

Determination of Optimum Carbon Content of LiFePO_4 Cathode Material for Lithium Ion Batteries

HÜSEYİN GÖKTEPE*, HALİL SAHAN and SABAN PATAT

Department of Chemistry, Faculty of Art and Science, Erciyes University, 38039 Kayseri, Turkey

Fax: (90)(352)(4374933); Tel: (90)(352)(4374901/33184)

E-mail: goktepe@erciyes.edu.tr

In order to optimize carbon content on LiFePO_4/C , six samples were synthesized. The samples of LiFePO_4/C were synthesized with the addition of 12.5, 25, 40, 50, 70 and 100 % wt. of white sugar as carbon precursor. The amount of carbon in synthesized samples were found to be 2, 4.5, 7, 10, 12 and 17 % wt., respectively. It is found that in this synthesis condition, ca. 17 % of the white sugar converted to carbon. All samples were characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), differential thermal analysis/thermal gravimetry DTA/TG and electrochemical properties of composite cathodes were investigated. The particle size of the powders which calcined at 700 °C for 10 h is about 1-2 μm . The electrochemical results showed that, the LiFePO_4/C (carbon content was 10 % wt.) cathode material delivers the first discharge capacity of 154 mAh g^{-1} , i.e. 91 % of the theoretical capacity (0.1 C-rate) between 2.5 and 4.5 V (vs. Li/Li^+).

Key Words: Rechargeable lithium batteries, Cathode material, LiFePO_4 .

INTRODUCTION

Last two decades, LiCoO_2 is the most widely used cathode material in the lithium-ion batteries. However, it is relatively expensive and has limited specific capacity. Many research groups are making efforts to find an effective cheap replacement for LiCoO_2 . In 1997 Padhi *et al.*¹ discovered that LiFePO_4 could be used as the cathode material for secondary lithium batteries and much effort has been made to identify the physical and electrochemical properties of this cathode material. LiFePO_4 has an orthorhombic olivine-type structure with the oxygen atoms arranged in a slightly distorted, hexagonal close-packed arrangement. The phosphorous atoms occupy tetrahedral sites while the lithium and iron atoms occupy octahedral sites². LiFePO_4 offers several advantages namely: (i) a relatively high theoretical specific capacity of 170 mAh g^{-1} ; (ii) a perfectly flat discharge voltage at 3.4 V vs. lithium, which provides for a wider safety margin of usage for organic electrolytes; (iii) good reversibility of cathode reactions; (iv) high thermal and chemical stability; (v) low material cost; (vi) low toxicity; (vii) improved safety³. For all these advantages associated with LiFePO_4 , a drawback of this material is its low ionic/electronic

conductivity (10^{-8} to 10^{-10} Scm⁻¹). Due to this low conductivity, the electrochemical properties of this material are limited, especially its rate capability. There are various attempts to solve this problem. Carbon coating is an efficient way to increase the electrochemical performance of these materials as well as to avoid formation of the Fe³⁺ oxidation state.

Various carbon sources have been reported for the LiFePO₄/C composite, *e.g.*, naphthalene tetracarboxylic dianhydride⁴, hydroxyethyl cellulose⁵, sugar⁶ resorcinol-formaldehyde gel⁷, polypropylene⁸ and carbon black⁹.

In this study, a simple synthesis method and inexpensive chemicals in order to keep production costs down and simple have been employed. In this synthesis, the sugar converts carbon at high temperature and inert argon atmosphere and carbon acts as conductive agent. It can control the particle size and conductivity of the result powder and thus affecting the electrochemical performance of LiFePO₄. In addition, excessive amount of carbon causes a significant decrease in the tap density⁶, which brings a drawback for practical applications. When optimizing the amount of carbon in cathode material, we consider the rate of capacity and tap density of cathode material. Therefore, we studied the effect of carbon on the electrochemical properties of materials, adding sugar between the rate of 12.5-100 % wt. into LiFePO₄.

