



Homogeneous precipitation synthesis and electrochemical performance of LiFePO₄/CNTs/C composite as advanced cathode materials for lithium ion batteries

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Homogeneous precipitation synthesis and electrochemical performance of $\text{LiFePO}_4/\text{CNTs}/\text{C}$ composite as advanced cathode materials for lithium ion batteries

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In this study, a series of $\text{LiFePO}_4/\text{CNTs}/\text{C}$ composite cathode materials for Li-ion batteries were synthesized by a simple homogeneous precipitation and subsequent annealing process. The investigation of the influence of CNTs on the structural and electrochemical characteristics of $\text{LiFePO}_4/\text{CNTs}/\text{C}$ composites shows that the resulting composite material exhibits smaller particle size, lower electron-transfer resistance, and faster lithium ion migration, which are attributed to improve lithium ion transfer by CNT incorporating. At 1C, the $\text{LiFePO}_4/\text{CNTs}/\text{C}$ composite delivers a stable specific capacity of $\sim 126 \text{ mAh g}^{-1}$ after 500 cycles. At high rates (e.g. 10C), the CNT-incorporated composite is still able to deliver stable capacities of up to $\sim 119 \text{ mAh g}^{-1}$, which is $\sim 42\%$ greater than its pristine counterpart.

Keywords: LiFePO_4 , CNTs, Composite, Homogeneous precipitation, Li-ion batteries

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1. Introduction

As an energy storage device, Lithium ion batteries (LIBs) have been widely used in wireless telephones, digital cameras, laptop computers, and other electronic devices since they were first introduced in the 1990s. Recently, the application of LIB technology in electrical energy storage systems for smart grids that are powered by conventional energy sources such as coal, as well as intermittent renewable energy sources such as solar and wind, has attracted considerable attention¹⁻³.

In the present LIB market, any Li-ion cathode needs to satisfy the demands of high energy density, fast charging capability, long shelf-life and safety. To address these requirements, great efforts have been made to develop phosphate-based cathodes because the strongly covalent $(\text{PO}_4)^{3-}$ units provide greater structural stability than commercial LiCoO_2 hosts even under deep charging conditions and elevated temperatures⁴⁻⁷.

Among the known phosphates, olivine LiFePO_4 cathode materials are being commercialized due to their low toxicity, low cost, long cycle life and safety. Although the theoretical specific capacity of LiFePO_4 is $\sim 170 \text{ mAh g}^{-1}$, its poor rate capability prevents its use in high power applications. Improvements in rate capability have been achieved by enhancing the low electronic conductivity and reported in many research literature, including carbon coating, doping with a conducting metal ion and particle-size control⁸⁻¹⁹. Many kinds of carbon materials (e.g. acetylene black, CNTs, graphene) are used to increase the electronic conductivity of LiFePO_4 . Larger amounts of carbon materials will increase rate capability and reduce volumetric

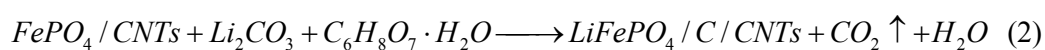
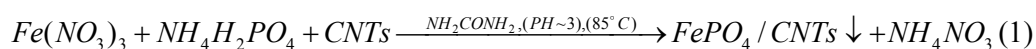
energy density of the cathode^{18, 20-26}. However, the amount and structure of carbon content will strongly influence the electronic conductivity of LiFePO₄/C composite materials. Therefore, to avoid decreasing the volumetric energy density, the amount of carbon should be kept low and more efficient in the industrial applications.

We report here a simple homogeneous precipitation method^[27-29] for obtaining LiFePO₄/C/CNTs composite with small amount of CNTs and carbon source by (i) homogeneous precipitation of Fe(NO₃)₃ in a suspension of CNTs using urea and (ii) subsequent annealing the mixture of the precursors, lithium carbonate (Li₂CO₃), and citric acid at 700 °C for 10 h under a nitrogen atmosphere. As an cathode material for Li-ion batteries, the LiFePO₄/C/CNTs composite exhibited a continuous and dispersive nano-carbon network which show the high electronic conductivity and rate capability. Our method of synthesis presents a promising route for large scale production of LiFePO₄/C/CNTs composites as electrode materials for Li-ion batteries.

