



Raman spectroscopy of carbon-coated LiCoPO₄ and LiFePO₄ olivines

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ABSTRACT

The effect of laser power on the Raman spectra of two carbon-coated nano-powders of LiCoPO₄ and LiFePO₄ olivine cathode materials were investigated. In the ambient atmosphere at a moderate laser power, the phenomenon of the removal of the carbon coating layer from both samples was detected. The olivine structure of LiCoPO₄-C powder therefore remains unchanged during the prolonged exposure to a 4.3 mW laser beam. The mild removal of the carbon layer makes it possible to analyze the details of the LiCoPO₄ structure in air without interference from carbon.

LiFePO₄-C powder, together with carbon layer gasification, undergoes oxidative decomposition by the oxygen with the formation of Li₃Fe₂(PO₄)₃ and Fe₂O₃, even at a laser power of 1 mW. Thus, care should be taken when measuring and interpreting the Raman spectra of this material both in air and in an inert atmosphere, as obvious decomposition of the LiFePO₄ olivine structure takes place even at a moderate power of the excitation laser.

A comparative study of the stability of these two carbon-coated nano powders under laser beam irradiation and heating was carried out with the use of TGA-mass spectrometry.

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1. Introduction

Li transition metal phosphates with olivine structure LiMPO₄ (M=Mn, Fe, and Co) have attracted much attention as cathode materials for Li-ion batteries due to their promising electrochemical properties [1,2]. One of the inherent difficulties which limits electrochemical response of these materials is their extremely low electronic conductivity. For LiFePO₄ at room temperature, its electronic conductivity is around 10⁻⁹ S cm⁻¹ [3] and the electronic conductivity of LiCoPO₄ is even much lower than that for LiFePO₄ and reach only ~10⁻¹⁵ S cm⁻¹ [4,5]. Several methods have been used to increase the electronic conductivity of phospho-olivines, among which are doping on either the Li⁺ or M²⁺ site with aliovalent elements and coating the particle surface with an electronic conductor, mostly with carbon. Another factor which substantially affects the performance of these substances is their particle size [6]. The use of nano-sized particles of olivine materials reduces the transport length for lithium ions and electrons, thus enhancing the electrodes' performance [7]. On this basis, carbon-coated nano-particles of phospho-olivines are the most commonly used form of an active electrode material for electrode preparation,

ensuring the optimal electrochemical performance of these materials.

Raman spectroscopy is a very sensitive tool for studying the structure of the lithium intercalation compounds used in Li-battery technology and for following the dynamics of lithium intercalation into different host materials [8–10]. Phospho-olivines, along with the most of the other electrode materials, are Raman active compounds [11–14]. The process of lithium intercalation and deintercalation into the olivine structure may be followed by Raman spectroscopy because the vibrational modes of the PO₄³⁻ anions are sensitive to the presence of lithium ions in the crystal structure. However, the presence of the carbon coating layer on the surface of the commonly used olivine electrode materials attenuates the signal from the olivine structure and hampers the analysis of the spectral features of the bulk material. In addition to that, it was shown that a FePO₄ olivine is unstable under local heating due to exposure to the laser beam [15]. Ramana et al. [14] pointed out the possibility of the photodecomposition of LiFePO₄ samples and their delithiated phases, and used an excitation laser power lower than 10 mW to prevent the destruction of the samples. Galinetto et al. [16] investigated the effect of laser irradiation on the thermal stability of LiFePO₄. They showed that its stability upon laser irradiation depends on the synthesis route, or more specifically, on the grain size and degree of order of the olivine structure. In the present work we show some peculiarities of the

