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The use of Raman and XPS spectroscopy to study the cathode material of LiFePO_4/C

VADYM GALAGUZ*, OLEKSANDR KORDUBAN, EDUARD PANOV
and SERGIY MALOVANYI

V. I. Vernadsky Institute of General and Inorganic Chemistry of the National Academy of Sciences of Ukraine, 32-34 Acad. Palladina Ave., Kyiv, 03142, Ukraine

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Abstract: Using Raman spectroscopy and X-ray photoelectron spectroscopy, synthesized lithium iron(II) phosphate (LiFePO_4) and carbon coated nanocomposites LiFePO_4/C , synthesized by annealing LiFePO_4 with glucose for 1 and 12 h at 700 °C, have been investigated. According to XPS data, the synthesis conditions of LiFePO_4/C nanocomposite (700 °C, 1 h) facilitate the reduction of iron, $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$, on the sample surface. Also according to C1s spectra, $\text{sp}^2\text{C}-\text{sp}^2\text{C}$ is the main bond type in the samples under investigation. Contributions relating to C–O, C=O, C–O–C, O–C=O functional groups are also present. According to X-ray diffraction analysis, a 12-h synthesis of LiFePO_4/C nanocomposite leads to the formation of impurities. According to Raman spectra, the annealing time does not affect the quality of carbon coating: the peak intensity ratio of bands D and G has a value of 1.06 for the material annealed for 1 h and 1.04 for LiFePO_4/C nanocomposite after annealing for 12 h.

Keywords: battery cathodes; functional groups; Li-ion.

INTRODUCTION

Lithium iron(II) phosphate (LiFePO_4) is one of the most promising materials for lithium-ion battery cathodes. It has a fairly high theoretical capacity (170 mAh g^{-1}) and can withstand a large number of charge/discharge cycles; LiFePO_4 is also an eco-friendly and cheap material. However, the disadvantages of LiFePO_4 are the low ionic conductivity (because of the low diffusion coefficient of lithium ions, $D_{\text{Li}} = 10^{-15} \text{ cm}^2 \text{ s}^{-1}$) and electronic conductivity ($10^{-9} \text{ S cm}^{-1}$). One of the main ways of increasing the electronic and ionic conductivity is the coating the LiFePO_4 particles with an electrically conductive addition and reducing the diffusion path of lithium ions by the synthesis of LiFePO_4 nanocrystals.^{1,2} The most commonly used component up to date is carbon and its modi-

* Corresponding author. E-mail: vgalaguz@ukr.net
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fications. The main role of the carbon coating is to increase the surface electronic conductivity of powder nanocrystals, which makes it possible to fully use LiFePO_4 active mass. The carbon coating also reduces the crystal growth rate and prevents the agglomeration of particles during synthesis. An important role of carbon is to create a reducing medium, which prevents the oxidation of Fe^{2+} . The carbon coating can be produced directly by adding carbon of various kinds to a mixture of precursors or during annealing in the pyrolysis of organic compounds. It is considered now that the coating produced during the thermal decomposition of organic compounds is more uniform, and that its structure and electronic conductivity depend on the carbon source and annealing temperature; the annealing time usually varies between 1 and 12 h and depends on the degree of crystallinity of synthesized LiFePO_4 . For an amorphous product, annealing is carried out longer (for ~ 12 h), for its goal in this case is not only to obtain a carbon phase, but also to form a crystal structure.^{1–4}

The paper present the results of investigating lithium iron(II) phosphate, which has been synthesized in an ionic liquid of the composition choline chloride/diethylene glycol, and a carbon composite based on it. To investigate the carbon coating of LiFePO_4/C and the effect of the high-temperature annealing stage on LiFePO_4 (assess possible iron oxidation), Raman spectroscopy and X-ray photoelectron spectroscopy were used.