EXPERIMENTAL

The sample was synthesized in two simple steps. In the first step, Fe(NO₃)₃·9H₂O (Merck), LiNO₃ (Riedel-de Haen) and (NH₄)H₂PO₄ (Merck) were dissolved according to the stoichiometric ratio of LiFePO₄ in distilled water. The above solutions were mixed and heated at 70 °C for 4 h with constant agitation to form homogeneous suspension. Then the gel was heated at 300 °C for 6 h to remove water and decomposition of nitrate without reductive atmosphere. The resulting powder was ground and different amounts of white sugar (12.5, 25, 40, 50, 70, 100 % wt.) were added respectively into the obtained powder. In the second step, the resulting mixture was calcined at 700 °C for 10 h under argon gas flow. As a result of this process, six different carbon-coated LiFePO₄ composites were obtained.

Thermogravimetric (TG) analysis of the samples were studied on a Perkin-Elmer, Diamond model thermal analysis apparatus with a heating rate of 10 °C min⁻¹ from ambient to 800 °C in an argon flow. The phase structure of the powder was analyzed by X-ray diffraction (XRD) on a Bruker AXS D8 diffractometer using CuK_α radiation. The Diffrac Plus and Win-Index programs were used to obtain information about the crystal structures and lattice parameters of the prepared samples. The morphologies of the powders were observed using a scanning electron microscopy (SEM, LEO 440), operated at 20 kV.

The amount of carbon in the lithium iron phosphate was determined by heating at 700 °C for 3 h in air¹⁰. The electrical conductivity of carbon coated samples was measured by 4-point probe method.

The electrochemical studies were carried out in two-electrode teflon cells. The cells were fabricated by using the LiFePO_4/C as a cathode and lithium foil as anode. A glass fiber separator soaked in electrolyte separated the two electrodes. The electrolyte consisted of 1 M solution of LiClO_4 dissolved in an ethylene carbonate (Aldrich)/diethyl carbonate (Merck) (EC/DEC, 1:1 ratio by volume). Diethyl carbonate, ethylene carbonate and acetylene black were used after being purified according to the methods given in the literature¹¹.

For the preparation of the cathode composite, a slurry mixed with 80 % wt. of cathode active material, 15 % wt. of carbon additive (including carbon black and carbon converted from sugar) and 5 % wt. of polyvinylidene fluoride (PVDF, Fluka) binder in 1-methyl-2-pyrrolidinone (NMP, Merck) was pasted on aluminium foil current collector with a diameter of 13 mm, followed by vacuum drying at 120 °C for overnight in a vacuum oven and uniaxial pressing between two flat plates at 2 ton for 5 min. The electrode loading was about 5-8 mg of cathode active material.

The test cell performance was measured on a computer-controlled multi channel charge/discharge apparatus (MLab100, Wenking). The electrochemical performances of the test cells were determined by charged/discharged with a constant current density of 0.1 C-rate within a voltage range between 2.5 V and 4.5 V (*vs.* Li/Li^+).

RESULTS AND DISCUSSION

The samples of LiFePO_4/C were synthesized with the addition of 12.5, 25, 40, 50, 70 and 100 % wt. of white sugar as carbon source and it converted into carbon. The percentages of carbon in the samples were found to be 2, 4.5, 7, 10, 12 and 17 % wt., respectively. These six samples are further referred as $\text{LiFePO}_4/\text{C}(X)$ where X denotes the carbon content in the samples. As a residual carbon content increases, the colour of the powder changes progressively from medium to dark grey even to deep black for the sample with 10-17 % wt. carbon. The conversion of sugar to carbon precursor depends appreciably on the processing condition, especially the annealing temperature and duration¹². In this study it is observed that 1 g sugar converted about 0.17 g of carbon.

The DTA/TG result of $\text{LiFePO}_4/\text{C}(10)$ is shown in Fig. 1. The weight loss at temperature between 50 and 140 °C is due to water vaporization. The weight loss in the next step at temperature between 150 and 240 °C is resulted from the decomposition of nitrates in precursor. The residual materials of ammonia was also decomposed before 380 °C. The exothermic peak exhibited at 440 °C in DTA curve is due to the crystallization of LiFePO_4 ¹³. Therefore, it is necessary to calcine the LiFePO_4 precursor above 500 °C to obtain the crystallized phase.