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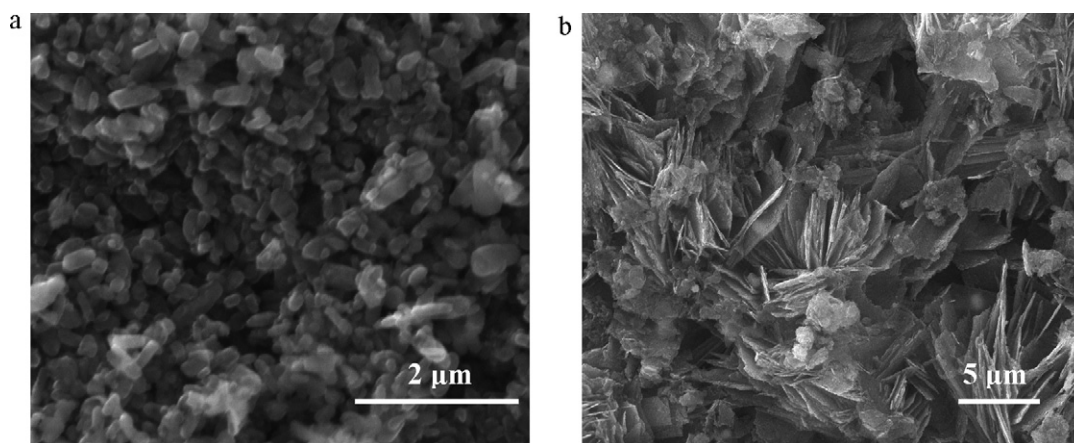


Fig. 1. SEM images of the carbon coated LiFePO₄ (a) and LiCoPO₄ (b) powders.

Raman spectroscopy analysis of carbon-coated nano-powders of phospho-olivines, and demonstrate the capabilities and limitations of Raman micro-spectrometry for the study of these materials.

2. Experimental

LiCoPO₄ was synthesized by hydrothermally treating a mixture prepared from aqueous solutions of LiOH, a soluble Co salt and H₃PO₄. The obtained hydrothermal product was filtered, washed, and subsequently mixed with a carbon precursor. After drying the mixture was pyrolyzed at 750 °C under inert atmosphere and a black powder of C-coated LiCoPO₄ was obtained [17]. The carbon content in the samples was determined by an Eager, Inc. Model 200 C, H, N, S analyzer. The surface area of the samples was calculated using the BET equation from the adsorption isotherm data, determined by N₂ gas adsorption at 77 K using an Autosorb-1-MP apparatus (Quantachrome Corporation). High resolution scanning electron microscopy (HR-SEM) imaging, using a JEOL-JSM 700F instrument was performed to estimate the average particle size and morphology. The results are shown in Table 1.

The cathode sheets were fabricated by spreading slurry (suspension of active cathode material powder and carbon black in a PVDF/N-methylpyrrolidone solution) on an aluminum foil current collectors with a doctor blade device. The electrolyte solution was 1 M LiPF₆ in an EC+DMC 1:1 mixture (Li-battery grade from Merck KGaA). Two electrode cells comprising LiFePO₄ or LiCoPO₄ composite electrodes, separators, electrolyte solution and Li foil negative electrodes were assembled in a glove-box filled with pure argon and sealed in 2032 coin-cells (NRC, Canada). Galvanostatic charge–discharge tests of the cells were carried out using an Arbin model BT2000 battery tester (Arbin Instruments, USA).

Raman spectra were measured in a back scattering configuration using a micro-Raman spectrometer HR 800 (Jobin Yvon Horiba), with a He–Ne laser (excitation line 632.8 nm) and a microscope objective (×50, Olympus LWD). The power of the laser beam on

the sample was varied between 0.37 and 4.3 mW. The diameter of the laser beam on the sample was ~1.4 μm.

The measurements of Raman spectra under inert atmosphere were conducted in an air-tight cell made of pyrex under the flow of pure helium. The cell was assembled in a glove box filled with ultra high-purity argon gas. For measurements in the inert atmosphere the samples were pre-dried in vacuum at 120 °C for 6 h.

Thermogravimetric analysis (TGA-MS) was performed using a TA TGA Q500 system combined with a mass spectrometer (MS), Thermostat Model, Pfeiffer. Experiments were carried out in alumina crucibles in air or pure argon (99.999%) with a heating rate of 10 °C min⁻¹ and a gas flow rate of 120 ml min⁻¹. Mössbauer measurements were carried out by Prof. Israel Novik at the Hebrew University, Jerusalem. The experimental details are described in [18]. Inductively coupled plasma (ICP) analysis was performed using the spectrometer model Ultima 2 from Jobin Yvon Horiba Inc.

