

High Rate Performance of Nano-Structured LiFePO₄/C Cathode Material Prepared by a Polymer-Assisted Method from Inexpensive Iron(III) Raw Material

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Abstract—A spherical carbon coated nano-structured LiFePO₄ composite is synthesized by a polymer-assisted method from inexpensive iron(III) raw material. The synthesis process includes two steps: (1) nano-FePO₄/polyaniline composites with core-shell structure are synthesized through the in-situ polymerization of aniline; (2) LiFePO₄/C composites are prepared through carbothermal reduction with the nano-FePO₄/polyaniline and sucrose as raw materials. The structure, surface morphology of the materials and the properties of the coated carbon are investigated by X-ray diffraction, Raman spectroscopy, scanning electron microscopy, and high-resolution transmission electron microscopy. The obtained nano-structured LiFePO₄/carbon composite has a spherical morphology composed of ordered olivine structure, which is coated with 2 nm thick amorphous layer of carbon. At the same time, the materials are linked together by amorphous carbon from sucrose decomposition. The aniline plays an important role during the synthesis process. The electrochemical properties of the materials are tested by charge-discharge measurements. The obtained nano-structured LiFePO₄/carbon composite shows excellent electrochemical properties, especially its high rate performance. It exhibits initial discharge capacities of 138, 136, 118, 103, and 92 mA h g⁻¹ at 0.2, 1, 10, 20, and 30 C rate between 3.65 and 2.0 V, respectively. That makes it a promising cathode material for advanced power Li-ion batteries. The excellent electrochemical properties of the materials can be ascribed to the two different amorphous carbons. The carbon coated on the surface of LiFePO₄ effectively reduces inter-particle agglomeration of the LiFePO₄ particles. The carbon interlinked between the composite improve the electronic conductivity. Those shorten the lithium ions diffusion length and improve the electric contact between LiFePO₄ particles.

Keywords: LiFePO₄, lithium-ion batteries, high rate, carbon coating

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INTRODUCTION

With the increasing concerns about environmental protection and energy saving, rechargeable lithium-ion batteries have been extensively used in a wide variety of portable electric devices owing to their high energy densities, high voltage and portability [1–3]. In recent years, there has been a dramatic increase in research and commercialization activities [3–7]. However, these batteries still need to be improved before they can be used in special applications which need high energy and high power, such as portable power tools, hybrid electric vehicles and other power supplies [8–12]. Olivine-structured lithium iron phosphate (LiFePO₄) has many advantages compared with

conventional cathode materials, such as LiCoO₂, LiNiO₂, and LiMn₂O₄. The insertion and extraction related to the LiFePO₄ electrode involves a two phase mechanism with the reversible reaction expressed as [13–15]:



It shows a plateau at around 3.5 V relative to lithium metal and high theoretical discharge capacity of 170 mA h g⁻¹. And it has excellent structural and chemical stability during intercalation and thermal cycling. However, a main obstacle of LiFePO₄ is its poor electronic conductivity and low lithium-ion diffusion coefficient, which is the most unfavorable issue

for the rate capability of batteries. And these hinder the application of LiFePO_4 in high power field, such as electric vehicles.

As the drawbacks mentioned above, various methods have been adopted to improve the conductivity of electrons in the materials, such as nanonization [8, 16–20], surface coating with carbon [11, 19–25], conductive organic polymer, and Li^+ site doping with Mg^{2+} , Mn^{3+} , Ce^{3+} , Zr^{4+} , Ti^{4+} , Ni^{2+} [12, 26]. In addition, some researches have focused on the electrochemical kinetics and mechanism studies of the lithium intercalation process of LiFePO_4 cathode materials, which makes the investigation more deep and extensive. Among these methods, coating nano-sized LiFePO_4 crystal with carbon can enhance conductivity and confine the crystal size of LiFePO_4 for solving the problem of high power performance [10, 11, 25, 27]. There are many literatures that reported the synthesis of LiFePO_4/C via various methods. However, these methods generally involve a high-temperature treatment to ensure the conductivity of the resulting carbon materials. But the increase of crystallite size is inevitable during the high temperature condition. And the carbon coated on the surface of the material is also incomplete, just like the description at the literature [19, 20, 22, 25, 28, 29].

