Journal of Ovonic Research Vol. 15, No. 3, May - June 2019, p. 199 - 204

PREPARATION AND CHARACTERIZATION OF CARBON DOPED LITHIUM IRON PHOSPHATE COMPOSITE AS CATHODE FOR RECHARGABLE BATTERY

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Carbon doped Lithium Iron Phosphate $LiFePO_4/C$ with orthorhombic olivine structure has been successfully prepared by sol-gel method with a new precursor agent. The structure and morphology properties were characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM), atomic force microscopy (AFM) and energy dispersive X-ray (EDX) spectrum. The XRD structural properties show orthorhombic olivine structure with space group (Pmnb), SEM results show that the addition of carbon source reduces the agglomeration of particles and lead to growth in particle morphology for $LiFePO_4/C$. AFM results shows that grains are up to around 65.70 nm for $LiFePO_4$ in diameter and 96.88 nm for $LiFePO_4/C$.

(Received 4 April, 2019; Accepted June 18, 2019)

Keywords: Lithium iron phosphate; Lithium ion battery; Cathode material, Powder fabrication, Composites

1. Introduction

The growing demand for sustainable energy sources and a clean environment has stimulated efforts towards the development of promising devices for energy storage, such as lithium-ion batteries [1,2,3]. Lightweight and high energy density make lithium-ion batteries interesting for portable electronic devices, as well as for electric or hybrid cars with the goal of decreasing CO_2 emissions [3, 4,5]. The carbon coating can considerably enhance the electronic conductivityof $LiFePO_4$, prevent particle growth, inhibit particle agglomeration and increase the contact area between $LiFePO_4$ material and electrolyte. These factors are beneficial to the diffusion of lithium-ion. However, higher carbon contact reduces the volumetric energy density of batteries [6]. Since cathode materials for lithium ion batteries have lower capacity compared with anode materials and it has a high free energy of reaction with the lithium the overall electrochemical performance of lithium–ion batteries is significantly determined by the properties of the cathode materials [7,8]. $LiFePO_4$ can be prepared by different methods, including solid-state reaction, -hydrothermal synthesis and co-precipitation method [9,10,11]. However, these methods include various successive steps of grinding and annealing, which cause an uncontrollable growth and agglomeration of the particles, leading to small surface area values [12]. In this work, we report a simple and easy synthesis route to obtain fine and uniform carbon doped $LiFePO_4$nanoparticles as cathode for lithium ion battery using low cost precursor agents and under normal oxygen atmosphere.

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2. Experimental section

2.1. Sample preparation

$LiFePO_4/C$ composite was prepared using sol-gel method. Stoichiometric weights (1:1:1:1/3) of Lithium Nitrate $LiNO_3$ (98%, Fluka, India), Ferric Nitrate $Fe (NO_3)_3.6H_2O$ (98%, TENAL, Germany), Ammonium Dihydrogen Orthophosphate $NH_4H_2PO_4$ (99%, Central Drug House, India) were dissolved in (60 ml) deionized water which were used as precursor agents. The mixture was heated under stirring at (70-80) °C for several hours, which made the mixture denser and formed the gel. The gels were heated at (100) °C in air for 8 hours so that all the distilled water gets evaporated. The dried gel was calcined in air at (750) °C for 2 hours. After calcination, the powder was ground and pressed to a disk-shaped pellet using up to 7 ton of pressure. Citric Acid $C_6H_8O_7$ (99.5%, SUNKOO Ltd., South Korea) was added as chelating agent and carbon source to $LiFePO_4$ to obtained $LiFePO_4/C$ composite.

2.2. Morphological and structural characterization

The crystalline structure of $LiFePO_4/C$ was analyzed using SHIMADZU (XRD-6000) diffractometer (Cu kα radiation 1.5405 °A). The microstructure of samples was investigated using a scanning electron microscope (SEM) model FEI inspect 50. The morphology was further characterized under an atomic force microscope AA3000 scanning probe microscopy Angstrom Advanced Inc. The chemical composition was determined with an inductively coupled plasma spectrometer and with energy dispersive X-ray spectrometer (EDX) coupled to a FEI inspect 50 scanning electron microscope.

3. Results and discussion

3.1. Crystallographic composition

The X-ray diffraction spectrum for C doped Lithium Iron Phosphate $LiFePO_4/C$ composite synthesized by sol-gel method is presented in Fig. 1. The X-ray analysis show the formation of orthorhombic olivine structure $LiFePO_4/C$ with space group Pmnb (JCPDS 40-1499) agreeing with the results obtained by [13], however, other crystalline phases attributed to $Li_4P_2O_7$ (JCPDS 13-0440), $Li_3Fe_2 (PO_4)_3$ (JCPDS 43-0526), and $Li Fe (P_2O_7)$ (JCPDS 37-0236) were identified using HighScorePlus XRD analyzer software.