3. Results and discussion

SEM images of LiFePO₄/C and LiCoPO₄/C powders are shown in Fig. 1, and initial charge–discharge curves for both cathode materials are demonstrated in Fig. 2.

A typical spectrum of a carbon-coated olivine is shown in Fig. 3a. The carbon layer makes it difficult to see the details of the spectrum of the olivine structure due to the attenuation of the signal and the overlapping of the spectral bands. Only a very weak sig-

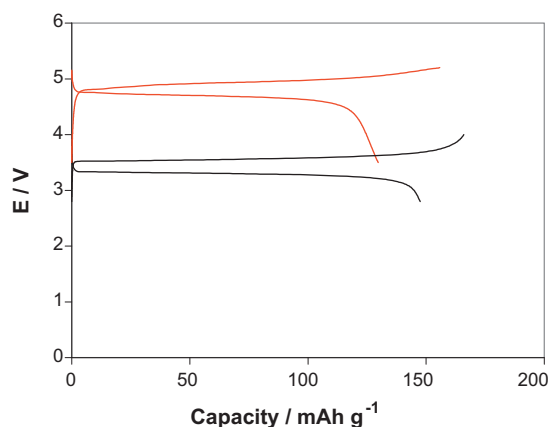


Fig. 2. Initial galvanostatic charge and discharge curves of LiFePO₄/Li (black) and LiCoPO₄/Li (red) cells, C/8, 30 °C. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Characteristics of the carbon-coated nano-powders.

Olivine powder	Carbon content (wt%)	BET surface area (m ² g ⁻¹)	Particles size (nm)
LiFePO ₄	2.4	13.5	Rods of 100–500 nm in length and of about 60–90 nm in diameter
LiCoPO ₄	1.8	21.3	Tens of nanometers

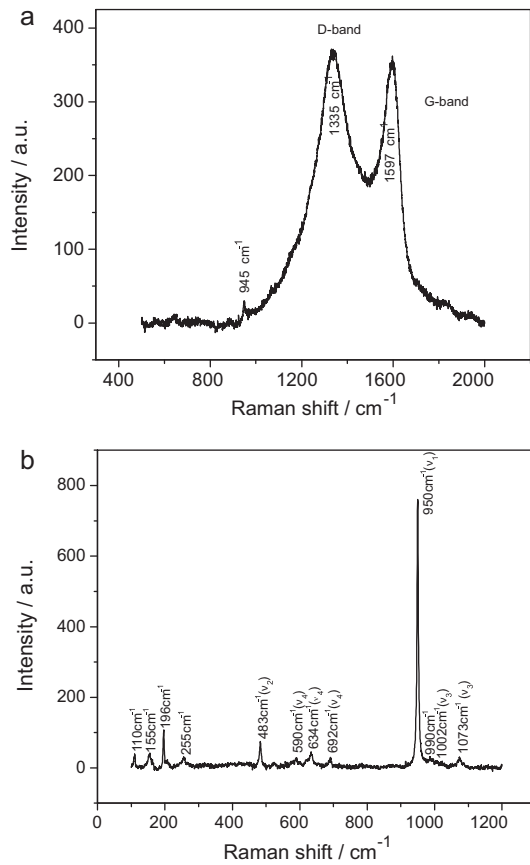


Fig. 3. Raman spectra of LiCoPO₄ olivines collected with 633 cm⁻¹ He–Ne laser: (a) carbon coated LiCoPO₄ olivine and (b) uncoated LiCoPO₄.

nal at 945 cm⁻¹ related to PO₄³⁻ anion symmetric stretching (the strongest peak in the olivine spectrum) is sometimes observed. The Raman spectrum of the uncoated LiCoPO₄ is shown in Fig. 3b. Three bands in the Raman spectrum of LiCoPO₄ are observed between 1100 and 900 cm⁻¹. The very sharp band at 950 cm⁻¹ is attributed to the A_g mode of ν₁ (intramolecular symmetric vibrations of the PO₄³⁻ anion), while the two weaker bands (1002 and 1070 cm⁻¹) belong to the asymmetric stretching modes of the PO₄³⁻ anion (ν₃). The bands observed between 400 and 800 cm⁻¹ ν₂ and ν₄ comprise bending modes of a PO₄³⁻ anion.

