One-pot synthesis of FePO$_4$·H$_2$O/carbon nanotube coaxial nanocomposite for high rate lithium ion batteries

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**ABSTRACT**

We developed an environmentally friendly, one-pot, solution-based method to synthesize a FePO$_4$·H$_2$O/carbon nanotube coaxial nanocomposite for lithium ion battery applications without using multi-step, time-consuming processes or hazardous reaction media. The resulting nanocomposite delivered a discharge capacity of 157 mAh g$^{-1}$ at a current density of 12.5 mA g$^{-1}$, 123 mAh g$^{-1}$ at 3750 mA g$^{-1}$ and 61 mAh g$^{-1}$ at 15,000 mA g$^{-1}$ (around 94 °C). This approach suggests eco-friendly synthesis of eco-friendly materials with excellent electrochemical performance, in the true sense of the word, since the synthesis process is environmentally benign as well as material itself.

**1. Introduction**

Phosphate materials ((Li)$_x$M$_y$(PO$_4$)$_z$, M = Fe, Mn, Co, Ni, V) have been considered as promising cathode materials for lithium ion batteries because of their high specific capacity (≥ 170 mAh g$^{-1}$) compared to the conventional cathode material (LiCoO$_2$, 145 mAh g$^{-1}$) [1–3]. Among them, LiFePO$_4$ has received the greatest attention due to its excellent structural stability, lack of toxicity, and environmental benignity [4–6]. Due to the similar advantages of the LiFePO$_4$, amorphous FePO$_4$·nH$_2$O (0 ≤ n ≤ 4) has been actively investigated as a potential cathode material [7–11]. Amorphous FePO$_4$·nH$_2$O provides a high charge–discharge capacity of 178 mAh g$^{-1}$ in its dehydrated state. However, it shows a poor rate capability due to its low electronic conductivity and lithium diffusion rate [8–11].

Recently, nanocomposites composed of FePO$_4$·nH$_2$O and nano-carbon such as carbon nanotube (CNT) and graphene have been investigated to improve the rate capability using bio-templating [8,9], mineralization [10] and precipitation [11] methods. Nano-carbons used in the preparation of such nanocomposites effectively increased the electronic conductivity of the electrode, thereby enhancing the high rate capability. In particular, amorphous FePO$_4$·nH$_2$O/graphene hybrid could deliver around 100 mAh g$^{-1}$ at a current density of 2500 mA g$^{-1}$ [11]. However, the fabrication of these nanocomposites requires multi-step, time-consuming processes or toxic organic solvents, such as strong acid or base, leading to potential environmental issues. Therefore, it is highly desirable to prepare FePO$_4$·nH$_2$O/nano-carbon composites with improved high rate capability using a simple and environmentally benign synthesis process.

In an attempt to address these issues, we herein report the solution-based one-pot synthesis of FePO$_4$·H$_2$O/CNT coaxial nanocomposite via an environmentally friendly method. The resulting nanocomposite delivered a reversible discharge capacity of 157 mAh g$^{-1}$ at a current density of 12.5 mA g$^{-1}$, 123 mAh g$^{-1}$ at 3750 mA g$^{-1}$ and 61 mAh g$^{-1}$ at 15,000 mA g$^{-1}$ (around 94 °C). This approach suggests eco-friendly synthesis of eco-friendly materials with excellent electrochemical performance, in the true sense of the word, since the synthesis process is environmentally benign as well as material itself.

