



Electrochemical properties of LiFePO₄-multiwalled carbon nanotubes composite cathode materials for lithium polymer battery

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ABSTRACT

LiFePO₄-multiwalled carbon nanotubes (MWCNTs) composites were prepared by a hydrothermal method followed by ball-milling and heat treating. Cyclic voltammetry, ac impedance and galvanostatic charge/discharge testing results indicate that LiFePO₄-MWCNTs composite exhibits higher discharge capacity and rate capability than pure LiFePO₄ at high-rate at room temperature. It is demonstrated that the added MWCNTs not only increase the electronic conductivity and lithium-ion diffusion coefficient but also decrease crystallite size and charge transfer resistance of LiFePO₄-MWCNTs composite.

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1. Introduction

Recently, lithium iron phosphate with an ordered olivine-type structure, LiFePO₄, has attracted extensive attention due to low cost, safety and high compatibility with environment [1–9]. However, it is difficult to attain the full capacity because the electronic conductivity ($\sim 10^{-9}$ S/cm) is very low, which leads to initial capacity loss and poor rate capability, and diffusion of Li⁺ ion across the LiFePO₄/FePO₄ boundary is slow due to its intrinsic character [1]. Many researchers have suggested solutions to this problem as follows: (i) coating with a conductive layer around the particles [10,11]; (ii) ionic substitution to enhance the electrochemical properties [12,13]; and (iii) synthesis of particles with well-defined morphology [14].

Li et al. [15] demonstrated that LiFePO₄/MWCNTs composite cathode displayed the initial discharge capacity of 155 mAh/g at 0.1 C rate and the gradual decrease in discharge capacity upon cycling. Whittingham et al. [16] indicated that the added MWCNTs in pure LiFePO₄ enhanced the electronic conductivity of the final product. Sakamoto et al. [17] suggested that V₂O₅/singlewalled carbon nanotubes composite electrode exhibited specific capacities in excess of 400 mAh/g at high discharge rates and retained this level of capacity on cycling. All the above papers used the liquid electrolyte. Zaghbi et al. [18] reported the electrochemical performance of natural graphite-fibers/polyethylene oxide (PEO)-based gel electrolyte/LiFePO₄ batteries. Appetecchi et al. [19] suggested that Li/LiFePO₄ polymer cells were capable of delivering

capacities exceeding 100 mAh/g at temperatures above 90 °C even at moderately high rates using PEO as a polymer matrix. However, up to now, there is no report on the electrochemical performance of LiFePO₄-MWCNTs composite using polymer electrolyte especially at room temperature.

In this study, MWCNTs were added to improve the electronic conductivity of pure LiFePO₄. For the first time, we used 25PVDFLiClO₄EC₁₀PC₁₀ as solid polymer electrolyte (SPE) to analyze the electrochemical properties of LiFePO₄-MWCNTs composite by cyclic voltammetry (CV), ac impedance and galvanostatic charge/discharge tests at room temperature.

2. Experimental

The preparation of pure LiFePO₄ was described in detail previously [20]. Five weight percentage of MWCNTs were added into the solution of LiFePO₄ hydrothermally synthesized at 170 °C and *N*-methyl-2-pyrrolidone (NMP), the mixture was ball-milled for 10h using a shaker type of ball mill (Planetary Mono Mill). After drying at 90 °C for 12h, the powders were pelletized and further heated at 500 °C for 1h in nitrogen atmosphere. After cooling to room temperature, the mixture of NMP and LiFePO₄-MWCNTs composite was ball-milled again for 10h. Finally, the mixture was dried at 90 °C for 12h. For comparison, pure LiFePO₄ without MWCNTs was synthesized by the same ball-milling and heating temperature.

The composite electrodes were prepared by mixing pure LiFePO₄ or LiFePO₄-MWCNTs composite with carbon black and polyvinylidene fluoride (PVDF) in a weight ratio of 70:25:5 in NMP. The

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synthesis of 25PVDFLiClO₄EC₁₀PC₁₀ was described in detail previously [21]. Li/SPE/LiFePO₄ and Li/SPE/LiFePO₄-MWCNTs coin-type batteries (CR2032) were assembled with lithium metal as anode and 25PVDFLiClO₄EC₁₀PC₁₀ as electrolyte. The automatic charge/discharge equipment (WBCS3000, WonATech Co. Ltd.) was used to perform the galvanostatic charge/discharge tests and CV measurements at room temperature.

The electronic conductivities of the samples were measured by a four-point probe method. The crystalline phases were identified with XRD (Dmax/1200, Rigaku) with Cu K α radiation. Electrochemical impedance spectroscopy measurements were performed using an IM6 impedance system (Zahner Elektrik Co.). The spectrum was potentiostatically measured by applying an ac voltage of 20 mV over the frequency range from 2 MHz to 0.1 or 0.01 Hz.

3. Results and discussion

Fig. 1 shows the XRD patterns for pure LiFePO₄ and LiFePO₄-MWCNTs composite. All the patterns can be indexed to a single-phase material having an orthorhombic olivine-type structure with a space group of *Pnma*, which is the same as the standard one. The crystallite size (*D*) was calculated by the Scherrer's equation: $D = 0.9\lambda/\beta \cos \theta$, from the full-width-at-half-maximum β of four strong and well-resolved reflection peaks corresponding to [1 0 1], [1 1 1], [2 1 1] and [3 1 1] crystallographic directions and the mean value was calculated [22,23]. The crystallite sizes are 34 nm for pure LiFePO₄ and 19 nm for LiFePO₄-MWCNTs composite, respectively. It is believed that the small particle size is useful for the intercalation/de-intercalation process of lithium ions. There is no impurity in pure LiFePO₄ and LiFePO₄-MWCNTs composite. There is no obvious carbon diffraction peaks in LiFePO₄-MWCNTs composite due to its low content and amorphous state. The added MWCNTs do not change the crystal structure of pure LiFePO₄.