In addition, to obtain phase-pure LiFePO_4 , oxidation of Fe^{2+} to Fe^{3+} during the synthesis must be avoided. Since Fe^{2+} can be easily oxidized during the prepare process, it is typically hard to obtain phase-pure LiFePO_4 by applying Fe^{2+} raw material. And these salts are much more expensive than Fe^{3+} salts. According to [30], H_2 and CO can reduce the iron to a lower oxidation state during the prepare process. This suggests that much cheaper iron (III) material may be used directly for the synthesis of LiFePO_4 . In 2015, R. Sehrawat and A. Sil have developed a polymer gel combustion method, which use different amount of aniline as the monomer of gel formation. The final particle size of the LiFePO_4/C depends on the initial monomer content used in the synthesis process. Prepared LiFePO_4/C cathode material performs a higher rate capability, due to small particle size, low charge transfer resistance, and higher Li^+ diffusion coefficient [31].

In this work, a spherical carbon coated nano-structured LiFePO_4 cathode composite is synthesized by a polymer-assisted method from inexpensive iron(III) raw material. The synthesis process of the composite includes two steps, in which the aniline plays an important role. There are two different amorphous carbons in the as-synthesized LiFePO_4/C composite, which greatly improve the electronic conductivity of the materials. The composite showed a high rate capacity (about 118 mA h g^{-1}) at 10 C rate and excellent cycling performance. That made it a promising cathode

material for advanced electrochemical devices such as power Li-ion battery and supercapacitor.

EXPERIMENTAL

Synthesis of $\text{FePO}_4/\text{PANI}$ and LiFePO_4/C Cathode Material

$\text{NH}_4\text{H}_2\text{PO}_4$ (Aldrich, 99%) and $(\text{NH}_4)_2\text{HPO}_4$ (Aldrich, 99%) with molar ratio of 1 : 1 were dissolved in deionized water. Then the aniline (Aldrich, 99.5%) and a little amount of tween-60 were added to the solution, marked as Solution A. The $\text{Fe}(\text{NO}_3)_3$ (Aldrich, 99.9%) in equimolar amount with $[\text{PO}_4]^{3-}$, were dissolved in deionized water, marked as Solution B. Then Solution B was slowly added to Solution A with stirring. Saturated NH_4HCO_3 (Sinopharm Group Co. LTD., 99%) solution was used as pH regulator. The reactive mixture was then stirred for 4 h at room temperature. And the resulting $\text{FePO}_4/\text{PANI}$ was filtered and washed several times with deionized water.

An equimolar mixture of $\text{CH}_3\text{COOLi} \cdot 2\text{H}_2\text{O}$ (Alfa Aesar, 99.9%) and $\text{FePO}_4/\text{PANI}$, with a contain amount of sucrose (Sigma-Aldrich, 99.5%) were dispersed in the ethanol as the precursor. After milling for about 1 h, the precursors were heated at 400°C for 4 h under Ar containing 5% H_2 (Jingxiang, 99.999%) in order to decompose the organic composition. The precursors were then remilled for about 1 h and finally calcined at 700°C for 10 h under argon containing 5% H_2 to obtain the composite.

Structural Characterization

The DSC–TGA of the precursor was performed by thermal gravimetric analysis (TA SDT Q600, American) under the mixture atmosphere ($\text{Ar} : \text{H}_2 = 95 : 5$). Raman spectrum of the samples was performed with Raman Spectrometers (Bruker RAM, Germany). The crystal structure of the obtained LiFePO_4/C powder was identified by X-ray diffraction (XRD) (D/Max-2500, Japan) using $\text{CuK}\alpha$ radiation scanned in the range 20° – 45° . The particle size and morphology were observed by a field emission scanning electron microscopy (FESEM) (S-4800, Hitachi, Japan). The nature and thickness of the coated carbon was measured using the images from high resolution transmission electron microscope (HRTEM) (JEM-2100, JEOL, Japan).