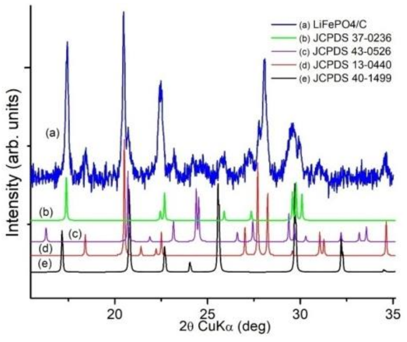

Fig. 1.X-RAY diffraction spectrum for $LiFePO_4/C$ composite.

3.2. Topography aspects

Characterization of the topographical properties of $LiFePO_4$ and $LiFePO_4/C$ synthesis by sol-gel process are presented in Fig. 2 (a and b), respectively. The images showed two distinct average grain size distributions. The large grains may be associated with the grain growth from the smaller grains, or may be agglomerate of small grains. On the other hand, $LiFePO_4/C$ image show regions of agglomerated small particles. In addition, the added carbon prevents the oxidation of Fe^{+2} to Fe^{+3}. It is clearly that the samples have developed grains of regular shape. As can be seen in Fig. 2(b) the particles are more homogeneous, and more uniform in terms of size distribution for the doped samples.

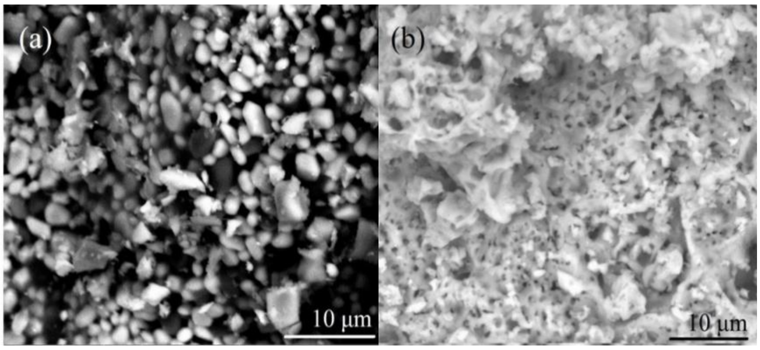

Fig. 2. SEM images of (a) $LiFePO_4$ and (b) $LiFePO_4$ /C.

AFM Atomic force microscopy micrograph of $LiFePO_4$, $LiFePO_4$/C, are presented in Fig. 3 and Fig. 4, respectively were a) 2D, b) 3D and c) Granularity cumulation distribution chart. It can be seen in Fig. 3 that sample is consisting of regular spherical shape and the grain distribution over the surface which seem to be uniform. Fig. 4 shows the effect of C doping on $LiFePO_4$. The average grain size and average surface roughness were listed in Table 1, which indicate a nanostructure dimensions for these samples.

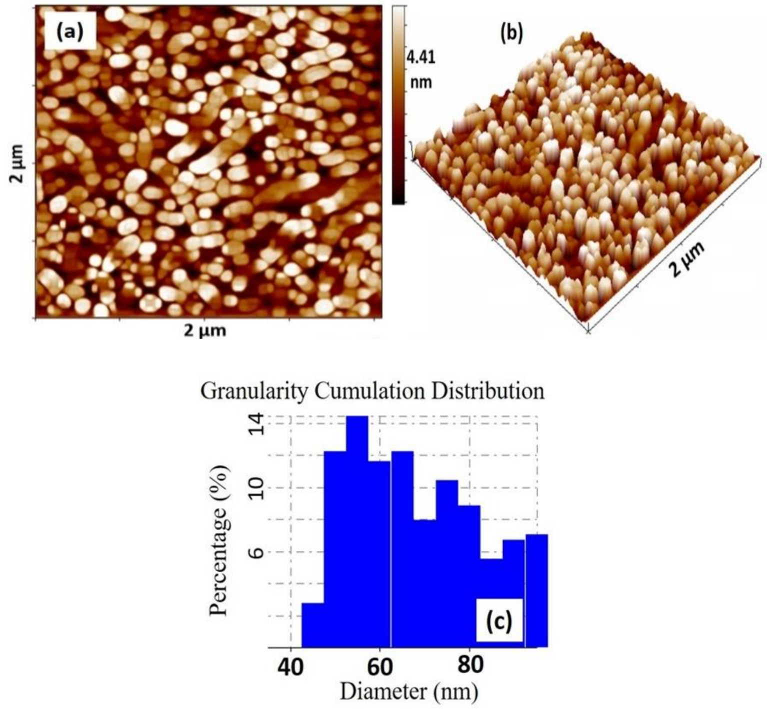

Fig. 3.AFM micrograph for $LiFePO_4$ (a) 2D (b) 3D and (c) Granularity cumulation distribution chart.

