



High performance LiFePO₄/CN cathode material promoted by polyaniline as carbon–nitrogen precursor

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HIGHLIGHTS

- Pyrolysis of PANI-Cl improves the LiFePO₄ performance much better than sucrose.
- PANI-Cl leads to the formation of thin carbon–nitrogen layer on LiFePO₄ particles.
- Crosslinked polymer chains upon pyrolysis inhibit the growth of crystalline grains.
- PANI-Cl reduces the LiFePO₄ particle size to nanometer scale but sucrose not.

ARTICLE INFO

Article history:

Received 23 January 2013

Received in revised form

13 March 2013

Accepted 7 April 2013

Available online 18 April 2013

Keywords:

Polyaniline chloride

LiFePO₄

Polymer pyrolysis

Carbon–nitrogen coating

Crosslinking

Solid state synthesis

ABSTRACT

A facile and efficient solid state synthesis of carbon and nitrogen coated lithium iron phosphate (LiFePO₄/CN) cathode material is achieved via polymer-pyrolysis method using polyaniline-chloride (PANI-Cl). The current investigation is comparatively analyzed with the results of the composite of LiFePO₄/C (LFP/C) synthesized using sucrose as carbon precursor. The optimized LiFePO₄/CN (LFP/CN) composite is synthesized at 700 °C using 10 wt.% PANI-Cl. The composite exhibits remarkable improvement in capacity, cyclability and rate capability compared to those of LFP/C. The specific discharge capacities as high as 164 mAh g⁻¹ (theoretical capacity: 170 mAh g⁻¹) at 0.1 C and 100 mAh g⁻¹ at 10 C rates were achieved with LFP/CN. In addition, the composite exhibits a long-term cycling stability with the capacity loss of only 10% after 1000 cycles. PANI-Cl shifts the size distribution of the composite to nanometer scale (approximately 150 nm), however the addition of sucrose does not have such an effect. LFP/CN contains 1.6 wt.% nitrogen and 15.8 wt.% carbon. LFP particles are mostly coated with a few nanometers thick C–N layer forming a core–shell structure. The possible crosslinking mechanism of PANI-Cl upon pyrolysis on size reduction and formation of uniform carbon/nitrogen coating on LFP are also discussed.

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1. Introduction

LiFePO₄ (LFP) is considered to be one of the most promising cathode material for the next generation high-power lithium ion batteries due to its low cost, high safety, non-toxicity and a competitive theoretical capacity [1,2]. They are envisioned to be used in electric vehicles and stationary energy storage systems for storing solar and wind power. Unfortunately, low electronic conductivity and slow diffusion of lithium ions across the two-phase boundary of LFP seriously limit its rate capability [3–6]. To overcome these intrinsic limitations, many efforts have been carried out including particle size reduction [7], doping with supervalent cations [8,9], coating with conductive polymers [6,10–12] and forming

a carbon layer (LFP/C) [5,6,13–18]. Uniform carbon coating greatly enhances specific capacity, rate capacity and cycling performance of LFP [5,6]. This is due to the pyrolytic carbon in the product, which suppresses the particle growth and thus leading both particle size minimization and intimate carbon contact [19]. However, it is quite difficult to obtain a homogeneously coated carbon shell on LFP particles during the heat treatment. In case of partial formation of carbon shell, an insufficient electronically conducting network would lead to decrease in the rate capability of the material.

Previous studies mostly focused on the synthesis of LFP/C composite materials by using low weight organic precursors [20,21], such as sucrose, glucose or citric acid, as the carbon source. Although the polymer pyrolysis method is a relatively simple and effective way to form carbon-coated materials such as ceramic/carbon composites [22,23], it has been rarely applied for coating the LFP particles [12,15,19]. In such a process, pyrolyzed polymers can lead to the formation of reduced size LFP/C particles coated uniformly with a

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Table 1

Experimental conditions for the synthesis of LFP/C and LFP/CN composites and carbon and nitrogen contents determined by elemental analysis.

Notation	Material/carbon source	Sintering temperature (°C)	Carbon source (wt.%)	Contents (wt.%)		
				C	N	N/C
LFP/C	LFP/C _{sucrose}	700	10	8.4	–	–
LFP/CN ₁	LFP/C _{PANI-Cl}	650	10	16.1	2.1	0.13
LFP/CN ₂	LFP/C _{PANI-Cl}	700	10	15.8	1.6	0.10
LFP/CN ₃	LFP/C _{PANI-Cl}	750	10	15.5	1.6	0.10
LFP/CN ₄	LFP/C _{PANI-Cl}	700	6	12.9	1.2	0.09
LFP/CN ₅	LFP/C _{PANI-Cl}	700	14	21.3	2.5	0.12
–	PANI-Cl	–	–	59.8	12.3	0.21

few nanometer thick carbon layers [15,19]. It is, however, important to choose the proper polymer precursor for tailoring the properties of LFP/C composite. Recently, Nien et al. [15] prepared LFP/C samples formed by calcinating amorphous LFP with various polymers such as polystyrene, polyethylene oxide, polybutadiene at 600 °C. They reported that polystyrene (5 wt.%) derivative with functionalized aromatic groups exhibited an improved performance. They achieved a capacity of 147 mAh g⁻¹ and 90 mAh g⁻¹ at 0.1 C and 3 C rates, respectively. Additionally, Yu and Fang [18] announced that LFP/C composite prepared using polystyrene nano-spheres (7 wt.%) sintered at 800 °C displayed a discharge capacity of 167 mAh g⁻¹ and 150 mAh g⁻¹ at 0.1 C and 1 C, respectively.