We found that at a moderate power of laser beam the carbon coating layer can be removed from the surface of LiCoPO₄ particles in air without damaging the structure of the underlying olivine (Fig. 4). It is known that transition metals, among which is Co, are effective catalysts in the carbon gasification processes, carried out under oxidative atmosphere [19,20]. Obviously, in our case Co²⁺ cations of LiCoPO₄ catalyze the process of carbon oxidation by oxygen in air. The photocatalysis of the laser can also not be excluded.

As a result of carbon gasification, the spectrum of the olivine becomes more pronounced. Fig. 4 illustrates this phenomenon for carbon-coated LiCoPO₄ powder. It is seen that during the exposure of the sample to the laser beam, the ratio of intensities of the olivine band at 945 cm⁻¹ (ν₁) and the bands related to carbon (D-band at 1340 cm⁻¹ and G-band at 1580 cm⁻¹) grows. All the peaks with a lower intensity related to the olivine structure progressively appear as the carbon layer is removed.

In Fig. 5 one can see Raman spectra of LiCoPO₄-C sample as a function of exposure time at a laser power of 4.3 mW. The figure demonstrates the retention of the olivine structure over 18 h of exposure of the electrode to the laser beam with power of 4.3 mW. Thus, LiCoPO₄ is sufficiently stable to be analyzed by Raman spec-

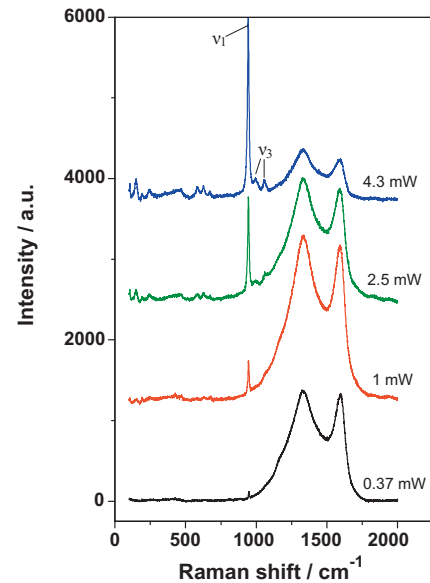


Fig. 4. Raman spectra of LiCoPO₄ carbon coated olivine powder as a function of power with 633 cm⁻¹ He–Ne laser collected in air.

troscopy in air when its carbon-coating layer undergoes oxidation. It is worth noting that such Raman analysis could be performed just in the air (oxygen) media, because in an inert atmosphere one cannot achieve the mild removal of the carbon coating layer as a result of its oxidation and gasification. Hence the spectra of the active mass are attenuated by the carbon coating, when the atmosphere of the measurement is inert.

A completely different type of situation occurs in the case of carbon coated olivine LiFePO₄. Fig. 6a demonstrates the process of the oxidative laser induced decomposition of LiFePO₄ carbon coated olivine powder. The spectra were collected subsequently with 633 cm⁻¹ He–Ne laser of different power levels in air. It is interesting that nearly the full gasification of carbon occurred, even at a laser power of 2.5 mW during the spectrum acquisition. As this takes place, the spectrum of the PO₄³⁻ units totally changes. Instead of three bands related to the vibrations of the phosphate anions in