**2. Experimental**

FePO$_4$·nH$_2$O/CNT coaxial nanocomposite was synthesized by one-pot aqueous solution-based method. The CNT powder (0.4 g) (Hanwha Nanotech) was submerged in urea solution (1 M, 720 ml) (Aldrich) and sonicated in an ice bath for 30 min without any pre-treatment of CNT such as acid treatment to enhance wettability of the CNT into the aqueous solution. Non-oxidized CNT could be effectively dispersed in urea solution due to stronger dispersion interaction of CNT with hydrophobic CNT than water [12]. Then FeSO$_4$·7H$_2$O (0.75 M, 24 ml) (Aldrich), citric acid (0.25 M, 8 ml) (Junsei), and (NH$_4$)H$_2$PO$_4$ (0.75 M, 24 ml) (Aldrich) solution were added drop-by-drop sequentially with vigorous stirring. After the reaction at 60 °C for 3 h, the solution was washed with distilled water and then dried at 60 °C for 24 h. The as-synthesized FePO$_4$·nH$_2$O/CNT coaxial nanocomposite was annealed at 300 °C for 6 h to remove the hydrated water.

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**Keywords:**

FePO$_4$·H$_2$O

Carbon nanotube

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The obtained FePO₄·nH₂O/CNT coaxial nanocomposite was characterized by field emission electron microscopy (FE-SEM; Jeol, 6701F), and transmission electron microscopy (TEM; Philips, CM200). Thermogravimetric analysis (TGA; Mettler Toledo, TGA/DSC 1) was used to determine the amount of hydrated water and the loading amount of FePO₄·nH₂O in the FePO₄·nH₂O/CNT coaxial nanocomposite, which was measured in air at the heating rate of 10 °C min⁻¹ from room temperature to 800 °C.

The working electrodes were fabricated by mixing 95 wt.% of FePO₄·nH₂O/CNT coaxial nanocomposite and 5 wt.% of polyvinylidene fluoride (PVDF; Aldrich) dissolved in N-methylpyrrolidone (NMP; Aldrich) as a binder without using extra conducting additives. The slurry was coated on an Al foil, dried and then roll-pressed. The coating amount of the slurry was about 1.5 mg cm⁻². Cyclic voltammetry was carried out using a three-electrode cell with a working electrode and two lithium foils as counter and reference electrodes in a glove box filled with Ar. Galvanostatic charge–discharge behavior was measured using coin cells (2032), with lithium foil as the counter electrode. The electrochemical characterization was performed within a voltage range of 2.0–4.3 V using a potentiostat/galvanostat (MPG2, Bio-logic). Electrochemical impedance spectroscopy (EIS) measurements were performed using potentiostat/galvanostat (VMP2, Bio-logic) over the frequency range from 100 kHz to 10 mHz with an AC signal of 5 mV. The electrolyte was 1 M LiPF₆ dissolved in a mixed solvent of ethyl carbonate (EC) and dimethyl carbonate (DMC) at a volume ratio of 1:1.

3. Results and discussion

The SEM image of the FePO₄·nH₂O/CNT coaxial nanocomposite in Fig. 1a shows that the FePO₄·nH₂O was uniformly coated on the entire surface of the CNT through heterogeneous nucleation and growth without any trace of separate FePO₄·nH₂O particles away from the CNT. Homogeneous nucleation of the nanoparticles in the solution could be suppressed under a very small driving force for the homogeneous nucleation so as to induce a heterogeneous nucleation of the FePO₄·nH₂O on the surface of CNTs [13,14]. More specifically, oxidation rate of Fe²⁺ to Fe³⁺ in the presence of H₂PO₄⁻ ions was carefully controlled to suppress homogeneous nucleation of the FePO₄·nH₂O nanoparticles in the solution and to promote the selective heterogeneous nucleation of the FePO₄·nH₂O only on the surface of CNT. TEM image of the FePO₄·nH₂O/CNT nanocomposite in Fig. 1b conforms the coaxial nature of the nanocomposite. CNT is covered with an approximately 15 nm-thick FePO₄·nH₂O layer, which is identified as amorphous phase by X-ray diffraction pattern (data not shown). The amorphous nature of the FePO₄·nH₂O is critical to its electrochemical properties because the amorphous FePO₄·nH₂O is electrochemically active while the crystalline FePO₄·nH₂O is less active [15]. Fig. 1c shows a TEM image of the FePO₄·nH₂O/CNT nanocomposite under irradiation of focused electron beam. It is noteworthy that FePO₄·nH₂O layer shrank rapidly during the TEM observation with the appearance of small pores trapped in the layer. This suggests that the FePO₄·nH₂O/CNT coaxial nanocomposite in Fig. 1b had a porous structure due to the removal of hydrated water during the heat treatment.