2. Experimental

The LiFePO₄/C/CNTs cathode materials were synthesized by homogeneous precipitation of Fe(NO₃)₃ in a suspension of CNTs using urea and a subsequent annealing process. Small amount of citric acid was used as both chelating agent and carbon source which used as reductant for iron ions and provides the networked structure of carbon for electronic conduction. All chemicals used in this paper were of analytical grade without any pretreatment.

First, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, soluble CNTs, NH_2CONH_2 and $\text{NH}_4\text{H}_2\text{PO}_4$ were mixed uniformly and dissolved in deionized water with continuous magnetic stirring for ~6 hours at ~85 °C under pH = ~3, then the precipitates were obtained (Equation 1). Subsequently, the precipitates was washed with water and dried in an oven at ~120 °C for ~3h. Afterward, the as-prepared precursor together with the lithium carbonate (Li_2CO_3), citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$) in the molar ratio of 1:0.5:0.1 was mixed in a moderate amount ethanol and ground by ball-milling for 6h, then pre-sintered at $\square 400$ °C for $\square 5$ h in a flowing N_2 atmosphere. This allowed the formation and release of H_2O and NH_3 as well as CO_2 associated with the decomposition of organic components. Finally, the obtained precursor was carefully grounded after cooling to room temperature, and was calcined at ~700 °C for ~10 hours to to yield the $\text{LiFePO}_4/\text{CNTs}/\text{C}$ composite (Equation 2).



The crystalline structural characterization of the samples was carried out by X-ray diffraction (XRD) using a diffractometer (Bruker D8 Focus X-ray diffractometer), and the diffraction patterns were recorded at room temperature in the 2θ range between ~10° and ~80°. The morphology and particle sizes of the powders were characterized under a scanning electron microscope (SEM, FEI Quanta200F) and transmission electron microscope (TEM, FEI Tecnai G2 F20, 200 kV).

Electrochemical properties were evaluated with model CR2025 coin-type cell. Cycling and galvanostatic charge–discharge performance of the two-electrode

electrochemical cells were tested on a multi-channel battery test system (Xinwei, Shenzhen, China), while cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were performed on an electrochemical workstation (PARSTAT 2273, Princeton, USA). For the two-electrode coin battery cell, a lithium metal foil of about 0.3 mm in thickness was used as the anode, and the cathode electrode was prepared as follows: The as-prepared powders, acetylene black and polyvinylidene fluoride (PVDF) binder in a weight ratio of 80:10:10 were mixed in N-methyl-2-pyrrolidone (NMP) to create a slurry. The resulting slurry was coated on an Al current collector with a thickness of $\approx 75 \mu\text{m}$. The cathodes were dried in a vacuum furnace at $\sim 65^\circ\text{C}$ for ≈ 20 h, following which they were roll-pressed at a pressure of ≈ 15 MPa. Circular electrodes (12 mm in diameter) were then punched out. We measured the average weight of several pure aluminum sheets (12 mm in diameter), and the weight of the dry Al current collector (sheets) of the same size coated with the cathode materials. Then we computed the mass of the cathode materials by subtraction. The typical weight of the cathode ranged between ≈ 7 and 8 mg. Finally, the cathode was dried again in a vacuum oven at $\approx 100^\circ\text{C}$ for ≈ 48 h prior to assembly. The cells were assembled in a high purity argon atmosphere inside a glove box (Mbraunlab Master130, Germany). Celgard[®] 2325 was used as the separator and the electrolyte was a solution of 1 M LiPF_6 dissolved in a mixture of ethylene carbonate (EC):dimethyl carbonate (DMC) (1:1 vol.%).

3. Result and Discussion

The XRD experiments were conducted to examine the structural changes of LiFePO₄/C/CNTs composites by incorporation of various amounts of CNT ($x = 0, 1\%, 3\%, 5\%$). As shown in Fig. 1, the LiFePO₄/C/CNTs composites retained the single phase of LiFePO₄. All fundamental peaks could be indexed to the typical olivine structure of LiFePO₄ (PDF No.83-2092) and no impurity was revealed^[30], which indicates that the incorporation of CNTs did not change the basic crystal structure of LiFePO₄. Therefore we expect that CNTs would provide the network structure together with the coated carbon for electronic conduction. Furthermore, the crystallinity of LiFePO₄ is maintained even after CNTs involved. This factor is critical as high crystallinity has the potential to significantly improve the cycling stability of the cathode^[31, 32].