EXPERIMENTAL

The synthesis of LiFePO_4 was carried out in a liquid-phase reaction medium, choline chloride (ChCl)–diethylene glycol (DEG), using precursors NH_4FePO_4 and CH_3COOLi . Nanocrystalline LiFePO_4 (sample 1) was prepared after 1 h of synthesis at 245 °C. The precipitate (LiFePO_4) was washed in the distilled water, ethanol and acetone separated by centrifugation and dried.⁵

To synthesize a LiFePO_4 -based carbon nanocomposite, synthesized LiFePO_4 powders were soaked in a glucose solution, dried and annealed in an inert argon atmosphere at 700 °C for 1 (sample 2) and 12 h (sample 3) to carbonize the precursor.

The X-ray diffraction analysis (XRD) patterns of powders were obtained using a DRON-4 diffractometer with $\text{CuK}\alpha$ radiation. The Raman spectra were taken with a DFS52 micro-Raman spectrometer, fitted with a CDD detector, using a solid-state laser with an emission wavelength of 532 nm. The research was carried out at room temperature in an optical vibration range of 800–1800 cm^{-1} . The electronic structure of the surface of LiFePO_4/C and LiFePO_4 was explored by method of X-ray photoelectron spectroscopy (XPS) by spectrometer with EC-2402 energy analyzer ($E_{\text{MgK}\alpha} = 1253.6$ eV, $P = 300$ W). The spectra of $\text{Fe}2p_{3/2}$ -level were decomposed into separate peaks, $FWHM = 1.9$ eV. The decomposition was carried out by Gauss–Newton method. The area of peaks was determined after subtraction of background by Shirley method.⁶

RESULTS AND DISCUSSION

For the LiFePO_4/C composite, synthesized at 700 °C for 1 and 12 h, XRD spectra have been obtained (Fig. 1). For LiFePO_4/C synthesized at 700 °C for 1 h, there are no additions (within the sensitivity of the XRD method, all reflect-

ions are consistent with JCPDS: 00-40-1499). On XRD spectra of LiFePO₄/C powder, which was synthesized for 12 h, Li₃PO₄, Li₃Fe₂(PO₄)₃, Fe₂O₃ or iron phosphides additions are present.

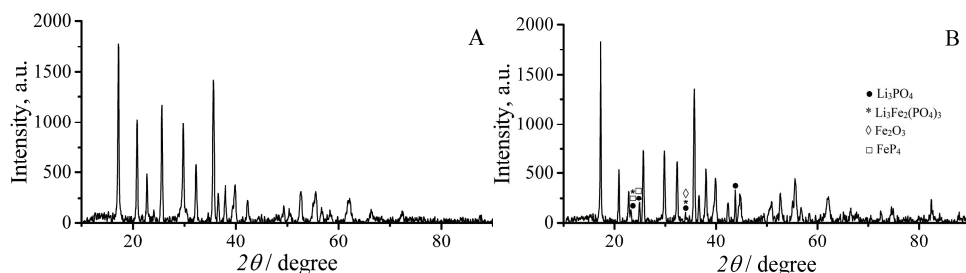


Fig. 1 XRD spectra of LiFePO₄/C after annealing for 1 (A) and 12 h (B).

Using Raman spectroscopy, we have studied the nature of the carbon coating on LiFePO₄ crystals. Raman spectra for two samples obtained after annealing for 1 (sample 2) and 12 h (sample 3) are shown in Fig. 2. The LiFePO₄/C samples showed two intense broad bands at ~1340 and ~1600 cm⁻¹, which are usually observed in disordered carbon black and are designated as bands D (disorder/defect band) and G (graphitic band).

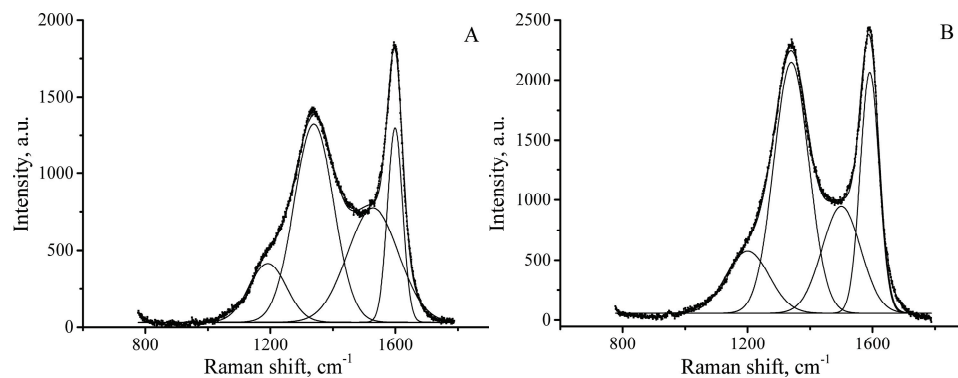


Fig. 2 Raman spectra of LiFePO₄/C obtained after the carbonization of glucose for 1 (A) and 12 h (B).