The decrease in the amount of hydrated water during the post annealing was quantitatively analyzed by TGA curves as shown in Fig. 1d. The as-synthesized FePO₄·nH₂O/CNT coaxial nanocomposite exhibited a weight loss of about 15% up to 500 °C due to removal of the hydrated water. To determine the amount of hydrated water precisely, FePO₄·nH₂O nanoparticles prepared in the absence of CNT (inset) were analyzed. For the as-synthesized FePO₄·nH₂O, the hydrated water was determined to be 31.4 wt.%, equating to n=4. As for the FePO₄·nH₂O heat-treated at 300 °C, the remaining hydrated water was 10.6 wt.%, corresponding to n=1. It indicates that three-quarters of the water molecules were removed from the as-synthesized FePO₄·nH₂O nanoparticles.

Fig. 1. (a) SEM image of the FePO₄·H₂O/CNT coaxial nanocomposite, (b) TEM image of the FePO₄·H₂O/CNT coaxial nanocomposite, (c) TEM image of the FePO₄·H₂O/CNT coaxial nanocomposite under irradiation of focused electron beam, and (d) TGA curves for the as-synthesized and heat-treated FePO₄·nH₂O/CNT coaxial nanocomposite. The inset is TGA curves for as-synthesized and heat-treated FePO₄·nH₂O nanoparticles.
FePO₄·nH₂O, leading to the formation of porous structure in the FePO₄·H₂O layer during the heat treatment. Considering the theoretical capacity of 178 mAh g⁻¹ for FePO₄, and hydrated water content, the theoretical capacity of the FePO₄·H₂O was calculated as 159 mAh g⁻¹ [16]. The loading amount of the FePO₄·H₂O in the nanocomposite was measured to be 76.4 wt.% by TGA.

Fig. 2a shows cyclic voltamograms (CVs) of the FePO₄·H₂O/CNT coaxial nanocomposite with increasing potential scan rates from 0.5 to 20 mV s⁻¹. The CV at a scan rate of 0.5 mV s⁻¹ (inset) shows one broad oxidation peak ranging from 2.5 to 4 V and a reduction peak spreading from 2.2 to 3.8 V, which is in good agreement with that of FePO₄·nH₂O [17]. The CVs maintain peak-shaped profiles to the potential scan rate of 20 mV s⁻¹ without distortion. In addition, the increase in peak separation according to the scan rate is quite small, indicating the facile transport of Li ions through the porous FePO₄·H₂O layer and of electrons from the CNT. These results suggest the excellent high rate capability of the FePO₄·H₂O/CNT coaxial nanocomposite.

Fig. 2b shows the charge–discharge profiles of the FePO₄·H₂O/CNT coaxial nanocomposite at increasing current density from 12.5 to 15,000 mA g⁻¹. It displays sloping charge–discharge profiles, implying that FePO₄·H₂O exhibits solid-solution behavior during the insertion/extraction of lithium ions. The discharge capacity was 120 mAh g⁻¹ based on the weight of FePO₄·H₂O/CNT coaxial nanocomposite (top axis) at a current density of 12.5 mA g⁻¹. This corresponds to 157 mAh g⁻¹ based on the weight of FePO₄·H₂O (bottom axis), which is close to its theoretical capacity of 159 mAh g⁻¹. At increasing current densities, the FePO₄·H₂O/CNT coaxial nanocomposite exhibited excellent high rate capability, with a discharge capacity of 146, 123, and 92 mAh g⁻¹ at current densities of 625, 3750 and 7500 mA g⁻¹, respectively. Furthermore, it retained a discharge capacity of 61 mAh g⁻¹ at a current density as high as 15,000 mA g⁻¹. It should be noted that FePO₄·H₂O in the nanocomposite exhibited a higher discharge capacity than the anhydrous FePO₄ reported in the literature at increasing current density, although the theoretical capacity of FePO₄·H₂O is smaller than that of FePO₄ (159 mAh g⁻¹ for FePO₄·H₂O, 178 mAh g⁻¹ for FePO₄) [11,16]. This excellent high rate capability could be attributed to the nanometer-thick FePO₄·H₂O layer, which shortens the travel length of both Li ions and electrons, that was in direct and intimate contact with CNT, thus enabling fast electron transfer. Furthermore, the porous nature of the FePO₄·H₂O coating layer could facilitate accessibility of the electrolyte.