Electrochemical Measurements

The electrochemical properties of the products were investigated using a two-electrode test cell with lithium foil as the negative. A positive electrode was made by coating a paste of the nano-structured LiFePO_4 composite, acetylene black and polyvinylidene fluoride (PVdF) binder (80 : 10 : 10 wt %) on an alumi-

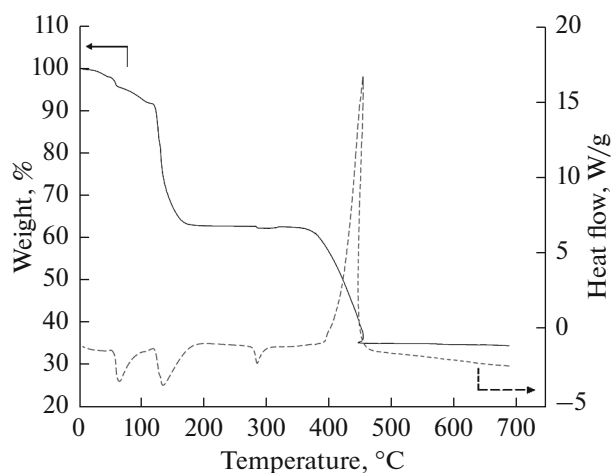


Fig. 1. The DSC–TGA curve of the precursor under the mixture atmosphere (Ar : H₂ = 95 : 5).

num-foil collector. The positive film was subjected to roll press and the electrodes of 10 mm diameter were punched out. The positive electrodes were dried at 120°C for 12 h in a vacuum oven. For comparison, a commercial LiFePO₄ powder with micron size (Marked as sample A), provided by Hao Run Technology Co. Ltd., is also used to prepare positive electrode with the same surface density as the synthesized LiFePO₄/C composite. The cells were assembled in an argon filled glove box with an electrolyte of 1 mol L⁻¹ LiPF₆ in DC–DMC (1 : 1, volume ratio) solution and a separator of Celgard 2400. The charge–discharge measurements were performed using a multi-channel battery tester (LAND CT2001A, China) operating in galvanostatic mode at various rates, between 2.0 and 3.85 V.

RESULTS AND DISCUSSION

Structure, Morphology and Physical Property

Figure 1 shows the DSC–TGA curve of the precursor under the mixture atmosphere (Ar : H₂ = 95 : 5). It can be seen that the weight loss is about 12 wt % from room temperature to 120°C because of the evaporation of water. Accompanied with the decalcination, there is a weight loss of 29 wt % from 120 to 150°C, which is caused by the pyrolysis of sucrose and polyaniline. The Fe³⁺ is reduced to Fe²⁺ and forms the LiFePO₄ with a weight loss of 26 wt % from 360 to 450°C. At the same time, there appears an exothermic peak in the DSC curve during 400 to 450°C. It indicates that the LiFePO₄ can be formed when the temperature is higher than 450°C. The XRD patterns shows that the element iron exist mainly as the form of FePO₄, Fe₇(PO₄)₆, Fe₃(PO₄)₂ and a small quantity exist as the form of LiFePO₄. The crystalline LiFePO₄ is formed with the increase of the temperature. The carbon,