In Fig. 2, the XRD patterns of $\text{LiFePO}_4/\text{C}(10)$ are completely amorphous at 300 °C and that the precursor is transformed into crystalline phase after heating at 700 °C for 10 h under argon gas flow. All peaks of XRD pattern are indexed on an orthorhombic olivine structure type and second phase is not found. The unit cell

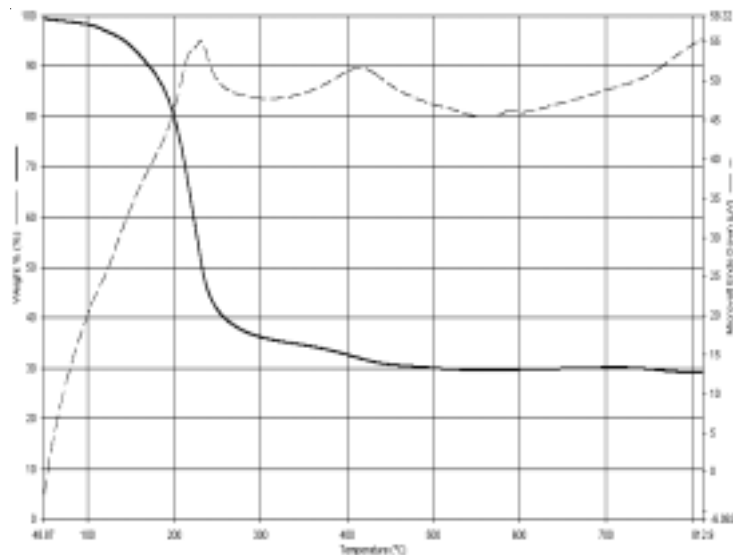


Fig. 1. The DTA/TGA curve for $\text{LiFePO}_4/\text{C}(10)$ over the temperature range from ambient to 800 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C min}^{-1}$ in argon atmosphere

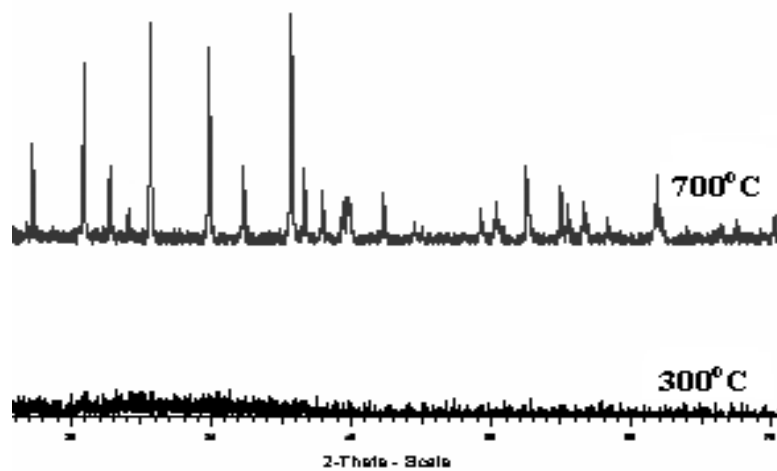


Fig. 2. X-ray diffraction profiles of $\text{LiFePO}_4/\text{C}(10)$ at 300 and 700 $^{\circ}\text{C}$, respectively

parameters for the orthorhombic cell are $a = 10.311 \text{ \AA}$, $b = 6.005 \text{ \AA}$ and $c = 4.689 \text{ \AA}$, which are very close to the Win-Index programs data ($a = 10.33 \text{ \AA}$, $b = 6.01 \text{ \AA}$ and $c = 4.69 \text{ \AA}$) given by JCPDS 81-1173. In addition, the other $\text{LiFePO}_4/\text{C}(X)$ composite samples are indexed on the same orthorhombic olivine structure and a space group of P_{nma} . The carbon in the powder is amorphous form. So, there are no additional peaks on the XRD patterns belonging to its crystal modification. The carbon coating has restricted the undesirable oxidation of Fe^{2+} to Fe^{3+} in the LiFePO_4 and hence resulted in the phase pure formation of sample.