Fig. 2c compares the high rate capability of the FePO₄·H₂O/CNT coaxial nanocomposite and the mixture of FePO₄·H₂O nanoparticles and CNT. The FePO₄·H₂O–CNT mixture electrode was fabricated with the same amount of CNT as that used in the FePO₄·H₂O/CNT coaxial nanocomposite. The FePO₄·H₂O–CNT mixture showed a capacity of 110 mAh g⁻¹ based on the weight of FePO₄·H₂O at a current density of 12.5 mA g⁻¹ and lost most of its capacity at a current density of 3750 mA g⁻¹. This was attributed to the limited contact of the FePO₄·H₂O nanoparticles with the mixed CNT, resulting in poor specific capacity and rate performance. On the contrary, the nanocomposite could deliver a discharge capacity of 123 mAh g⁻¹ based on the weight of FePO₄·H₂O at a current density of 3750 mA g⁻¹, 92 mAh g⁻¹ at 7500 mA g⁻¹, and 61 mAh g⁻¹ at a current density as high as 15,000 mA g⁻¹. The best reported capacity for the FePO₄·nH₂O was...
FePO₄/graphene hybrid, which could deliver the specific capacity of around 100 mAh g⁻¹ at 2500 mA g⁻¹ [11]. To the best of our knowledge, the FePO₄·H₂O/CNT coaxial nanocomposite prepared in this study showed the best rate performance among FePO₄·nH₂O/nano-carbon composite materials reported in the literature.

The excellent rate performance is further supported by the result of the EIS measurement, as shown in Fig. 2d. The impedance spectra has been explained on the basis of an equivalent circuit (inset) composed of uncompensated resistance (R₀), parallel elements relating to the solid–electrolyte interface, electrode roughness and inhomogeneous reaction at the electrode surface (C₁, R₁), and charge transfer resistance (Rct), double layer capacitance (Cdl), and Warburg impedance (ZW) [18]. The FePO₄·H₂O/CNT coaxial nanocomposite shows a single semicircle in the high and medium frequency region (inset) while the FePO₄·H₂O–CNT mixture shows two semicircles. Compared to the mixture, the coaxial nanocomposite exhibited negligible impedance of the parallel elements originated from the inhomogeneous reaction, through the wiring up of the FePO₄·H₂O with CNT. In addition, the coaxial nanocomposite displayed a significant decrease in charge transfer resistance compared to the mixture because of enhanced electronic conductivity afforded by the direct and intimate contact of FePO₄·H₂O and conductive CNT.

4. Conclusion

We developed one-pot synthesis of FePO₄·H₂O/CNT coaxial nanocomposite via solution-based method without any hazardous reaction media. Nanometer-thick FePO₄·H₂O with a porous structure was uniformly coated along the surface of CNT, forming a coaxial nanocomposite. The nanocomposite exhibited high capacity close to its theoretical capacity and excellent high rate capability due to the high conductivity of the nanocomposite, which was attributed to the intimate contact between nano-structured FePO₄·H₂O and CNT, and to easy access of electrolyte due to the porous structure of FePO₄·H₂O. We demonstrated the effectiveness of this proposed approach for improving high rate capability of the insulating materials by forming a composite with conductive phases through a simple and environmentally friendly synthesis method.

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References