For D and G, a procedure of decomposing peaks using Gaussian–Lorentzian function was employed. We analyzed four peaks at ~1200, 1340, 1520 and 1600 cm⁻¹, which are analogous to the curves presented in literature.^{7–11} Two broad bands of them at ~1340 and ~1600 cm⁻¹ correspond to D and G (graphitic band) carbon particles respectively. The range ~1600 cm⁻¹ is associated with graphite stretching mode E_{2g}. Band D with a frequency of ~1340 cm⁻¹ is associated with A_{1g} mode vibration. It is related to different disorder types in the graphite structure (in the graphene layer): graphite domains of finite size, grain faces, sub-

stitution of C atoms by N or other additions, sp^3 hybridized carbon, *etc.*^{7–9} Two additional bands, which are necessary for satisfactory analysis, are located at ~ 1200 and 1520 cm^{-1} related to sp^3 -type carbon, which is often observed in amorphous carbon compounds. To assess the nature of the carbon coating using decomposed spectra, the peak intensity ratio of bands D and G ($I_D/I_G = I_{1340}/I_{1600}$) is used. Smaller I_D/I_G values indicate a more conductive structure (mainly sp^2 bond). The ratio sp^2/sp^3 of carbon, $I_{sp^2}/I_{sp^3} = (I_{1340} + I_{1600})/(I_{1200} + I_{1520})$, is also determined. It is considered that the bands at ~ 1340 (D range) and 1600 cm^{-1} (G range) correspond to a graphite-like structure and the other two bands at ~ 1200 and $\sim 1520\text{ cm}^{-1}$ to sp^3 -like disordered carbon. Higher ratios sp^2/sp^3 correlate with the more graphite-like nature of the carbon coating and hence with higher electronic conductivity.^{7–11} In our work, a fraction of sp^2/sp^3 carbon is estimated using only one excitation line at 523 nm and can be used, as was shown in⁷, as a semiquantitative estimate.

The Raman spectra (Fig. 2) of the LiFePO_4/C composite obtained from a powder annealed with glucose for 1 and 12 h have pronounced D and G peaks, as well as two additional bands, obtained after the decomposition of the peaks. The peak intensity ratio of bands D and G has a value of 1.06 for the material annealed for 1 h and 1.04 for LiFePO_4/C after annealing for 12 h, which is a good indicator and correlates with the results of other investigations of the carbon coating LiFePO_4/C (I_D/I_G of 1–3).^{7–11} For samples 2 and 3, synthesized for 1 and 12 h, the sp^2/sp^3 values of carbon are 2.23 and 2.76, respectively. This indicates that the optimal annealing regime is the carbonization of carbon precursor for 1 h at $700\text{ }^\circ\text{C}$. Increasing the annealing time results in a partial oxidation of LiFePO_4 , but does not affect the nature of pyrolytic carbon.

For LiFePO_4/C nanocomposite samples, XPSs of C1s, $\text{Fe}2p_{3/2}$ -, Li1s-, P2p- and O1s- inner levels have been obtained. To assess the nature of the carbon coating, a deconvolution of the C1s spectrum has been performed (Fig. 3). The

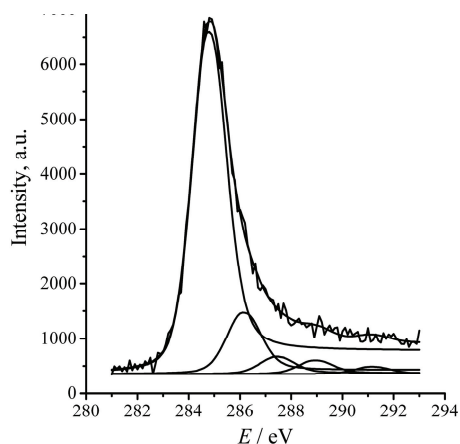


Fig. 3. XPS of the C1s level of a LiFePO_4/C composite (sample 2).