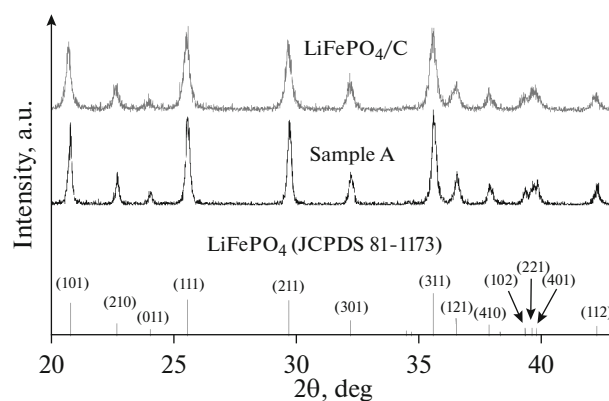


Fig. 2. XRD patterns of LiFePO₄ powder and nano-structured LiFePO₄/C composite.

which forms because of the pyrolysis of sucrose and polyaniline, has two effects during the process. It can reduce Fe³⁺ into Fe²⁺. At the same time, it can restrain the increase of the LiFePO₄ crystal.

Figure 2 shows XRD patterns of commercial sample A and nano-structured LiFePO₄/C composite. It can be found clearly that there are four strong diffraction peaks at 2θ = 20.68° (101), 25.50° (111), 29.69° (211), and 35.54° (311) in the XRD patterns of sample A and nano-structured LiFePO₄/C composite. And there appears another weak peaks at 2θ = 22.63°, 23.99°, 32.18°, 36.46°, 37.83°, 39.24°, and 42.16°. All the peaks are consistent with the standard LiFePO₄ (JCPDS 81-1173), which indicates the presence of the LiFePO₄ phase as an ordered olivine structure. According to the Scherrer's equation, the crystal size of the nano-structured LiFePO₄/C composite is about 50.2 nm, indicating the samples have a high crystal degree. At the same time, there is no diffraction peaks attributed to carbon, most likely because there may be amorphous or a low content of crystalline carbon in the nano-structured LiFePO₄/C composite.

Figure 3 shows the Raman spectrum of the nano-structured LiFePO₄/C composite. Raman spectroscopy is an important method for the investigation of the properties of the carbon. The typical characteristic of carbon in the Raman spectrum are the two broad bands at 1350 and 1582 cm⁻¹, which are called as D-band (disorder/defect band) and G-band (graphitic band), respectively. These two bands are observed in Raman spectrum of the nano-structured LiFePO₄/C composite. It indicates that the carbon is composed of amorphous phase and a little amount of graphitic carbon. The electronic conductivity of the composite has a complicated correlation with the peak intensity ratio and the bands are a ratio of the D vs. G band. The ration of I_D/I_G of the synthesized powder is 0.92, indicating that the coated carbon might be amorphous phase. The result is consistent with that of

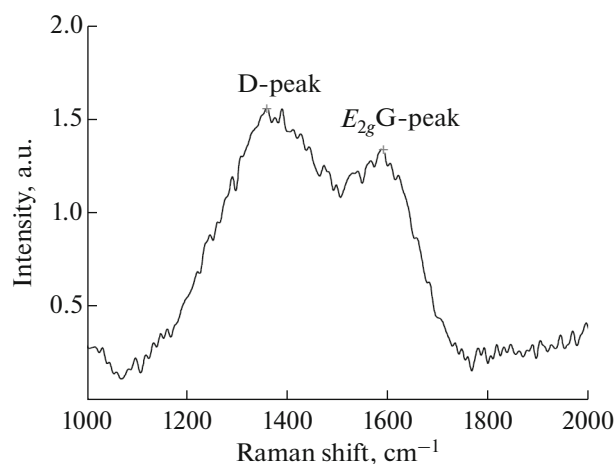


Fig. 3. Raman spectrum of nano-structured LiFePO_4/C composite.

XRD analysis, which shows that no diffraction lines caused by graphite have been found in XRD patterns of the nano-structured LiFePO_4/C composite.