The particle morphology of the powders observed by SEM is shown in Fig. 3. The SEM images show that the average particle size is in the range of 1-2 μm . In addition, the carbon content affects the particle size and homogenous distribution of particles. However, the SEM analysis was difficult to discern carbon from LiFePO_4 powder.

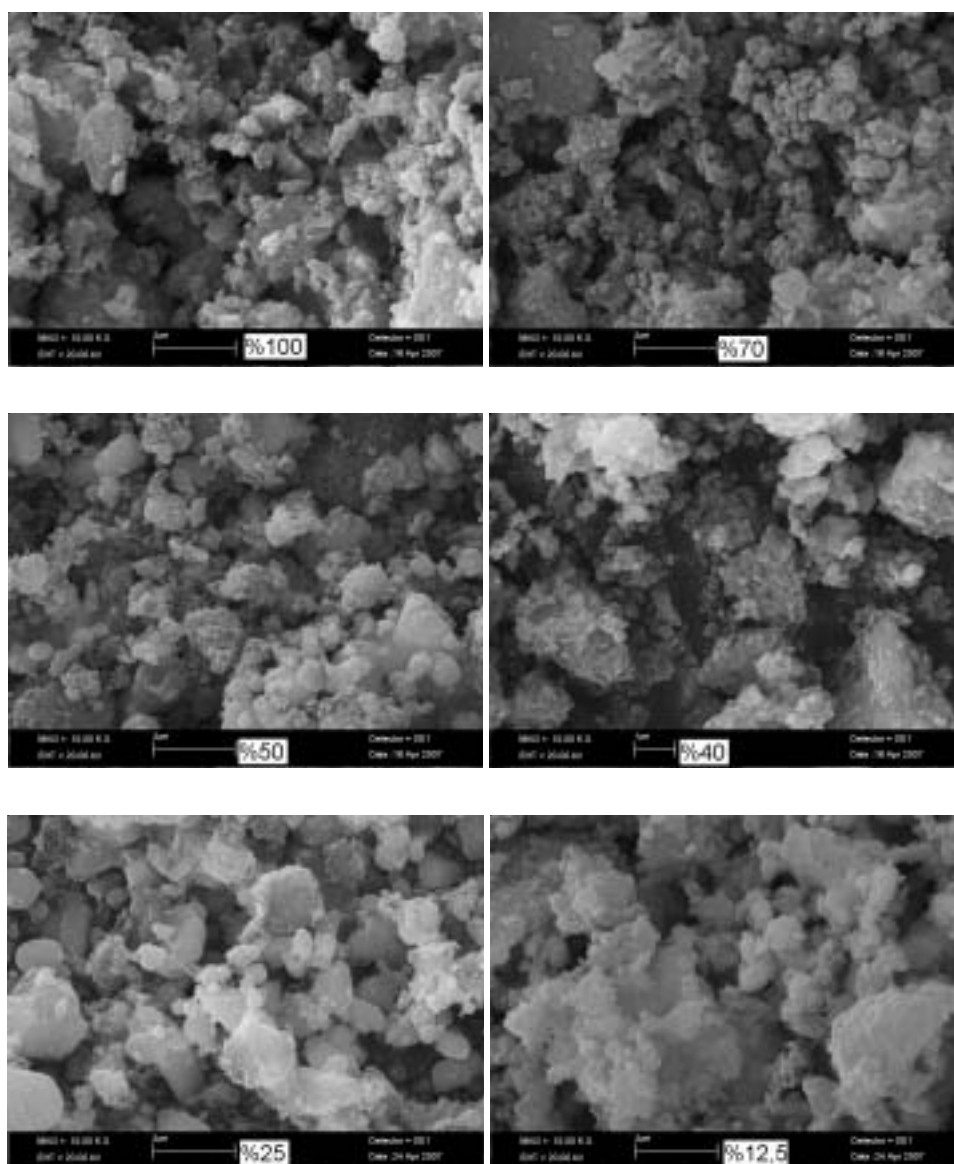


Fig. 3. SEM morphology of the LiFePO_4/C compounds synthesis with different amount of white sugar (12.5, 25, 40, 50, 70, 100 % wt. added into samples)