Fig. 2 shows the SEM image of LiFePO₄-MWCNTs composite. SEM observation shows that the MWCNTs intertwine with LiFePO₄ particles together to form a three-dimensional network. The dispersed MWCNTs provide pathways for electron transference. Therefore, the electronic conductivity of LiFePO₄-MWCNTs composite is improved from 5.86×10^{-9} S/cm for pure LiFePO₄ to 1.08×10^{-1} S/cm (measured by a four-point probe method).

Fig. 3 shows the cyclic voltammograms of pure LiFePO₄ and LiFePO₄-MWCNTs composite. For pure LiFePO₄, oxidation and reduction peaks in the second cycle appear at around 3.65 and 3.17 V, respectively. The potential interval between two peaks is

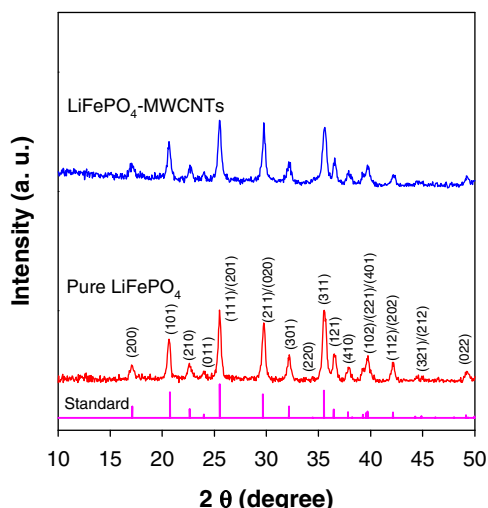


Fig. 1. The XRD patterns for pure LiFePO₄ and LiFePO₄-MWCNTs composite.

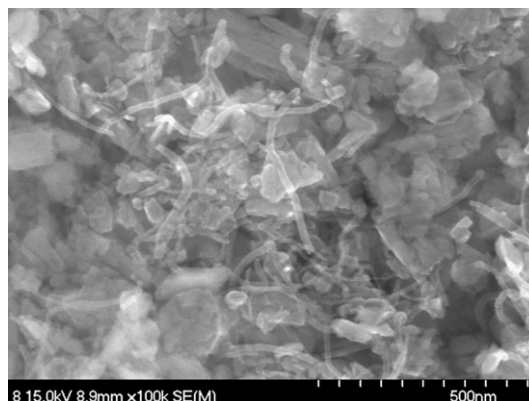


Fig. 2. The SEM image of LiFePO₄-MWCNTs composite.

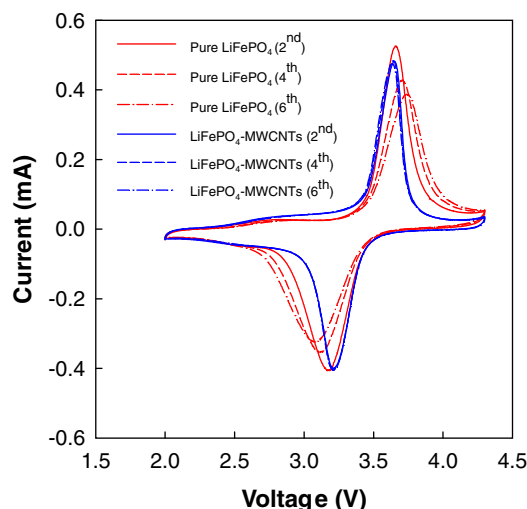


Fig. 3. The cyclic voltammograms of pure LiFePO₄ and LiFePO₄-MWCNTs composite at a scan rate of 0.1 mV/s.

0.48 V. However, in the case of LiFePO₄-MWCNTs composite, the oxidation and reduction peaks in the second cycle appear at around 3.64 and 3.2 V, respectively. The potential interval between two peaks is 0.44 V less than that of pure LiFePO₄. The redox peak profile of LiFePO₄-MWCNTs composite is more symmetric and spiculate than that of pure LiFePO₄, demonstrating that the reversibility and reactivity of LiFePO₄-MWCNTs composite are enhanced due to improvement of electronic conductivity and the reduced diffusion length resulting from a decrease in the crystallite size by MWCNTs.

Fig. 4 shows (a) the cycling performance of pure LiFePO₄, pure LiFePO₄ with ball-milling and LiFePO₄-MWCNTs composite and (b) the relationship between capacity and discharge rate of pure LiFePO₄ and LiFePO₄-MWCNTs composite. The discharge capacity of pure LiFePO₄ after 1 cycle is 111 mAh/g, and decreases to 96 mAh/g after 30 cycles. For pure LiFePO₄ with ball-milling, the discharge capacity after 1 cycle is 110 mAh/g, and decreases to 99 mAh/g after 7 cycles, and subsequently retains the stable discharge capacity. However, LiFePO₄-MWCNTs composite displays more stable discharge capacity retention than pure LiFePO₄ and pure LiFePO₄ with ball-milling until 30 cycles and the discharge capacity is 115 mAh/g. In conclusion, the improvement of pure LiFePO₄ is due to MWCNTs and not ball-milling. Fig. 4b demonstrates that high-rate capability of LiFePO₄-MWCNTs composite

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