The surface morphology of the precursor particles and the LiFePO_4/C sample as well as the shape of the carbon coating is investigated by SEM and HRTEM, as shown in Fig. 4. Figure 4a shows that the precursor powder $\text{FePO}_4/\text{PANI}$ has a spherical morphology and its diameter is about 30 nm. As shown in Fig. 4b, the diameter of nano-structured LiFePO_4/C composite is about 55 nm. In contrast to the precursor $\text{FePO}_4/\text{PANI}$, the diameter of nano-structured LiFePO_4/C composite becomes bigger. The HRTEM images of Fig. 4c show that the FePO_4 is amorphous and there is no clear interface between the FePO_4 and PANI. In Fig. 4d, it is clearly founded that regular crystal plane of LiFePO_4 particle and coating layer with little crystallinity. It shows that the thickness of the coated carbon layer is about 2 nm. These findings combined both XRD and Raman spectra can help us to understand these grains have a core-shell structure with LiFePO_4 crystallite as the core and carbon coating as the shell. The LiFePO_4 grains are sphere-like and surrounded completely by carbon layers. The resultant LiFePO_4/C composites show an enhanced rate property due to the improve-

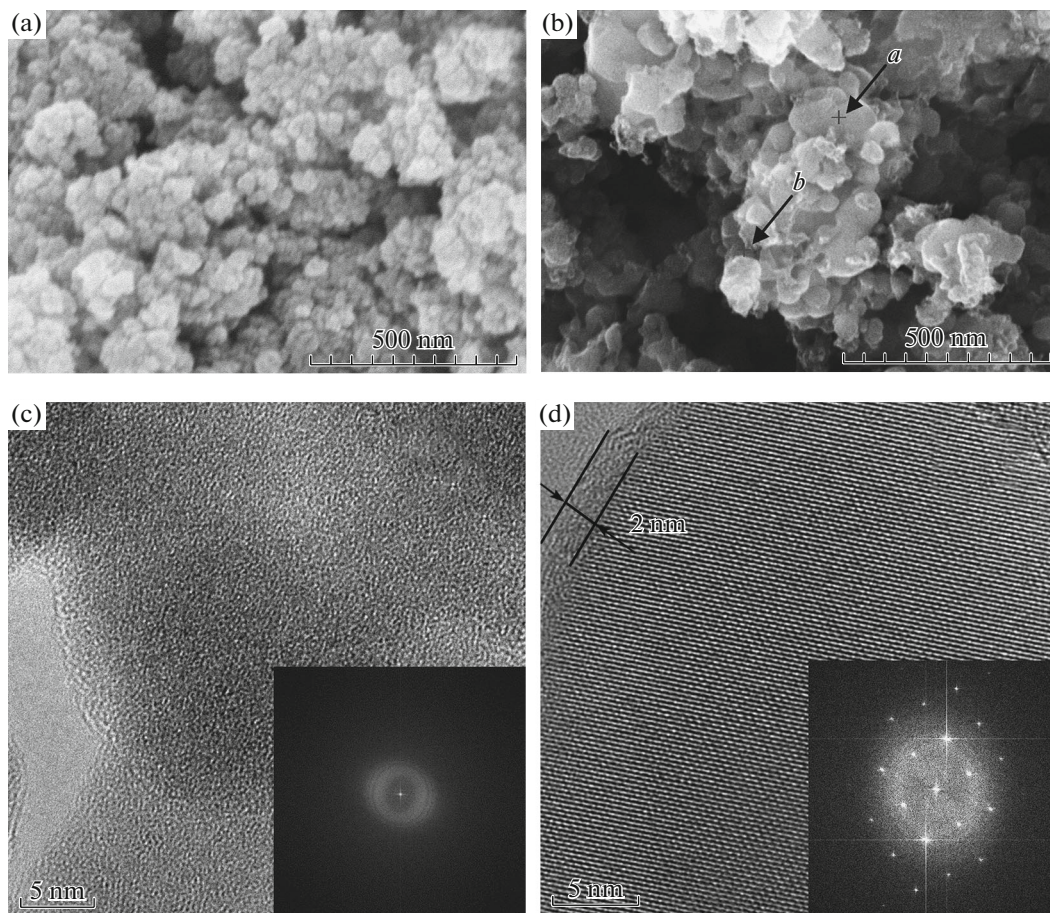


Fig. 4. SEM images of (a) the precursor particles and (b) the nano-structured LiFePO_4/C composite, HRTEM images of (c) the precursor powder $\text{FePO}_4/\text{PANI}$, and (d) the LiFePO_4 particle and carbon layer.