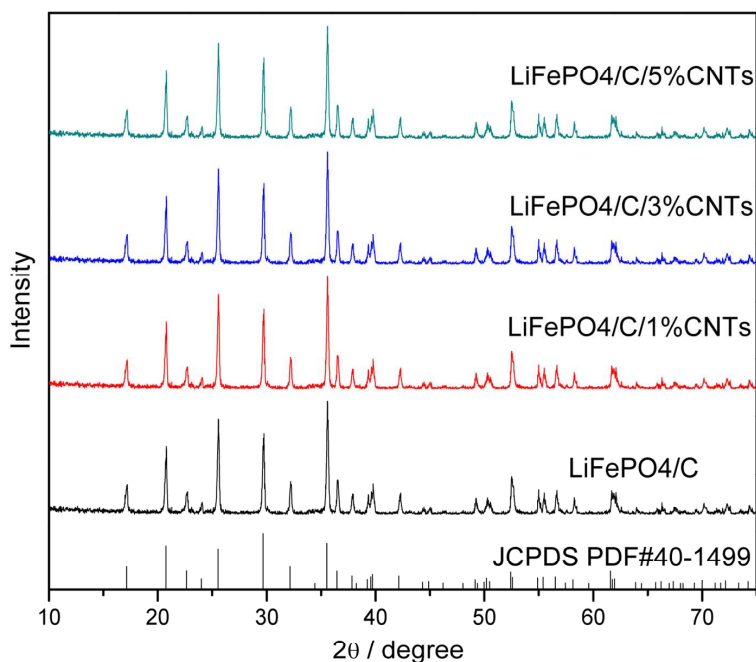


Figure 1. X-ray diffraction patterns of $\text{LiFePO}_4/\text{CNTs}/\text{C}$ composites: the amount of CNTs= 0 (a); 1wt% (b); 3 wt% (c); 5 wt% (d).

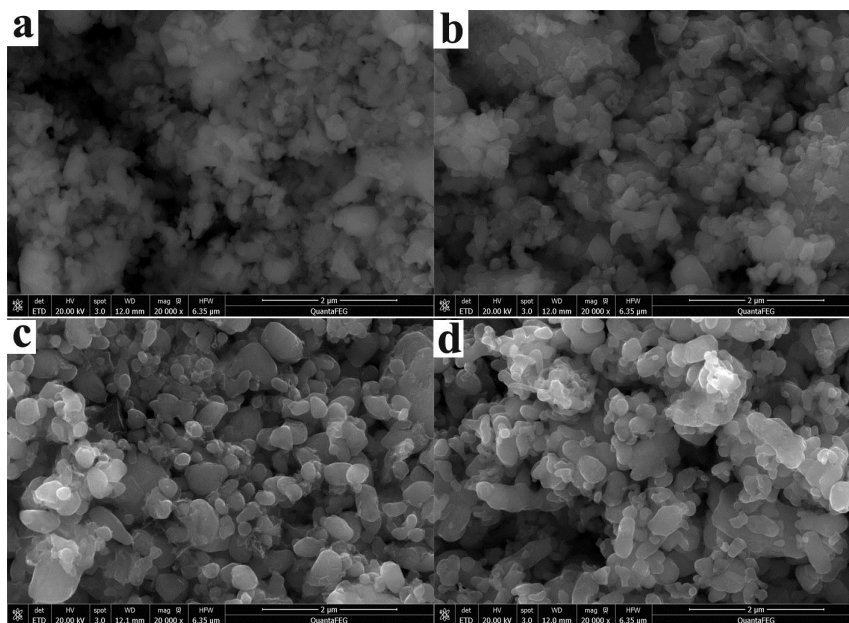


Figure 2. SEM images of $\text{LiFePO}_4/\text{CNTs}/\text{C}$ composites: the amount of CNTs= 0 (a); 1wt% (b); 3 wt% (c); 5 wt% (d).

