_2O . This should be ascribed to the decomposition of the electrolyte at low voltage to form a SEI layer and further lithium storage via interfacial charging at $\text{Mn}/\text{Li}_2\text{O}$ interface [6]. The discharge voltage

plateau of $\text{Mn}_3\text{O}_4/\text{CNTs}$ electrode has shifted to 0.5 V from the second cycle, which is higher than the first discharge, indicating that the lithium insertion reaction has become easier [7].

The first reversible charge capacity is $809.9 \text{ mA h g}^{-1}$, which is much higher than the capacity of commercial graphitic carbon. There is a significant irreversible capacity loss for the first cycle, which is common to almost all systems based on conversion reactions.

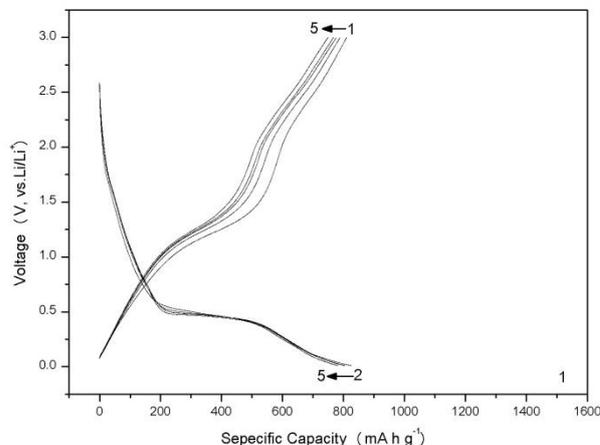


Fig. 3 Galvanostatic discharge/charge curves of the $\text{Mn}_3\text{O}_4/\text{CNTs}$ composite at a current density of 40 mA g^{-1}

The cycling performance under a constant current density of 160 mA g^{-1} with a potential window from 0.01 V to 3.0 V of $\text{Mn}_3\text{O}_4/\text{CNTs}$ composites electrode is shown in Fig. 4. The $\text{Mn}_3\text{O}_4/\text{MWCNTs}$ composite maintains a significantly higher reversible capacity, which is slightly increased from $644.2 \text{ mA h g}^{-1}$ to $796.1 \text{ mA h g}^{-1}$. This could be attributed to the intimate interaction between the MWCNTs substrates and the Mn_3O_4 nanoparticles directly coated on them

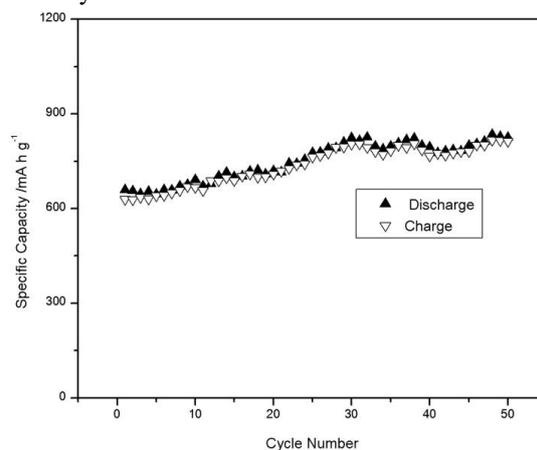


Fig. 4 Cycling performance of $\text{Mn}_3\text{O}_4/\text{CNTs}$ composite electrode at a current density of 160 mA g^{-1}

The excellent electrochemical performance of $\text{Mn}_3\text{O}_4/\text{CNTs}$ composite could be attributed to its special architecture. First, the CNTs in the obtained composite can not only accommodate the strain induced by volume expansion/contraction of Mn_3O_4 nanoparticles during the Li ion insertion/extraction process, but also efficiently

prevent the aggregation of Mn_3O_4 nanoparticles and the cycling. Secondly, CNTs can improve the conductivity of the electrode materials and stabilize the electrode structure during the charge/discharge process because of the intimate interaction between CNTs and Mn_3O_4 nanoparticles directly grown on them.

4. Conclusion

We synthesized a $\text{Mn}_3\text{O}_4/\text{CNTs}$ composite via a one-step hydrothermal method. It displays a high specific discharge capacity of up to $796.1 \text{ mA h g}^{-1}$ after 50 cycles at 160 mA g^{-1} . The excellent electrochemical performance of the $\text{Mn}_3\text{O}_4/\text{CNTs}$ composite could be attributed to its unique architecture.

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References

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