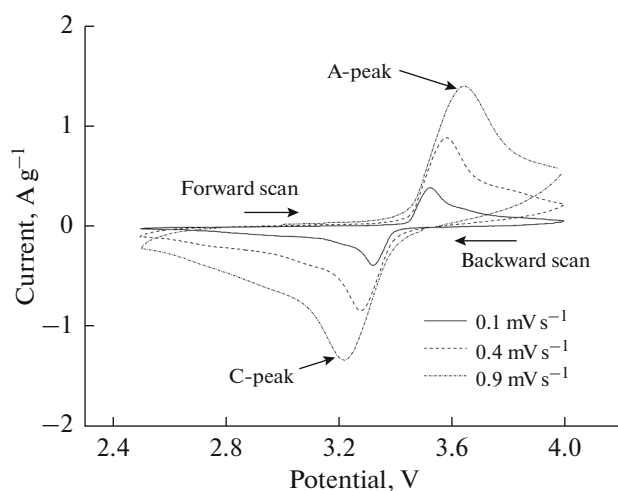


Fig. 5. Cyclic voltammetry test of nano-structured LiFePO_4/C composite at different scanning rate.

ment of electronic conductivity from the effective carbon coating.

The EDX analysis shows that the content of the carbon is different in the different region of the nano-structured LiFePO_4/C composite. As shown in Fig. 4b, the carbon content of in the dot *b* region is much higher than that in the dot *a* region. The ratio is about 4 : 1, most likely because the carbon in the dot *b* region come from the decomposition of sucrose and the carbon in the dot *a* region come from the decomposition of PANI. These results can help us to understand the carbon distribution in nano-structured LiFePO_4 and the reason why the composites having excellent rate properties.

Electrochemical Performance

In order to evaluate the potential application of the nano-structured LiFePO_4/C composite as cathode materials for lithium-ion batteries, the electrochemi-

Table 1. Discharge capacities and the discharge capacity retention s at various values of $Q_{nC}/Q_{0.2C}$ for nano-structured LiFePO_4/C composite at different rates

Discharge rate	Discharge capacity, mA h g^{-1}	$Q_{nC}/Q_{0.2C}$, %
0.2 C	138	100
1 C	136	98.6
10 C	118	85.5
20 C	103	74.6
30 C	92	66.7

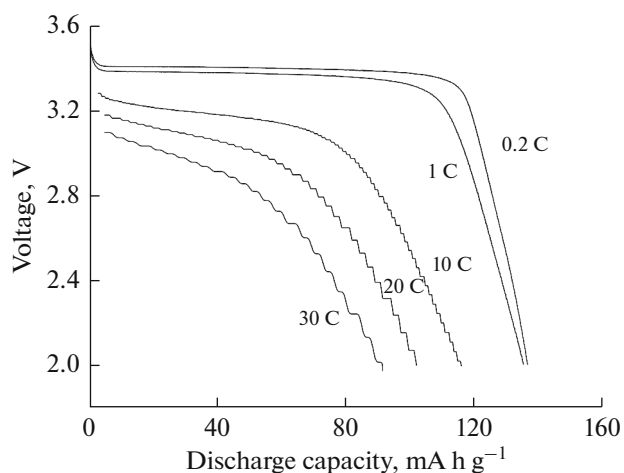


Fig. 6. The 4th charge–discharge curves of nano-structured LiFePO_4/C composite at different rates.

cal performances with respect to Li insertion/extraction have been investigated. Figure 5 shows the cyclic voltammetry test of nano-structured LiFePO_4/C composite at different scanning rate. It is can be seen that a couple of redox peaks are observed between 3.3 and 3.5 V (vs. Li/Li^+) in the cyclic voltammetry curve obtained at a scanning rate of 0.1 mV s^{-1} . These peaks correspond to the extraction and insertion of lithium ions. These redox peaks can still be clearly observed at a scanning rate of 0.9 mV s^{-1} . It indicates that the composite has good high power performance. The result is consistent with that of the two-electrode test cell as shown in Fig. 6 and Table 1.

