Materials Chemistry and Physics 121 (2010) 302–307

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

The preparation and electrochemical performances of $LiFePO_4$-multiwalled nanotubes composite cathode materials for lithium ion batteries

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ARTICLE INFO

Article history:
Received 13 February 2009
Received in revised form 2 November 2009
Accepted 21 January 2010

Keywords:
Composite materials
Annealing
X-ray diffraction topography
Electrochemical properties

ABSTRACT

$LiFePO_4$-MWCNTs (multi-walled carbon nanotubes) composite cathode materials were prepared by mixing $LiFePO_4$ and MWCNTs in ethanol followed by heat-treatment at 500 °C for 5 h. The structural, morphology and electrochemical performances of $LiFePO_4$-MWCNTs composite materials were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), galvanostatic charge–discharge cycle tests, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The results indicated that MWCNTs adding improved the electronic conductivity, the discharge capacity, cycle stability and lithium ion diffusion kinetics of $LiFePO_4$, but MWCNTs adding did not charge the orthorhombic olivine-type structure of $LiFePO_4$. In all these prepared $LiFePO_4$ with x wt.% MWCNTs ($x = 4, 7, 10$) composites, 7 wt.% MWCNTs adding composite cathode shows the best electrochemical performance, which gets an initial discharge capacity of 152.7 mAh g^{-1} at 0.18 C discharge rates with capacity retention ratio of 97.77% after 100 cycles.

1. Introduction

Rechargeable lithium ion batteries exhibiting high energy and high power density are in great demand as energy sources for a variety of advanced devices such as cellular phones, notebook computers and electric/hybrid vehicles [1]. However, the development and application of lithium ion batteries are mainly limited by the cathodes [2]. At present, the most widely used commercial cathode material for lithium ion battery is $LiCoO_2$ due to its ease of production, stable electrochemical cycling and acceptable specific capacity [3–5]. This cathode was successful, but serious problems such as safety, cost and toxicity still remained unsolved. Possible alternatives are $LiMn_2O_4$ [6–13], $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ [14–20], LiV_3O_8 [21,22] and $LiFePO_4$ [23–40] etc.

Among these cathode materials, olivine structured $LiFePO_4$ have attracted the most interest due to the low cost, low toxicity and the high approaching to the theoretical, practical capacity of larger than 160 mAh g^{-1} at low rates with flat charge–discharge potential plateaus around 3.4 V vs. Li^+/Li owing to the Fe^{3+}/Fe^{2+} redox couple [27]. However, the low electronic conductivity (10^{-8} to 10^{-10} S cm^{-1}) of $LiFePO_4$ made it difficult to utilize the full theoretical capacity at useful rate. To overcome this problem, tremendous efforts have been made, such as doping with foreign atom [25,26,29–31], decreasing the particle size [24,27] and coating electronically conductive reagent [23,28], etc.

Carbon nanotubes are readily electronic conductive [33,34]. Li et al. [32], Liu et al. [35] and Sheem et al. [36] applied MWCNTs as the conducting additive in $LiFePO_4$ and $LiCoO_2$ electrodes. They demonstrated MWCNTs were better conductor than carbon black. The reversible discharge capacity of $LiFePO_4$-MWCNTs composite cathode was 150 mAh g^{-1} at 0.1 C rates while the $LiFePO_4$-carbon black composite was 140 mAh g^{-1} at the same rate [32]. Compared with the batteries carbon black additive, those with CNT additive show better electrochemical performances with capacity retention ratio of 99.2% after 50 cycles at 0.1 C rates. Chen and Whittingham [37] and Gu and co-workers [38] prepared $LiFePO_4$-MWCNTs via hydrothermal method and indicated that the added MWCNTs in pure $LiFePO_4$ enhanced the electronic conductivity of the final product. Wang et al. [39] prepared $LiFePO_4$-MWCNTs by microwave routes and indicated and the electrochemical capacity of $LiFePO_4$-MWCNTs was 145 mAh g^{-1} at 0.5 C rates and cycle ability was stable. However, these above methods were not convenient and most of these need more than two heating process.

In this work, a liquid mixing method followed by heat-treating was used to prepare $LiFePO_4$-MWCNTs composite cathodes. The mixing process of $LiFePO_4$ and MWCNTs was simple and the following heating process was easy to control. The structural, morphological and electrochemical properties of the $LiFePO_4$-MWCNTs composite were investigated.