The SEM images of CNTs and pristine LiFePO_4/C composites are shown in Fig. 2(a-d), respectively. From SEM observations, the LiFePO_4/C sample shows a flake-like morphology, the particles are about $1\ \mu\text{m}$ in diameter and slightly agglomerated with each other as shown in Fig. 2(a) while the size of $\text{LiFePO}_4/\text{C}/\text{CNTs}$ composites (the amount of CNTs = 1 wt%, 3 wt%, 5 wt%) particles is smaller and more uniform compared to the baseline with diameters of less than 500 nm as indicated in Fig. 2(b-d). It indicates that the addition of CNTs influences the geometry and shape of the particles. This result is similar to what has been reported previously^[24]. Among the CNTs incorporated samples, the LiFePO_4/C composite (3

wt% CNTs) has the smallest particle size (i.e. highest specific surface area) and a uniform morphology; we expect that such a microstructure will facilitate the penetration of the electrolyte ensuring better wettability and thereby shortening the diffusion distance of lithium ions from the cathode bulk phase to the electrolyte^[33-35].

The image of TEM and HRTEM of the LiFePO₄/C composite (3 wt% CNTs) is shown in Fig. 3(a-d). From the TEM observation, the morphology and particle size of all the samples were found to be consistent with the SEM imaging shown in the previous figure. As compared to the smooth surface of pure LiFePO₄, it can be seen that the thickness of the amorphous carbon layer is about ~5 nm on the surface of the LiFePO₄ grains (Fig. 3c). The lattice fringes with widths of 0.40 nm and 0.35 nm correspond to the (-210) and (111) plane of LiFePO₄, and the (-210) and (111) axes are also indicated in Figure 3c (inset). The same pattern can be observed for all the particles. Then, CNTs would form the network structure together with the coated carbon in the composites, as shown in Fig.3d. CNTs have outstanding electrical conductivity due to their special graphite wall structure. Such a conductive carbon network could provide good grain-to-grain electronic contact, thereby reducing the grain-to-grain electrical contact resistance leading to an improvement in electrochemical properties.

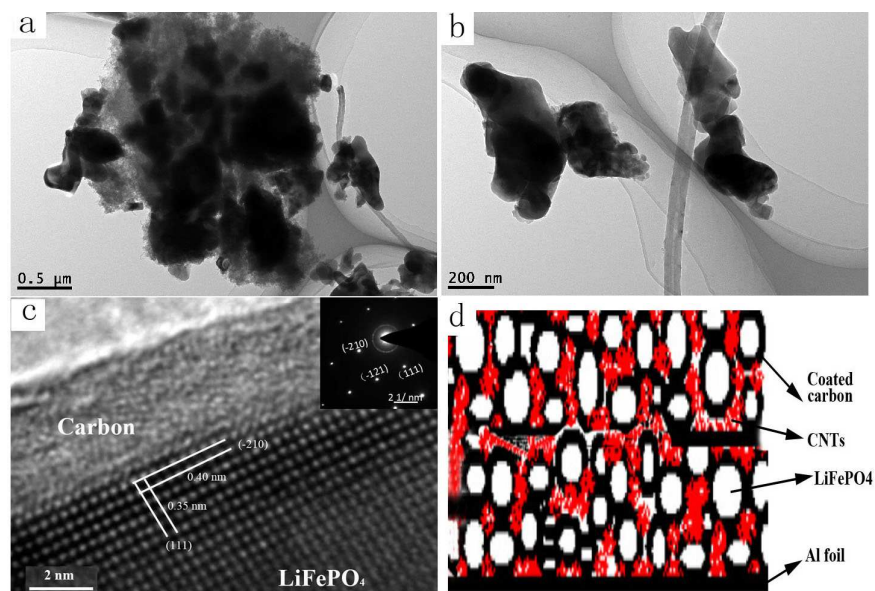


Fig. 3 The image of TEM and HRTEM of $\text{LiFePO}_4/\text{C}/3 \text{ wt}\%$ CNTs composites (a-c); The SAED pattern of LiFePO_4 particles (c, inset); Figure Schematic diagram of the structure for $\text{LiFePO}_4/\text{C}/\text{CNTs}$ composite at the anode (d).

