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Short communication

High purity lithium iron phosphate/carbon composites prepared by using secondary lithium source

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ABSTRACT

Various lithium salts including lithium carbonate, lithium hydroxide, lithium acetate and lithium citrate were used as secondary lithium sources for the synthesis of lithium iron phosphate/carbon composites with cheap iron sources in the form of Fe and $FePO_4$. Samples were characterized by X-ray diffraction, scanning electron microscopy, cyclic voltammetry and constant-current charge–discharge tests. The results showed that lithium carbonate derived product generated a high purity $LiFePO_4$ phase with high tap densities. Furthermore, satisfactory electrochemical performance with an initial discharge capacity of 146.1 mAh g^{-1} at 0.5 C rate and good capacity retention of 95.2% after 50 cycles were achieved.

1. Introduction

Finding a low-cost synthetic route to yield high performance lithium iron phosphate products remains a challenge. In this regard, the selection of a cheap source of iron and lithium is a paramount. Cheap source of iron could take the form of iron phosphate [1,2], instead of divalent ferrous source such as iron(II) chloride [3], iron (II) oxalate [4,5], iron(II) acetate [6] or iron(II) sulfate [7,8]. Low cost source of lithium could take the form of lithium phosphate. However, using Li_3PO4 as raw materials starting material, would require an optimum control of the amount of usage, as it may lead to low Li content in the final product ($LixFePO_4$ pahse with $x<1$) [9]or an over dosage if an excess of Li_3PO4 is used. Another problem associated with the use of an excess of Li_3PO4 is the inevitable formation of intermediate compounds that would impede electrode performance. In particular, during the synthesis of $LiFePO_4$, the formation of $Li_4P_2O_7$ as a by-product has been a significant problem limiting electronic conduction and induces side reactions leading to the formation of impurities when $LiFePO_4$ is exposed to air [10]. Several approaches have been proposed to suppress the formation of Li_3PO_4. These include: a) controlling the sintering temperature [10] and atmosphere [2,11] during the post heat-treatment process of LiFePO4, b) introducing reductive reagent [11,12] and c) synthesizing $LiFePO_4$ material in a nonstoichiometric way [13].

In the present case, our strategy was to use a low starting amount of Li_3PO_4 to avoid any formation of by-product and a secondary lithium source to compensate the Li loss inevitability occurring during the sintering/synthesis process of $LiFePO_4$ [14–18].To this aim, we used a mechano-chemical-solid-state synthesis method with lithium phosphate as the main Li source and various Li salts as secondary Li sources. Fe and $FePO_4$ were used as an iron source since widely available. We found that compared to the single lithium phosphate source, using appropriate amounts of a secondary Li source could eliminated the formation of impurities. In particular, the use of lithium carbonate as secondary Li source leads to very good electrochemical properties for the resulting $LiFePO_4$. The role of secondary Li salt addition on the physical and electrochemical properties of the resultant $LiFePO_4$/C composites is discussed.

2. Experimental

2.1. Synthesis of $LiFePO_4$/C

The $LiFePO_4$/C composites were prepared by a ball-milling assisted solid-state reaction method using sucrose as a carbon source. The raw materials in their stoichiometric ratios (Table 1) were mixed with 10 ml ethanol and then ball-milled at a speed of 150 rpm for 3 h, and then 350 rpm for 8 h. The precursor obtained was put into a vacuum drying oven to remove the ethanol, and then placed in a tube furnace under a nitrogen atmosphere at 450 °C for 3 h and then at 700 °C for 8 h. The products were cooled naturally to room temperature and labeled from a-e respectively.

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Table 1
Tap densities of $LiFePO_4$/C composites prepared from different lithium sources.

Sample	Secondary Li source	Molar ratio of raw materials				Tap densities (g/cm^3)	Carbon coating (%)	Phases
		Lithium phosphate	Secondary Li source	Fe	$FePO_4$			
a	Li_2CO_3	1	0.075	1	2	1.36	3.8	$LiFePO_4$
b	LiOH	1	0.15	1	2	1.33	3.6	$LiFePO_4$
c	CH_3COOLi	1	0.15	1	2	1.35	3.7	$LiFePO_4$
d	$C_6H_5Li_3O_7$	1	0.05	1	2	1.32	3.7	$LiFePO_4$
e	Li_3PO_4	1	0.05	1	2	1.28	3.5	$LiFePO_4$ Li_3PO_4 $Li_4P_2O_7$ $Fe_2P_2O_7$

2.2. Characterization

The crystallographic structure of the samples was characterized by power X-ray diffraction (XRD, PNAlytical, X'Pert Pro) with Cu·Kα radiation. Data were collected in the 2θ range of 10°–80° at a step interval of 0.02°. The morphologies of samples were observed by Scanning Electronic Microscopy (SEM, Hitachi S-4700). The particle size was analyzed with a laser particle size analyzer (Mastersizer 2000). The carbon content of the $LiFePO_4$/C materials was determined with a Flash EA 1112 tester (Conflo-III, Thermo Electron Corporation, America).The tap density was obtained by the following method: *ca.* 3 g of the respective $LiFePO_4$/C powders was poured into a small pre-weighed calibrated measuring cylinder. The later was tapped by hand until the volume of the powder ceased to decrease. The volume, V, was read and the tap density, ρ, thus calculated from $\rho = m/V$ (where m is the mass of the powder).