To test the working voltage and rate properties, the LiFePO_4/C electrodes have been discharged at different rates, as shown in Fig. 6. The electrode is charged at 0.2 C for each charging step and then discharged at gradually increased rates. At low discharge rate (0.2, 1 C), the nano-structured LiFePO_4/C composites has the similar charge–discharge curves with close discharge capacity (138.0 , $142.5 \text{ mA h g}^{-1}$) and flat plateaus. And the electrode exhibits flat voltage plateaus at each C-rate. Even at a 20 C rate, the discharge voltage plateau is still higher than 3.0 V (vs. Li^+/Li), and the delivered capacity is more than 103 mA h g^{-1} . Moreover, the charge–discharge plateau voltage differences are 0.1, 0.15, 0.5 and 0.7 V at 0.2, 1.0, 10, and 20 C-rate, respectively. The results indicate that the nano-structured LiFePO_4/C electrode has low polarization, good electrical conductivity, as well as good rate capability.

The retention of discharge capacity ($Q_{nC}/Q_{0.2C}$, $n = 0.2, 1, 10, 20, 30$) for LiFePO_4/C at different discharge currents are listed on Table 1. It can be seen that the nano-structured LiFePO_4/C composites has good rate capability. The discharge capacity retention is

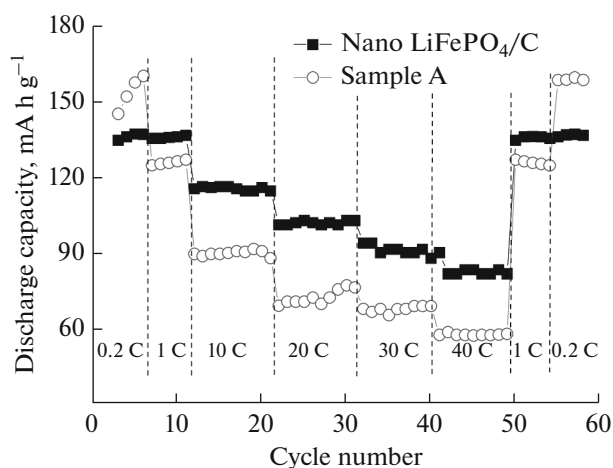


Fig. 7. Cycling performance of the nano-structured LiFePO_4/C composite at different rates compared to a commercial sample A.

85.5, 74.6, 66.7% at 10, 20, and 30 C-rate respectively, while the discharge capacity is 118, 103 and 92 mA h g^{-1} . From the results, it could be concluded that the nano-structured LiFePO_4/C composites present better rate performance, which can be attributed to the structure of the LiFePO_4/C composites.

Figure 7 shows the discharge capacity at various rates (0.2, 1.0, 10, 20, 30, and 40 C-rate) as a function of cycle number for the nano-structured LiFePO_4/C composites and a commercial sample A. At 0.2 C rate, the nano-structured LiFePO_4/C composites and sample A reached a reversible capacity of 138 and 158 mA h g^{-1} , respectively. After 50 cycles at various

rates, the reversible capacity of the two materials maintained at about 138 and 158 mA h g^{-1} , which indicated a favorable reversible capacity and cycling stability retention even under high-rate discharge conditions. But from the figure, it can be seen that the reversible capacity of the nano-structured LiFePO_4/C composites is higher than that of sample A at high discharge rate. It can be seen the nano-structured LiFePO_4/C composites has good rate-cycle performance.