The initial charge-discharge curves of $\text{LiFePO}_4/\text{C}/\text{CNTs}$ samples (the amount of CNTs = 0, ~1 wt%, ~3 wt%, ~5 wt%) at a charge/discharge rate (C-rate) of ~0.1C in the voltage range of ~2.0–4.2 V are presented in Figure 4a. As can be seen in Fig. 4a, almost all the samples obtained exhibit stable voltage plateaus at around ~3.45 V in the charge process, and at around ~3.35 V in the discharge process, which correspond to a phase transition processes in LiFePO_4 [36]. It can also be seen that the initial discharge capacities of $\text{LiFePO}_4/\text{C}/\text{CNTs}$ composites depend on the CNTs amounts. It is found that the charge specific capacities of $\text{LiFePO}_4/\text{C}/\text{CNTs}$ (the amount of CNTs = 0, 1 wt%, 3 wt%, 5 wt%) are about ~154.3, ~155.7, ~160.8 and ~156.1, mAh g^{-1} , respectively, and the corresponding coulombic efficiencies are ~93%, ~97%, ~97%, and ~94%, respectively. Furthermore, it is found that $\text{LiFePO}_4/\text{CNTs}/\text{C}$ composites

exhibits a smaller potential difference between charge and discharge curve. The high coulombic efficiencies are indicative of reversible phase transformations in LiFePO_4 associated with lithiation and delithiation steps, thereby ensuring repeatability and reversibility upon successive cycling^[31]. However, it is clearly observed that the discharge specific capacity is enhanced considerably when the CNTs amount is $\sim 3\text{wt}\%$. The high discharge capacity of $\text{LiFePO}_4/\text{C}/\text{CNTs}$ can be attributed to the decrease of grain size and improved homogeneity as shown in Figs. 2 and 3.

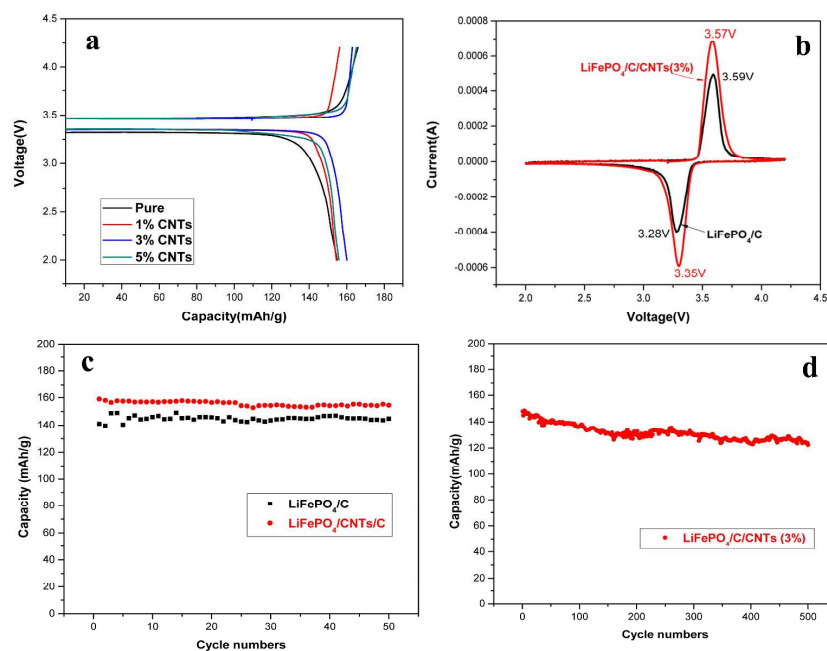


Fig. 4 (a), Charge-discharge tests for LiFePO_4 composite samples at 0.1C; (b) Cyclic voltammetry of LiFePO_4/C and $\text{LiFePO}_4/\text{C}/\text{CNTs}$; The cycle performance of LiFePO_4 composites at 0.1C (c) and 1C (d).

The electrode reaction reversibility of LiFePO_4 can also be investigated by the cyclic voltammetry curve. Figure 4b shows the cyclic voltammetry of LiFePO_4/C composite and $\text{LiFePO}_4/\text{CNTs}/\text{C}$ composite ($\sim 3\%$ CNTs) in the second cycle at $\sim 0.1\text{mV/s}$ between 2.0 and 4.2V. A pair of redox peaks and the sharp peaks appears in the curves

for the two samples. The anodic and cathodic peaks are equivalent to the two-phase charge and discharge reaction of the $\text{FePO}_4/\text{LiFePO}_4$ redox couple. For LiFePO_4/C composite, the oxidation and reduction peaks appear at $\sim 3.28\text{V}$ and $\sim 3.59\text{V}$ and the potential interval between the two peaks is $\sim 0.31\text{V}$. For $\text{LiFePO}_4/\text{CNTs}/\text{C}$ composite, the oxidation and reduction peaks appear at $\sim 3.35\text{V}$ and $\sim 3.57\text{V}$, the potential interval between the two peaks is $\sim 0.22\text{V}$. The less potential interval indicates that $\text{LiFePO}_4/3\%\text{CNTs}/\text{C}$ shows a better electrode reaction reversibility. The peak profiles of $\text{LiFePO}_4/\text{CNTs}/\text{C}$ composite are more symmetric and it demonstrates a smaller conductivity restriction than that of LiFePO_4/C ^[37-38].