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doi:10.1016/j.matchemphys.2010.01.038

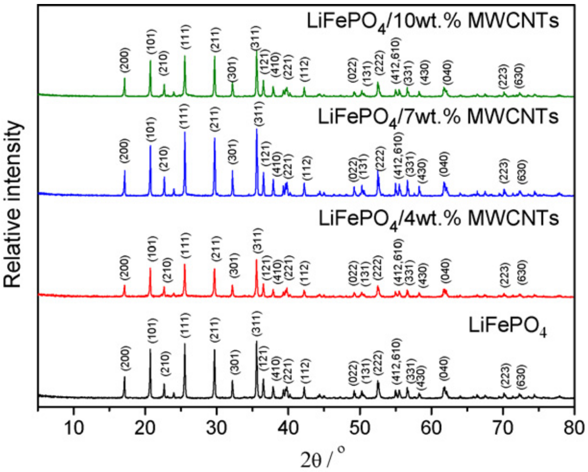

Fig. 1. XRD patterns of $LiFePO_4$ and $LiFePO_4$-MWCNTs.

2. Experimental

$LiFePO_4$ was prepared from stoichiometric amount of $LiOH{\cdot}H_2O$, $FeC_2O_4{\cdot}2H_2O$ and $NH_3H_2PO_4$ (molar ratio 1:1:1, respectively). The mixture was ball milled for 1 h and pre-pyrolyzed at 400 °C for 5 h in pure argon flow. The resulting product was reground by ball milling for 1 h and then heated at 700 °C for 16 h in pure argon flow. MWCNTs (Shenzhen Nanotech Port, China) were soaked in concentrated nitric acid and refluxed for 5 h. The product was washed by distilled water and acetone, and then dried in a vacuum at 60 °C. As-treated MWCNTs and as-prepared $LiFePO_4$ were mixed in absolute alcohol at 60 °C with vigorous stir (the weight content of MWCNTs adding was 4, 7, 10 wt.% of $LiFePO_4$). Until all the liquid was evaporated, the solid was dried in a vacuum at 120 °C for 1 h and then heated at 500 °C for 5 h in pure argon flow. The resulting composite powder was ground in agate mortar to obtain objective product.

The phase structures of the $LiFePO_4$-MWCNTs composite and pure $LiFePO_4$ were analyzed by X-ray diffraction (XRD) using Rigaku X-ray powder diffractometer D/MAX-2500 with graphite monochromatic CuKα radiation in the 2θ range of 3–80°. Morphologies of the composite were investigated by Shimadzu SS-550 scanning electron microscopy (SEM) with an accelerating voltage of 15 kV. Transmission electron microscopy (TEM) images were collected by using PHILIPS Tecnai G^2 F20 (operating at 200 kV) transmission electron microscopes. The electronic conductivities of all prepared samples are measured with the four-electrode method by SDY-5 four-point probe meter (Guangzhou, China).

For electrochemical tests, cathode electrodes were prepared by mixing the active material ($LiFePO_4$-MWCNTs), conductive additive (acetylene black, ENSACO, Switzerland) and binder (PTFE, Sigma Aldrich, China) in a weigh ratio of 85:10:5, respectively. The materials, as a cathode, were assembled into lithium batteries in an argon filled glove box, with the use of Celgard 2300 as a separator, Li foil as counter and reference electrodes, and 1 mol dm^{-3} $LiPF_6$ in ethylene carbonate (EC), propylene carbonate (PC) and dimethyl carbonate (DMC) (1:1:1 by volume respectively, Jinniu, China) as electrolyte, to form laboratory-made coin-type cells (size: CR 2032). Galvanostatic charge–discharge cycle tests were performed on a LAND 2001A battery testing system (Jinnuo, China) in the potential range of 2.5–4.3 V respectively vs. Li$^+$/Li. Cyclic voltammetry (CV) tests were performed on a CHI 660C electrochemical workstation (Chenhua, China) at a scan rate of 0.1 mV S^{-1} at a potential interval 2.5–4.3 V vs. Li/Li$^+$. Electrochemical impedance spectroscopy (EIS) was also performed on a CHI 660C electrochemical workstation. The EIS measurement conditions were: AC amplitude 5 mV; testing potential 3.4 V vs. Li$^+$/Li at approximate 50% DOD (depth of discharge); frequency range 10^5–0.1 Hz.

3. Results and discussion

The XRD patterns of as-prepared $LiFePO_4$ and $LiFePO_4$-MWCNTs are shown in Fig. 1. The patterns of $LiFePO_4$-MWCNTs composites can be indexed to a single-phase material having an orthorhombic olivine-type structure with a space group of *Pnma* [40], which are the same as the $LiFePO_4$ one. No diffraction peak for MWCNTs or carbon was present in either of these XRD patterns. That is because of the low content and the amorphous state of carbon in the composite materials. The XRD peak of amorphous carbon was covered by the main phases of $LiFePO_4$. Therefore, the MWCNTs adding do not change the crystal structure of pure $LiFePO_4$.