Polyaniline (PANI) exhibits an interesting behavior upon pyrolysis compared to many other polymers by forming a network structure as a result of crosslinking of polymer chains [24–29]. Mentus et al. reported that a disordered nitrogen-containing graphite structure is formed upon carbonization of sulfuric acid doped PANI with conductivity higher than that of pristine PANI [26]. In this article, we introduce the chloride doped PANI (PANI-Cl) as a carbon–nitrogen source for the solid state synthesis of LFP/CN composite which has very good properties as cathode material in high power lithium ion batteries. This composite seems to be a

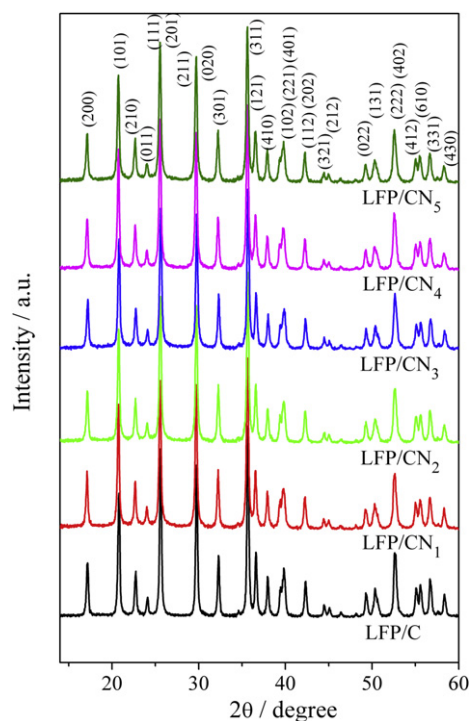


Fig. 1. XRD patterns of LFP/C and LFP/CN composites synthesized at different conditions (see Table 1).

promising alternative route for an industrial-scale production due to its facile fabrication and low cost. A mixture of nanometer and micrometer size LFP/CN particles are formed as a result of the pyrolysis of PANI-Cl. It is believed that the crosslinked polymer chains inhibit the growth of crystalline grains. LFP/CN composite synthesized at 700 °C using PANI-Cl (10 wt.%) exhibits superior electrochemical performances in wide operation discharge rate range compared to LFP/C synthesized using sucrose as a carbon precursor.

2. Experimental

2.1. Synthesis of LiFePO₄/C and LiFePO₄/CN composites

As the starting materials for the solid-state synthesis, stoichiometric amounts of analytical grade 2.24 g of Li₂CO₃ (Alfa-Aesar), 10.99 g of FeC₂O₄·2H₂O (Aldrich), 6.98 g of (NH₄)₂HPO₄ (Carlo-Erba) as well as 2.25 g of PANI-Cl or 2.25 g of sucrose (Carlo-Erba) as carbon source precursors were thoroughly planetary milled in mortar for 2 h (300 rpm) in the mixture solvents of 30 ml of ethanol and 30 ml of N-methylpyrrolidone (NMP, Merck). The resulting gel was dried at 100 °C in a furnace and then heated to 350 °C for 6 h in

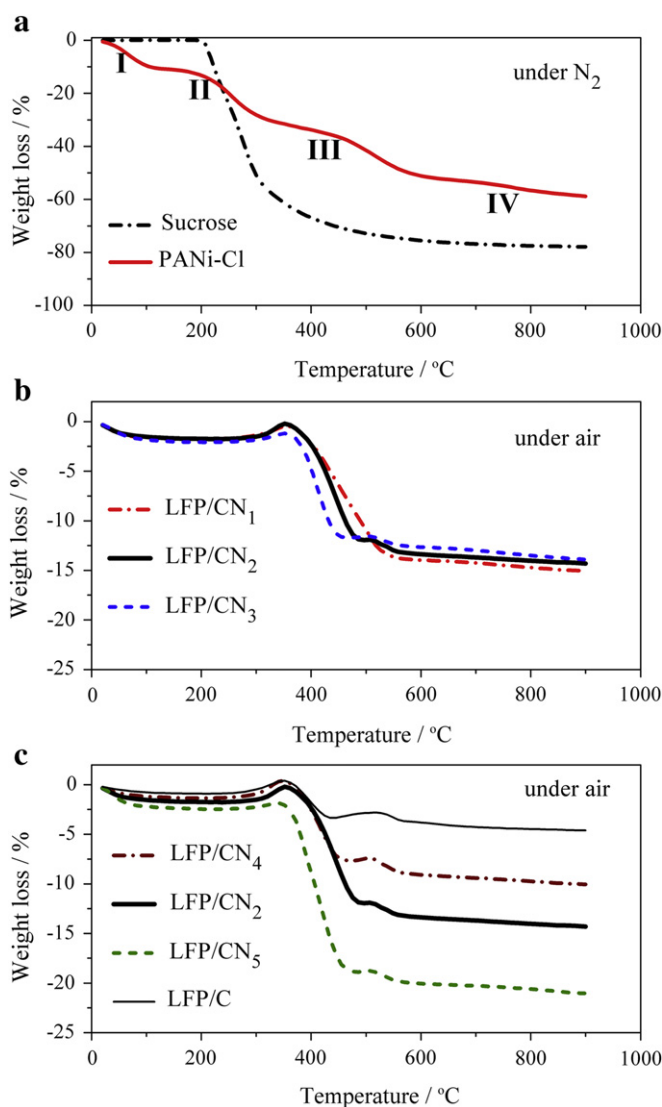


Fig. 2. Thermogravimetric curves of (a) sucrose and PANI-Cl under N₂ flow; (b) LFP/CN sintered at 650, 700, 750 °C under air, (c) LFP/CN synthesized using 6, 10, 14 wt.% PANI-Cl and LFP/C sintered at 700 °C under air.

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