dominating contribution to the C1s spectrum (77.5 %) with $E_b \approx 284.75$ eV relates to the sp²-hybridization of carbon (sp²C–sp²C) with C–C or C=C bonds (Table I). Components are also present, which can be assigned to oxygen-containing C–O ($E_b = 286.1$ eV); C=O ($E_b = 287.4$ eV); C–O–C; O–C=O ($E_b = 288.9$ eV) functional groups, peak at 291.2 eV can be determined as π – π shake-up satellite.^{12–14}

TABLE I. Results of the deconvolution of the C1s spectrum of a LiFePO₄/C composite (sample 2)

E_b C1s / eV	Content, at. %	Components
284.75	77.5	C–C, C=C (sp ²)
286.1	13.5	C–O
287.4	4.0	C=O
288.9	3.2	C–O–C, O–C=O
291.2	1.8	π – π

To assess possible iron oxidation by the action of oxygen and water, which escapes during the pyrolysis of organic precursors, Fe2p_{3/2} spectra of starting LiFePO₄ (sample 1, Fig 4, A) and a LiFePO₄/C composite (sample 2, Fig. 4, B), synthesized at 700 °C for 1 h, have been examined. The spectra of 709.6–711.3 eV relate to the Fe²⁺ states of iron, and those formed by components in a range of 712.6–714.5 eV relate to the Fe³⁺ states of iron in LiFePO₄; these data correlate with the results from the references.^{15–17} The peaks with energies of 716.1 and 718 eV are satellites, which correspond to the Fe²⁺ and Fe³⁺ states, respectively (Table II).

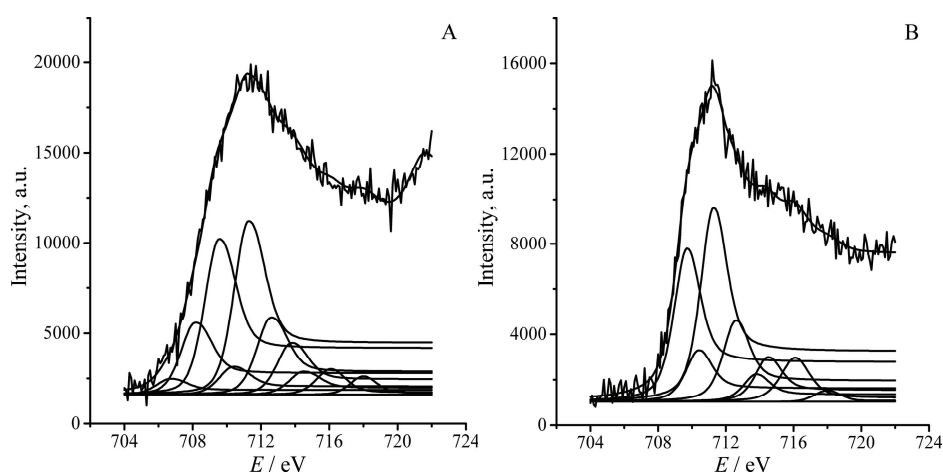


Fig. 4. XPS of the Fe2p_{3/2} levels of the starting compound LiFePO₄ – sample 1 (A) and a LiFePO₄/C composite – sample 2 (B).

In the Fe2p_{3/2} spectrum of sample 1, components at E_b Fe2p_{3/2} 706.7 and 708.2 eV, are also present, which are described in literature as “pre-peaks”.¹⁸ These low-energy peaks may results from the deeper reduction iron. The peaks with energies close to 708.2 eV are described in¹⁸ as corresponding to Fe²⁺ in the FeO (708.4 eV) and Fe₃O₄ (708.3 eV) phases.