The electrochemical cycling performance of pristine and $\text{LiFePO}_4/\sim 3\text{wt}\%\text{CNTs}/\text{C}$ samples at room temperature and at $\sim 0.1\text{C}$ rate is shown in Fig. 4c. As observed from Fig. 4c, the specific capacities of LiFePO_4/C and $\text{LiFePO}_4/\text{C}/\sim 3\text{wt}\%\text{CNTs}$ composites display excellent capacity retention ($\sim 100\%$) with cycle index. When the C-rate increases to $\sim 1\text{C}$, as shown in Fig 4d, the discharge specific capacity of $\text{LiFePO}_4/\text{C}/\sim 3\%\text{CNTs}$ composites still shows the excellent capacity retention, and the discharge specific capacities can still keep about $\sim 126\text{mAh g}^{-1}$ after 500 cycles. These results indicate that the cycling stability of LiFePO_4 can be significantly enhanced by incorporating with optimal amount of CNTs ($\sim 3\text{wt}\%$). This improved cycling stability can be attributed to the olive structure of LiFePO_4 stabilized by CNTs.

The rate performance of the LiFePO_4/C composites and $\text{LiFePO}_4/\sim 3\text{wt}\%\text{CNTs}/\text{C}$ composites is compared in Fig. 5a. For the LiFePO_4/C sample, a specific capacity of $\sim 138.2\text{mAh g}^{-1}$ is obtained at $\sim 1\text{C}$ rate. The specific capacity drops to $\sim 94\%$ of this

value when the operating C-rate is increased to $\sim 2C$. The $\text{LiFePO}_4/\sim 3\text{wt}\%\text{CNTs}/\text{C}$ composite delivers $\sim 149.4 \text{ mAh g}^{-1}$ at $1C$ rate and retains a capacity of $\sim 143.0 \text{ mAh g}^{-1}$ ($\sim 96\%$) when the C-rate is increased from $\sim 1C$ to $\sim 2C$. However when the rate is increased from $\sim 5C$ to $\sim 10C$, there is a significant difference in the specific capacity between the LiFePO_4/C and $\text{LiFePO}_4/\sim 3\text{wt}\%\text{CNTs}/\text{C}$ samples. The specific discharge capacity is $\sim 119.8 \text{ mAh g}^{-1}$ ($\sim 82\%$) for the $\text{LiFePO}_4/\sim 3\text{wt}\%\text{CNTs}/\text{C}$ composite, while the pristine LiFePO_4/C only shows a specific capacity of $\sim 84.0 \text{ mAh g}^{-1}$ ($\sim 61\%$) when the C-rate is $\sim 10C$. Faster lithium ion migration and more uniform particle distribution via the homogeneous precipitation method are responsible for the obtained high-rate performance after the $\sim 3\text{wt}\%$ CNTs incorporated.

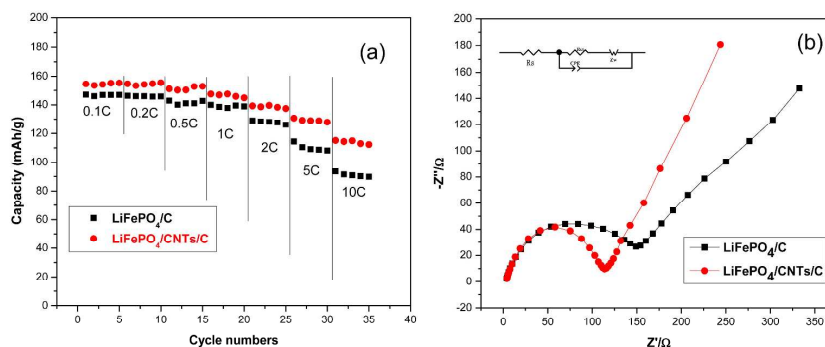


Figure 5. (a) Rate performance of LiFePO_4/C and $\text{LiFePO}_4/\sim 3\text{wt}\%\text{CNTs}/\text{C}$ composites, (b) Electrochemical impedance curves of LiFePO_4/C and $\text{LiFePO}_4/\sim 3\text{wt}\%\text{CNTs}/\text{C}$ composites.

