Mn$_3$O$_4$/CNTs composite as anode materials for lithium-ion batteries

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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, Mn$_3$O$_4$/CNTs composite is prepared via a facile one-step solvothermal method. The results of XRD and SEM showed that Mn$_3$O$_4$ 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$_x$O$_y$, M=Fe, Co, Ni, Cu, etc.) through heterogeneous conversion reaction: M$_x$O$_y$ + 2Li$^+$ + 2ye$^-$ → xM + yLi$_2$O. 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 Mn$_3$O$_4$ is about 937 mA h g$^{-1}$, which is nearly three times higher than that of graphite. But Mn$_3$O$_4$ exhibits extremely low electrical conductivity ($\sim 10^{-7}$-$10^{-8}$ 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 Mn$_3$O$_4$ have better cycle stability than undoped Mn$_3$O$_4$, 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 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 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$^{-1}$ LiPF$_6$ in 1:1 mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). Pure lithium foil was used as counter electrode. The batteries were discharged/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.

2. Experimental

CNTs was first functionalized by sonicating with a concentrated solution of H$_2$SO$_4$/HNO$_3$ (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 KMnO$_4$ 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 Ka radiation (λ=1.5406 Å). The general morphology and particle size of the synthesized products were investigated by a 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$^{-1}$ LiPF$_6$ in 1:1 mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). Pure lithium foil was used as counter electrode. The batteries were discharged/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 Mn$_3$O$_4$/CNTs composite power. The crystal structure of Mn$_3$O$_4$/CNTs composite can be indexed to the tetragonal phase of Mn$_3$O$_4$ (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 Mn$_3$O$_4$ with tetragonal structure. The
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.

![X-ray diffraction pattern of Mn₃O₄/CNTs composite (Fig. 1)](image)

To investigate the morphology of the products, field emission scanning electron microscope (FESEM) images were collected fo the Mn₃O₄/CNTs composite, as shown in Fig. 2. Fig. 2(a) presents the overall FESEM images of the as prepared Mn₃O₄/CNTs composite sample. It exhibits homogeneous nanotube architecture. At high magnification (Fig. 2(b)), it can be easily seen that Mn₃O₄ are uniformly coated on the surface of CNTs. The average diameter of the nanotube is about 50 nm. So the coating thickness of Mn₃O₄ is about 10 nm, and Mn₃O₄ particle that coated on CNTs is very small.

![FESEM images of (a) low magnification and (b) high magnification of the Mn₃O₄/CNTs composite (Fig. 2)](image)

Fig. 3 shows the typical voltage profiles of the first five cycles for the Mn₃O₄/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 Mn₃O₄. A well-defined voltage plateau at around 0.38 V can be attributed to the Li⁺ charge reaction: Mn₃O₄ + 8Li⁺ + 8e⁻ → 3Mn (0) + 4Li₂O [5]. The initial specific discharge capacity extends to 1528.7 mA h g⁻¹, slightly higher than the theoretical capacity of 937 mA h g⁻¹ for the conversion reaction to Mn and Li₂O. 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 Mn/Li₂O interface [6]. The discharge voltage plateau of Mn₃O₄/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 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.

![Galvanostatic discharge/charge curves of the Mn₃O₄/CNTs composite at a current density of 40 mA g⁻¹ (Fig. 3)](image)

The cycling performance under a constant current density of 160 mA g⁻¹ with a potential window from 0.01V to 3.0V of Mn₃O₄/CNTs composites electrode is shown in Fig. 4. The Mn₃O₄/MWCNTs composite maintains a significantly higher reversible capacity, which is slightly increased from 644.2 mA h g⁻¹ to 796.1 mA h g⁻¹. This could be attributed to the intimate interaction between the MWCNTs substrates and the Mn₃O₄ nanoparticles directly coated on them.

![Cycling performance of Mn₃O₄/CNTs composite electrode at a current density of 160 mA g⁻¹ (Fig. 4)](image)

The excellent electrochemical performance of Mn₃O₄/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 Mn₃O₄ nanoparticles during the Li ion insertion/extraction process, but also efficiently
prevent the aggregation of Mn$_3$O$_4$ nanoparticles and the cracking of the electrode material upon continuous 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$_3$O$_4$ nanoparticles directly grown on them.

4. Conclusion

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

References

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