TABLE II. Bond energies (E_b) of components in Fe2p_{3/2} spectra

LiFePO ₄ (Fig. 4, A)		LiFePO ₄ /C (Fig. 4, B)		Component
E_b , (Fe2p _{3/2}) / eV	Content, at. %	E_b (Fe2p _{3/2}) / eV	Content, at. %	
706.7	1.8	–	–	Pre-peak
708.2	11	–	–	
709.6	25.6	709.7	24.2	Fe ²⁺
710.4	3.9	710.4	8.2	
711.3	28.4	711.3	32.0	Fe ³⁺
712.6	12.1	712.6	13.2	
713.8	8.0	713.8	4.6	
714.5	3.3	714.5	7.4	
716.1	3.8	716.1	8.4	Fe ²⁺ sat
718.0	2.1	718.0	2	Fe ³⁺ sat

To assess influence of the annealing of the original sample with glucose, Fe²⁺/Fe³⁺ ratio values have been obtained for sample 1 (LiFePO₄) and sample 2 (LiFePO₄/C), which are $61.7/25.5 = 2.4$ and $72.8/27.2 = 2.7$, respectively. This indicates that the conditions of LiFePO₄/C synthesis at 700 °C for 1 h not only prevents the rise of the oxidation of LiFePO₄, but also initiate a reduction reaction, Fe³⁺ → Fe²⁺, on the LiFePO₄ surface through the pyrolysis of an organic precursor.

CONCLUSION

A procedure for the preparation of LiFePO₄/C nanocomposite (LiFePO₄ nanocrystals with conductive carbon coating) has been optimized, and the methods of its diagnosis: routine monitoring (X-ray photoelectron and Raman spectroscopy) of the iron (II) content of the LiFePO₄ surface layer and the nature of carbon in LiFePO₄/C have been proposed. According to the Raman spectra, the annealing time does not affect the quality of the carbon coating. The peak intensity ratio of bands D and G has a value of 1.04–1.06 for the materials annealed for 1–12 h; however, the increase of the annealing time results in the formation of impurities. According to XPS, the dominating contribution to the C1s spectrum (77.5 %) with $E_b \approx 284.75$ eV relates to sp²C–sp²C (C–C or C=C) bond. There are also components which can be assigned to oxygen-containing C–O, C=O, C–O–C and O–C=O functional groups. Using an XPS analysis, it has been found that the prosed LiFePO₄/C nanocomposite formation conditions (700 °C, 1 h) not only prevents the rise of the oxidation of LiFePO₄, but also initiate

the reduction $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ on the material surface through the pyrolysis of glucose.

ИЗВОД

ИСПИТИВАЊЕ КАТОДНОГ МАТЕРИЈАЛА LiFePO₄/C РАМАНСКОМ И XPS СПЕКТРОСКОПИЈОМ

VADYM GALAGUZ, OLEKSANDR KORDUBAN, EDUARD PANOV и SERGIY MALOVANYI

V. I. Vernadsky Institute of General and Inorganic Chemistry of the National Academy of Sciences of Ukraine, 32-34 Acad. Palladina Ave., Kyiv, 03142, Ukraine

Синтетисани литијум-гвожђе(II)-фосфат (LiFePO₄) и нанокмозити LiFePO₄/C прекривени слојем угљеника, добијени одгревањем LiFePO₄ са глукозом у току 1 и 12 сати на 700 °C, испитивани су коришћењем раманске спектроскопије и фотоелектронске спектроскопије X-зрачења. XPS резултати показују да услови синтезе LiFePO₄/C нанокмозита (700 °C, 1 h) подстичу редукцију гвожђа, $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$, на површини узорка. Такође на основу C1s спектра, $\text{sp}^2\text{C}-\text{sp}^2\text{C}$ је главни тип везе у испитиваним узорцима. Доприноси који потичу од C–O, C=O, C–O–C, O–C=O функционалних група су такође детектовани. Резултати дифракције X-зрачења указују да дванаесточасовна синтеза LiFePO₄/C нанокмозита доводи до формирања нечистоћа. На основу раманских спектра закључено је да време одгревања не утиче на квалитет слоја угљеника: однос интензитета D и G трака има вредност 1,06 за материјал одгреван један сат и 1,04 за нанокмозит LiFePO₄/C одгреван 12 h.

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