This excellent high rate performance of the nano-structured LiFePO_4/C composite is ascribed to the carbon coated on the surface of the LiFePO_4 and the carbon interlinked between the particles, as shown in Fig. 8. According to the literature, although the conductive carbon is added to the electrode film during the preparation process, it cannot form a convenient conductive network because of dispersion reasons. Thus, during the intercalation process of LiFePO_4 , the electrons cannot reach all the positions where Li^+ ion intercalation takes place, resulting in polarization of the electrode, especially at high rate circumstance. In the composite prepared by a polymer-assisted method, the LiFePO_4 is completely coated with conductive carbon that comes from PANI. Lithium ions can easily intercalate into the LiFePO_4 through the carbon shell (about 2 nm). Moreover, the completely carbon coated- LiFePO_4 is interlinked by the carbon that comes from sucrose, which form a convenient conductive network in the composite. When the Li^+ ion intercalation takes place, the electrons can reach from all the positions with the conductive network. Thus it could further alleviate this polarization phenomenon and present excellent high rate performance.

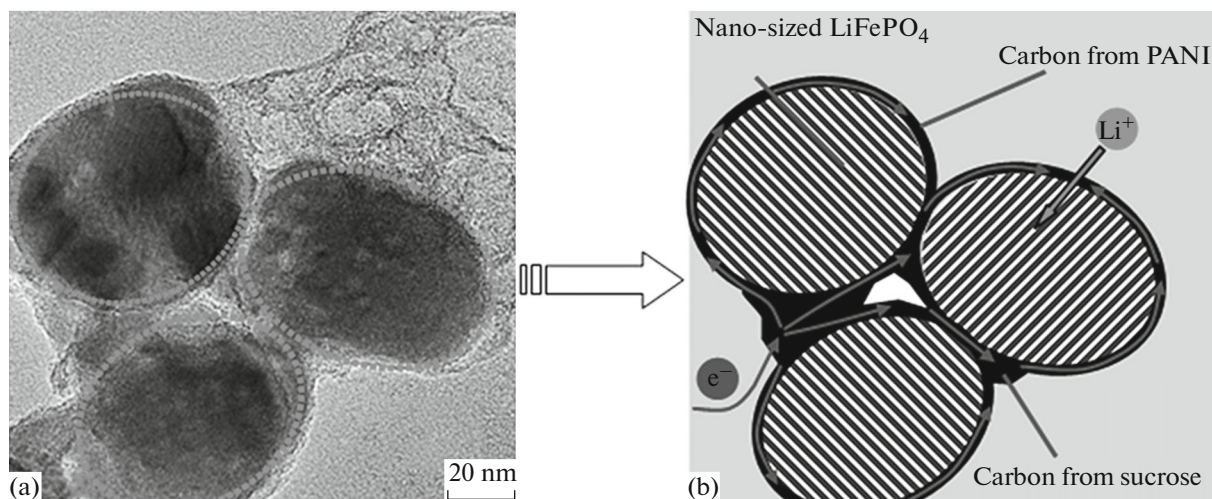


Fig. 8. (a) HRTEM images of the carbon coated LiFePO_4 particles and (b) electron-transfer pathway for LiFePO_4 particles with nano-size and two type of carbon.

CONCLUSIONS

In summary, a spherical carbon coated nano-structured LiFePO₄ composite is synthesized by a polymer-assisted method from inexpensive iron(III) raw material. The cathode material shows a discharge capacity of 138, 136, 118, 103 and 92 mA h g⁻¹ at 0.2, 1, 10, 20, and 30 C-rates. The nano-structured LiFePO₄ composite provides an excellent rate performance and a good cycling stability at high rates. This excellent behavior of the nano-structured LiFePO₄ composite is ascribed to the carbon coated on the surface of the LiFePO₄ and the carbon interlinked between the particles. Such a synthesis using Fe(III) cheap raw material in combination with sucrose as an organic carbon source is a facile and energy-saving way for the synthesis of high-rate performance LiFePO₄/C composite for high power lithium-ion batteries.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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