In order to better understand the kinetics of the LiFePO_4/C and $\text{LiFePO}_4/\sim 3\text{wt}\%\text{CNTs}/\text{C}$ electrodes, the electrochemical impedance spectra was also measured under fully discharge state after several galvanostatic charge and discharge process

and shown in Fig. 5b. The inset equivalent circuit is used to simulate the impedance spectra. The curve in high frequency corresponds to the interfacial resistance at the surface of the cathode and the intercept is related to the electrolyte resistance (R_s). The semicircle in the medium frequency is related to the charge transfer resistance (R_{ct}), which shows Li^+ interfacial transfer between the interface of LiFePO_4 particles and the surface film. The semicircle in low frequency represents the diffusion of Li^+ in the bulk of the electrode and this process is associated with the Warburg impedance (Z_w). As shown in Fig. 5, the charge-transfer resistance of the $\text{LiFePO}_4/\sim 3\text{wt}\%\text{CNTs}/\text{C}$ composite ($\sim 110 \Omega$) is significantly lower than that of the LiFePO_4/C ($\sim 146 \Omega$), which we expect is associated with the increase in electron conductivity associated with the CNTs introduced.

Another interesting phenomenon obtained from the impedance spectra is the low impedance related to diffusion of lithium ions (low frequency spike) in the $\text{LiFePO}_4/\sim 3\text{wt}\%\text{CNTs}/\text{C}$ composites. The low impedance can be attributed to higher surface area, uniform particle size distribution and better electrolyte wettability associated with homogeneous precipitation of the composite material. The aforementioned factors translate to greater accessibility to active sites for the lithium ions, shorter diffusion distances and quicker lithium ion diffusion, thereby explaining the significantly better rate capability of the $\text{LiFePO}_4/\sim 3\text{wt}\%\text{CNTs}/\text{C}$ composite electrode.

Conclusions

In this work, the LiFePO_4/C and $\text{LiFePO}_4/\text{CNTs}/\text{C}$ composites have been synthesized by a facile homogeneous precipitation and annealing process. The influence of CNTs on the structural and electrochemical characteristics of LiFePO_4/C is analyzed. We show that small amount CNTs can provide the networked structure of carbon for electronic conduction and the resulting composite exhibits small particle size, lower electron-transfer resistance, and faster lithium ion migration kinetics, which are attributed to CNT incorporating. At $\sim 1\text{C}$, the $\text{LiFePO}_4/\sim 3\text{wt}\%\text{CNTs}/\text{C}$ composite delivers a stable specific capacity of $\sim 126 \text{ mAh g}^{-1}$ after 500 cycles. At high rates (e.g. $\sim 10\text{C}$), the $\text{LiFePO}_4/\sim 3\text{wt}\%\text{CNTs}/\text{C}$ composite is still able to deliver stable capacities of up to $\sim 119 \text{ mAh g}^{-1}$, which is $\sim 42\%$ greater than its pristine counterpart.

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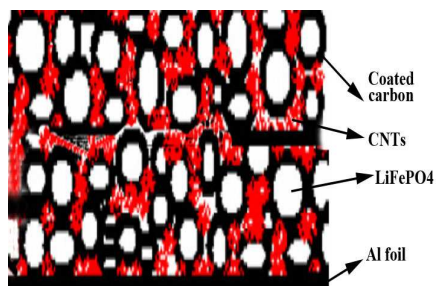
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Graphical Abstract



CNTs-doped $\text{LiFePO}_4/\text{CNTs}/\text{C}$ composites synthesized by a simple homogeneous precipitation and subsequent annealing process.

CNTs provides the networked structure of carbon for electronic conduction and the resulting composite exhibits small particle size, lower electron-transfer resistance, and faster lithium ion migration kinetics

At 1C, the $\text{LiFePO}_4/\text{CNTs}/\text{C}$ composite delivers a stable specific capacity of $\sim 126 \text{ mAh g}^{-1}$ after 500 cycles.

At high rates (e.g. 10C), the CNT-doped composite is still able to deliver stable capacities of up to $\sim 119 \text{ mAh g}^{-1}$.