The samples of LiFePO₄/C have been evaluated as cathode materials for their electrochemical performance in lithium cells at room temperature. The initial charge/discharge performances of the cell with LiFePO₄/C cathodes which has various carbon contents at a constant current density (0.1 C-rate) are compared in Fig. 4. In all of these cathodes, the highest specific capacity is achieved for LiFePO₄/C(10). This cathode exhibits a discharge capacity of 154 mA h g⁻¹ corresponding to 91 % of the theoretical capacity. The first discharge capacities for LiFePO₄/C(2), LiFePO₄/C(4.5), LiFePO₄/C(7), LiFePO₄/C(12) and LiFePO₄/C(17) were 131, 139, 145, 146 and 142 mA h g⁻¹, respectively. It was known that, the carbon coating reduces particle size and enhances the electronic conductivity⁷. In present experiment we measured the electronic conductivity of LiFePO₄/C(10) as $1.4 \cdot 10^{-3} \text{ S cm}^{-1}$ by 4 point probe method. This is a favourable rate as against carbon free LiFePO₄ (10^{-8} - $10^{-9} \text{ S cm}^{-1}$). In Fig. 4, the specific capacity of LiFePO₄/C increases as carbon content increases in the sample. However, when the carbon content is further increases (12-17 % wt), the discharge capacity decreases. This result shows that a large amount of carbon decreases the energy density and electrochemical performance of cathode material. The same result was observed by Huang *et al.*¹⁴.

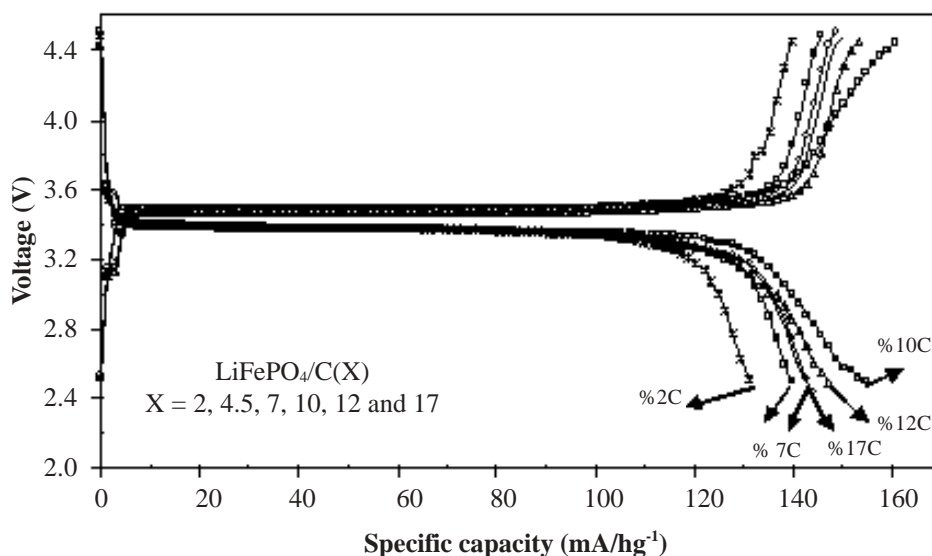


Fig. 4. Initial charge and discharge capacities of lithium cells with LiFePO₄/C samples with various carbon contents as cathodes (current density = 0.1C)

Conclusion

The LiFePO₄/C composites were successfully synthesized by simple and cheap method. White sugar is used as the carbon source and reductive agent. In the synthesis *ca.* 17 % of sugar converted to carbon. It is found that LiFePO₄/C(10) has the best

electrochemical performance which corresponds to 91 % of its theoretical capacity. On the other hand, the lower electrochemical performance is observed, when the carbon content is increased up to a large amount as 12-17 % wt. We studied carbon content between the rate of 2-17 % wt and found that 10 % wt carbon is optimum rate for high electrochemical performance. These results prove that carbon content is an important factor for favourable cathode material. Therefore, battery producers of LiFePO₄ must keep a careful watch on the effect of carbon content on capacity, rate capability and tap density.

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