Table 1
The electronic conductivity of $LiFePO_4$ and $LiFePO_4$-MWCNTs composites.

Samples	Electronic conductivity (S cm^{-1})	
	Original materials	As-prepared electrodes
$LiFePO_4$	3.1×10^{-9}	7.4×10^{-4}
$LiFePO_4$/4 wt.% MWCNTs	5.5×10^{-4}	1.1×10^{-3}
$LiFePO_4$/7 wt.% MWCNTs	4.7×10^{-3}	5.2×10^{-3}
$LiFePO_4$/10 wt.% MWCNTs	2.3×10^{-3}	3.2×10^{-3}

Fig. 2 shows the SEM images of $LiFePO_4$ and $LiFePO_4$-MWCNTs composites. The particle size of pure $LiFePO_4$ was 1–5 μm, while that of $LiFePO_4$ with 7 wt.% MWCNTs composite was 3–5 μm. In Fig. 2d, f and h, it is clear that networks of MWCNTs appeared in the interstitial grain-boundary region, which can improve the electrical continuity between $LiFePO_4$ particles and makes the crystal structure stable. Moreover, the dispersed MWCNTs provide pathways for electron transference.

The electronic conductivity of $LiFePO_4$ with 7 wt.% MWCNTs and $LiFePO_4$ with 10 wt.% MWCNTs composite is about a factor of $\sim 10^6$ higher than the pure $LiFePO_4$, reaching to about 10^{-3} S cm^{-1} (measured by a four-point probe method, Table 1). The conductivity value of original materials and as-prepared electrode materials (active material + conductive + binder) are all shown in Table 1. The reason of the improvement of the electronic conductivity of the composite is that the MWCNTs offer the electronic transport channels in the composites. Therefore, MWCNTs adding improves the electronic conductivity of $LiFePO_4$.

Fig. 3 shows the TEM images of $LiFePO_4$, $LiFePO_4$ with 7 wt. % MWCNTs and $LiFePO_4$ with 10 wt.% MWCNTs composites. From Fig. 3a, the pure $LiFePO_4$ sample exhibits the irregular particles. From Fig. 3c, the MWCNTs coated on the surface of $LiFePO_4$ and connected the particles of $LiFePO_4$ which can be clearly seen. These results agree with SEM images in Fig. 2. The MWCNTs in the $LiFePO_4$/7 wt.% MWCNTs composite were covered around every particle of $LiFePO_4$ and they have good connection with the $LiFePO_4$ particles. The MWCNTs distribution of $LiFePO_4$/10 wt.% MWCNTs was disorderly and their orientation was lacking direction.

Discharge capacities of $LiFePO_4$ and $LiFePO_4$-MWCNTs composite at 0.18 C (1 C = 170 mA g^{-1}) are shown in Fig. 4. With the MWCNTs weight ratio increasing in the as-prepared composite, discharge capacity and cycle stability of the $LiFePO_4$-MWCNTs composite are both improved. The $LiFePO_4$ with 7 wt.% MWCNTs shows the best cycling performance among the as-prepared composites. At first cycle, the discharge capacity of $LiFePO_4$ with 7 wt.% MWCNTs is 152.7 mAh g^{-1} at 0.18 C discharge rates while that of pure $LiFePO_4$ was 141.4 mAh g^{-1}. After 100 cycles of charge–discharge, the discharge capacity of $LiFePO_4$ with 7 wt.0% MWCNTs is 149.3 mAh g^{-1} and the capacity retention is 97.77%, which are both higher than those of pure $LiFePO_4$ (125.3 mAh g^{-1} and 88.57%). That is because the MWCNTs webs covered the $LiFePO_4$ particles to protect the cathode crystal structure from distortion during charge–discharge test and also delivered good conductivity of cathode material [32,34,35].

In the case of $LiFePO_4$-MWCNTs composite, the $LiFePO_4$ with 7 wt.% MWCNTs has the best discharge capacity and cycle stability, not the 10 wt.% MWCNTs one. Here we analysis some reasons about this behavior. Firstly, Less MWCNTs content (4 wt.%) could not provide sufficient aforementioned effects and because of the little electrochemical activity of MWCNTs compared with $LiFePO_4$ active material, more MWCNTs content (such as 10 wt.%) would decrease the active material percentage leading to the decrease of discharge capacity. So the 7 wt.% MWCNTs is the best one. Additionally, from TEM images in Fig. 3d, the MWCNTs distribution of $LiFePO_4$ with 10 wt.% MWCNTs was disorderly and their orientation was lacking direction. However, the MWCNTs in the $LiFePO_4$ with