

Effect of multi-walled carbon nanotubes on the electrochemical performance of LiVPO_4F cathode material for rechargeable lithium-ion batteries

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ABSTRACT

A novel network cathode material for lithium-ion batteries, pristine and multi-walled carbon nanotubes modified LiVPO_4F composites have been successfully synthesized via a microwave assisted sol–gel route. The crystal-line structure and morphology of as-synthesized samples are investigated systematically by X-ray diffraction, scanning electron microscopy, and transmission electron microscopy. Their electrochemical performances are also studied and compared in detail. The achieved results indicate that the multi-walled carbon nanotube modified LiVPO_4F sample has excellent C-rate performance, and delivered discharge capacities of 137.6, 131.2, 120.5 and 108.9 mAh g^{-1} at 0.5, 1, 2 and 5 C in the voltage range of 3.0–4.5 V at room temperature, respectively. Moreover, the capacity retention is 96.2% with the discharge capacity of 132.4 mAh g^{-1} at 0.5 C after 100 cycles. Electrochemical impedance spectroscopy results reveal that the charge-transfer resistance of multi-walled carbon nanotube modified LiVPO_4F is much smaller than that of the pristine LiVPO_4F . The outstanding features are desirable and enable the multi-walled carbon nanotube modified LiVPO_4F to be an excellent cathode material for lithium-ion batteries.

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1. Introduction

Lithium-ion batteries with both high energy and high power densities are essential to electric vehicles and hybrid electric vehicles. Cathode material is one of the crucial factors that determine the performance of lithium-ion batteries; therefore it is the key to developing high-performance cathode materials. Nowadays, LiCoO_2 , LiMn_2O_4 , $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, LiFePO_4 and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ [1–7] are the main cathode materials. However, each of the materials has its own shortcoming which limits its wide use in lithium-ion batteries.

Recently, a new fluorophosphate cathode material, LiVPO_4F , has been firstly proposed by Barker et al. [8,9]. It promises to deliver good rate capability, long cycle life, safety, high energy density and high voltage in lithium-ion batteries. LiVPO_4F is isostructural with the naturally-occurring mineral tavorite, $\text{LiFePO}_4 \cdot \text{OH}$ [10] or ambylgonite, LiAlPO_4F [11], crystallizing with a triclinic structure (space group $\text{P}\bar{1}$). The reversible Li extraction/insertion reaction for $\text{Li}_{1-x}\text{VPO}_4\text{F}$, based on the $\text{V}^{3+/4+}$ redox couple, operates at about 4.2 V versus Li. Besides, the thermal stability of LiVPO_4F is better than that of oxide-based cathode materials, such as LiMn_2O_4 , LiNiO_2 and LiCoO_2 [9]. Usually, LiVPO_4F was synthesized by conventional two-step solid state reactions [12,13]

and sol–gel method [14,15]. Moreover, microwave solid-state route as a novel method has been successfully employed in the preparation of electrode materials for lithium-ion batteries [16]. Different from the conventional solid state synthesis by sintering the target materials from the surfaces to inners, microwave heats the material at the molecular level, leading to a uniform heating distribution [17]. In our experiment, we combine the sol–gel and microwave solid-state method to synthesize the multi-walled carbon nanotube modified LiVPO_4F cathode.

However, the pristine LiVPO_4F has poor electronic conductivity, like LiFePO_4 [18], which presents a major drawback to practical implementation. Tremendous effort has been devoted to improve the electrochemical performance of LiVPO_4F . Carbon coating [19,20] is considered an excellent alternative because of the enhanced electronic conductivity between LiVPO_4F particles. Nevertheless, high carbon content may inhibit the Li^+ ion diffusion through the carbon layers and reduce the tap density of active materials. Recently, carbon nanotube is taken as a novel carbon source showing exceptional electronic and mechanical properties [21], which may be attributed to the high specific surface area and good conductivity. Furthermore, the carbon nanotube also provides a direct path for Li^+ ion transport to improve its electrochemical properties [22]. Recently, there are a lot of reports about using the multi-walled carbon nanotubes as the carbon source to improve its performance in the material of LiCoO_2 [23], LiFePO_4 [24] and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ [25]. So far, the effect of multi-walled carbon nanotube doping on the

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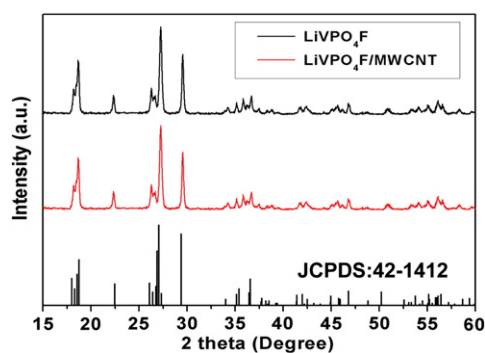


Fig. 1. X-ray diffraction patterns of (a) pristine and (b) multi-walled carbon nanotubes modified LiVPO₄F samples synthesized under the same route.

electrochemical performance of LiVPO₄F has not been reported. Therefore, this paper is focused on the study of LiVPO₄F modified with multi-walled carbon nanotubes on the electrochemical performance of lithium-ion batteries.

In this work, the multi-walled carbon nanotube modified LiVPO₄F was synthesized via a microwave assisted sol–gel method. The effects of multi-walled carbon nanotube doping on the crystalline structure, morphology and electrochemical performance of LiVPO₄F are studied in detail.