2.3. Electrochemical test

The electrochemical performance of the samples as cathode was evaluated by assembling a CR2032-type coin-type cell in an argon filled glove box. The electrode was prepared by dispersing 80 wt.% active materials, 12 wt.% acetylene black and 8 wt.% polyvinylidene fluoride (PVDF) in 1-methyl-2-pyrrolidone (NMP) to ensure the homogeneity, the slurry was then coated on an aluminum foil current collector and dried at 120 °C for 12 h. A lithium foil was used as the counter electrode, the electrolyte was formed by 1 M $LiPF_6$ in EC: DMC: EMC (1:1:1, v/v/v). Cyclic voltammetry (CV) was calculated by a CHI 660B electrochemical station at a scan rate of 0.5 mV/s between 2.5 and 4.2 V. The cells were charged and discharged between 2.5 and 4.2 V by applying a battery test system (Land CT2001A) at 25 °C.

3. Results and discussion

Using Fe and $FePO_4$ as raw materials, pure $LiFePO_4$ can be theoretically obtained according to reaction (1) whereby the iron powder reduces the trivalent Fe (III) in $FePO_4$ into bivalent Fe (II) in the product.

$$Li_3PO_4 \cdot 0.5H_2O + Fe + 2FePO_4 \cdot 4H_2O \rightarrow 3LiFePO_4 + 8.5H_2O \quad (1)$$

However, overdosing the amount of Li_3PO_4 generates impurities, e.g. $Li_4P_2O_7$ and $Fe_2P_2O_7$, in addition to the ordered olivine phase $LiFePO_4$, as observed by XRD (Fig. 1). It can be assumed that the formation of impurities when using Li_3PO_4 as the main Li source was due to the following reactions: a) During the sintering process, the reaction between $FePO_4$ and Li_3PO_4 according to Eq. (2) and [19], and b) further reaction of $Li_4P_2O_7$ with Fe and $FePO_4$ according to Eq. (3).

$$2FePO_4 + 4Li_3PO_4 \rightarrow 3Li_4P_2O_7 + Fe_2O_3 \quad (2)$$

$$1.5Li_4P_2O_7 + Fe + 2FePO_4 \cdot 4H_2O \rightarrow 1.5Fe_2P_2O_7 + 2Li_3PO_4 + 8H_2O \quad (3)$$

However, if an adequate amount of a secondary Li source is present, the formation of $Li_4P_2O_7$ impurities can be eliminated with the additional Li source. Indeed, we obtained a pure $LiFePO_4$ phase when secondary Li source was added to the reaction mixture (Fig. 1).

Further information on the structural parameters for the $LiFePO_4$/C composite were obtained by refining the XRD patterns using reflex model of Materials studio. Fig. 2 presents an example of a Rietveld refinement result for the $LiFePO_4$/C composites prepared by using lithium carbonate (Li_2CO_3) as the secondary lithium source. The lattice parameters of Li_2CO_3 derived-sample were found to be of $a = 0.60075$ nm,

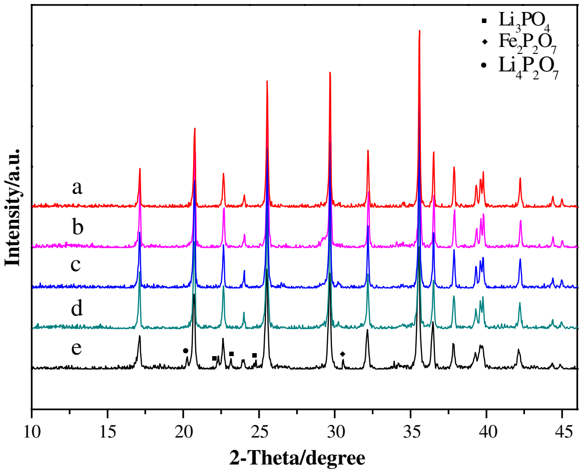

Fig. 1. XRD patterns of $LiFePO_4$/C composites prepared from different secondary lithium sources: (a) Li_2CO_3 (b) LiOH (c) CH_3COOLi (d) $C_6H_5Li_3O_7$ and (e) Li_3PO_4.

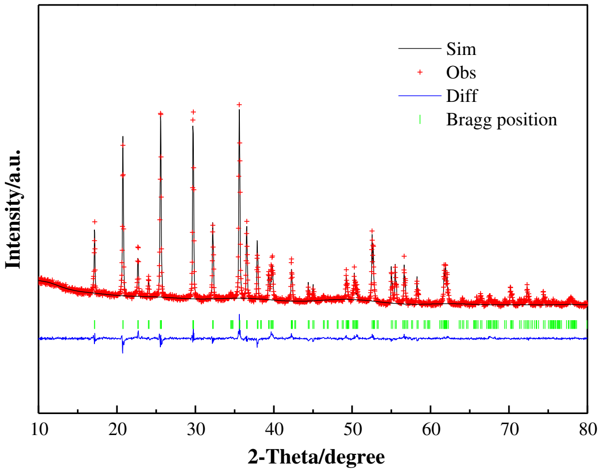

Fig. 2. The Rietveld refinement of the XRD pattern for $LiFePO_4$/C composites using Li_2CO_3 as the secondary lithium source.