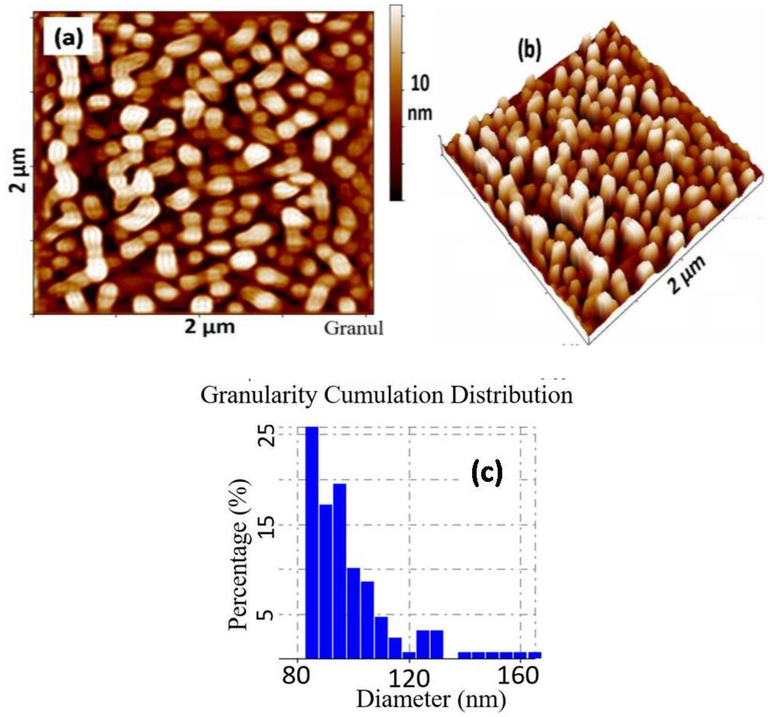

Fig. 4. AFM micrograph for $LiFePO_4/C$ (a) 2D (b) 3D and (c) Granularity cumulation distribution chart.

Table 1. Shown average grain size and surface roughness for pure $LiFePO_4$ and C doped $LiFePO_4$ using AFM.

Sample	average grain size(nm)	Average surface roughness(nm)
$LiFePO_4$	65.70	0.998
$LiFePO_4/C$	96.88	2.58

Furthermore, in order to characterize the elemental composition of $LiFePO_4/C$ cathode material, energy dispersive X-ray (EDX) was used. The EDX quantifications for $LiFePO_4/C$ composite presented in Table 2. The results reveal the existence of C, O, Fe, and P atoms; Li is not detected by standard EDX detectors so it cannot be quantified through this technique. However, one can observe there are no other peaks for impurities present in Fig. 5, showing pure $LiFePO_4$ and C as a weak peak as EDX is not very sensitive for C characteristic radiation. The atomic ratio Fe:P:O:C was found to be approximately (10:19:6:5) as shown in Table 2 for $LiFePO_4/C$, however, EDX is not a rigorous technique for chemical analyze but it is good enough for element identification.

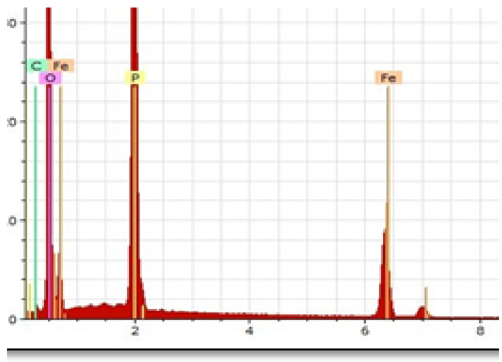

Fig. 5.EDX spectrum for $LiFePO_4/C$.

Table 2. EDX elemental ratio for C doped LiFePO$_4$.

Element	Weight (%)	Atomic (%)	Error (%)
O	47.31	66.35	5.38
P	26.58	19.26	0.98
Fe	23.44	9.42	0.64
C	2.66	4.97	0.73

The $LiFePO_4$ cathode material have been doped with carbon as conductive additive to improve the electrical conductivity of the $LiFePO_4$ nanostructure which are known to have low electrical conductivity [14,15], and additionally, the carbon additive increases the porosity of cathode material, consistent with the SEM and AFM results, carbon coatings lead to increase the surface area, therefore leading to an improvement in the cathode capacity [16,17,18]. It is an indication that the combination of carbon layer and the nano-scale particle size is crucial to the quick intercalation/deintercalation for sodium ions with the olivine structure.

4. Conclusions

Olivine cathode materials $LiFePO_4$ and $LiFePO_4$/C were successfully prepared through an innovative sol-gel method using citric acid as carbon sources. $LiFePO_4$/C shows sharp diffraction peaks, which indicates that the samples have good crystalline structure. SEM images show a uniform particle distribution for $LiFePO_4$ and this distribution became less because the additives, these results were ensured by AFM result. EDX quantification of C, O, Fe and P is consistent with XRD analysis and proves chemical purity of the $LiFePO_4$/C composite.

Acknowledgements

This work was supported by the Ministry of Science and Technology in Baghdad-Iraq and Baghdad University.

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