2. Experimental

The multi-walled carbon nanotube modified LiVPO₄F cathode material was synthesized via a microwave assisted sol–gel method, using V₂O₅, H₃PO₄, LiF, citric acid and multi-walled carbon nanotubes as the raw materials. Firstly, the V₂O₅·nH₂O hydro-gel was prepared. The stoichiometric H₃PO₄, LiF and excess citric acid (reducing agent) were added to the V₂O₅·nH₂O hydro-gel with constant intensive stirring at room temperature for 5 h and then at 70 °C. In order to prevent the

multi-walled carbon nanotubes from aggregating, the multi-walled carbon nanotubes were added until there was a small amount of water. Secondly, the mixture was dried to evaporate the liquid, and then the resulting product was calcined at 600 °C for 5 min in flowing N₂ using a microwave tube furnace. Finally, the sample was cooled to room temperature in the microwave oven. The pristine LiVPO₄F was also synthesized for comparison through the same method.

The crystalline structure of as-prepared samples were analyzed by X-ray diffraction (Phillips, PW1700) with scanning steps of 0.02 over the range from 15 to 60 (2θ). Scanning electron microscopy (JEOL JSM-6510) was used to investigate the particle morphology. The nano-scale microstructure of the multi-walled carbon nanotube modified LiVPO₄F sample was examined by transmission electron microscopy (JEM-2010, JEOL). Carbon contents of the samples were measured by elemental analyzer (Vario EL III, Elementar).

Electrochemical measurements were carried out with CR2032 coin cells. The cathode was prepared by mixing 85 wt.% active material with 10 wt.% conductive carbon black and 5 wt.% poly (vinylidene fluoride) in a N-methyl-2-pyrrolidone solvent, which was then applied onto an etched aluminum foil current collector and dried at 120 °C for 12 h in an oven. Lithium metal was used as the anode and Celgard 2300 film was used as the separator. The electrolyte implemented was 1 M LiPF₆ in a mixture of ethylene carbonate and dimethyl carbonate (1:1, volume). The cells were finally assembled in a glove box filled with argon gas. In describing batteries, charge and discharge current is often expressed as a C-rate. A C-rate is a measure of the rate at which a battery is discharged relative to its maximum capacity. Charge/discharge tests were performed between 3.0 and 4.5 V (versus Li/Li⁺) with a land CT2001 tester (Wuhan Land Electronic Co. Ltd., China) with different current densities. The charge and discharge capacity was calculated according to the LiVPO₄F based capacity. Electrochemical impedance spectroscopy was also performed on an electrochemical working station (Princeton, United States) with the frequency range from 0.01 Hz to 100 kHz. All the electrochemical measurements were carried out at room temperature (25 °C).

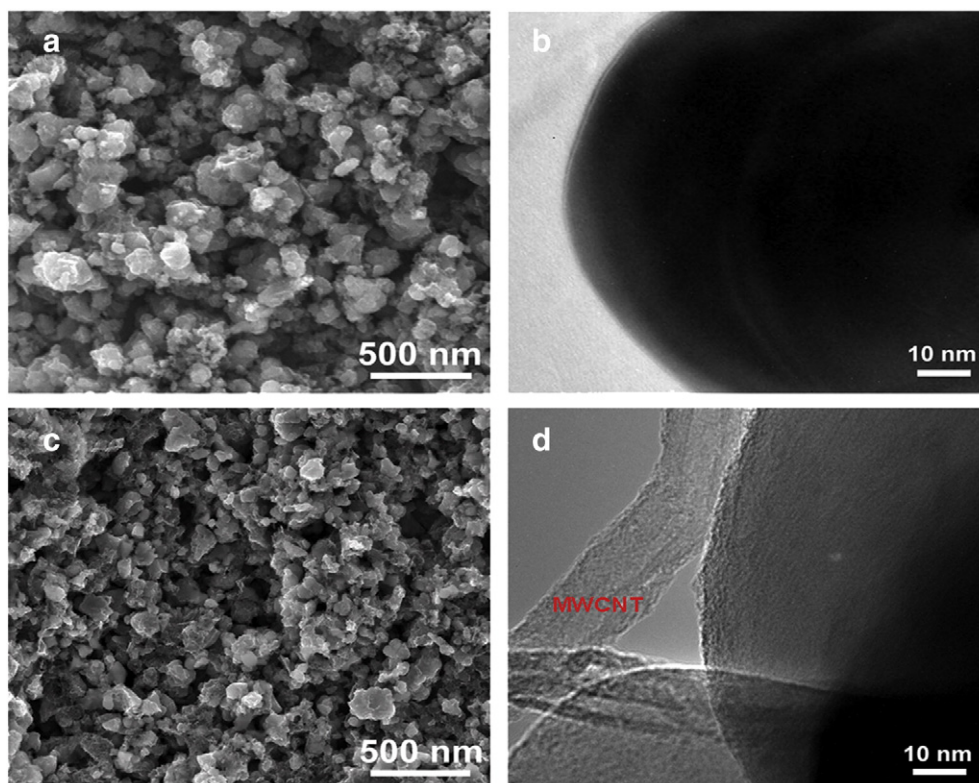


Fig. 2. Scanning electron microscopy and transmission electron microscopy images of pristine sample (a) and (b), and multi-walled carbon nanotube modified sample (c) and (d).

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