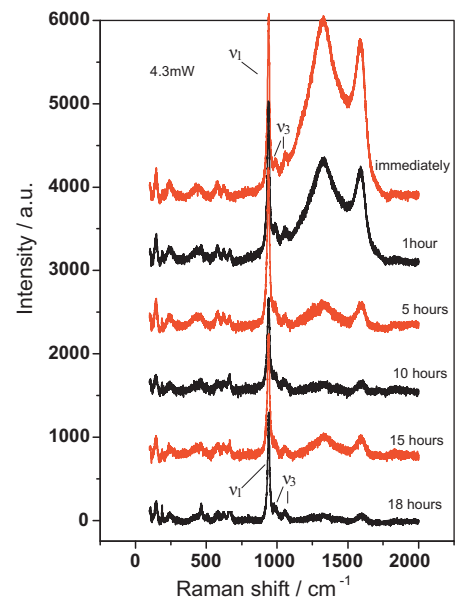


Fig. 5. Raman spectra of LiCoPO₄ carbon coated olivine powder collected in air as a function of exposition time at laser power of 4.3 mW.

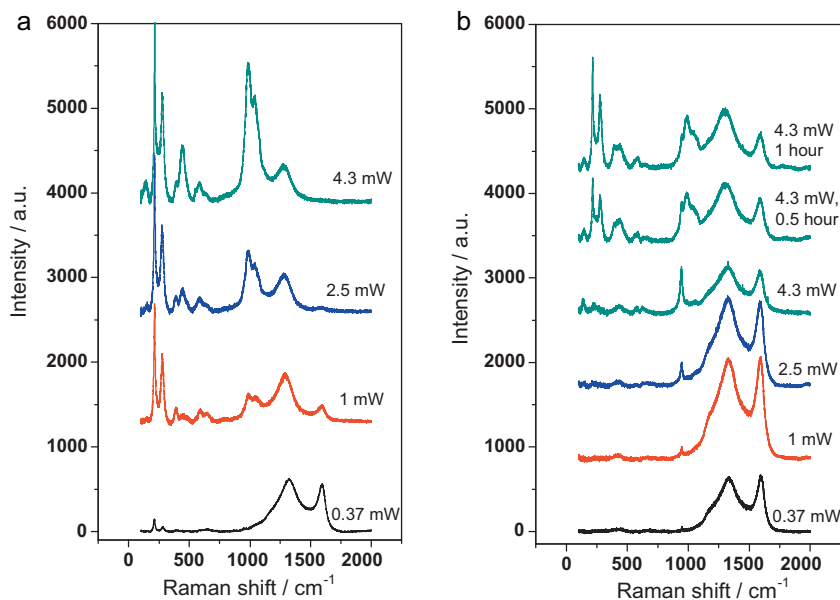


Fig. 6. Raman spectra of LiFePO₄ carbon coated olivine powder collected as a function of power with 633 cm⁻¹ He–Ne laser: (a) in air and (b) in inert atmosphere of helium (99.99%).

Table 2

Wavenumbers and assignment of Raman peaks in the spectrum obtained as a result of laser-induced decomposition of carbon coated olivine LiFeCO₄.

Wavenumber (cm ⁻¹)	Assignment	References
217	A _{1g} vibrations	[25–28]
277	E _g vibrations	[25–28]
395	E _g , O–Fe–O bending of α-Fe ₂ O ₃	[25–28]
448	E, PO ₄ ³⁻ deformation of γ-Li ₃ Fe ₂ (PO ₄) ₃	[21–23]
586	F _{2g} , PO ₄ ³⁻ deformation of γ-Li ₃ Fe ₂ (PO ₄) ₃	[21–23]
600	E _g , Fe–O stretching vibrations of α-Fe ₂ O ₃	[25,26,28]
646	LO, disorder band appearing due to the presence of point defects of α-Fe ₂ O ₃ (odd symmetry IR-active phonon, probably activated by disorder)	[25,28–32]
990	Internal stretching vibrations of the PO ₄ ³⁻ units of γ-Li ₃ Fe ₂ (PO ₄) ₃	[21–23]
1040	Internal stretching vibrations of the PO ₄ ³⁻ units of γ-Li ₃ Fe ₂ (PO ₄) ₃	[21–23]
1119	Internal stretching vibrations of the PO ₄ ³⁻ units of γ-Li ₃ Fe ₂ (PO ₄) ₃	[21–23]
1280	2LO, second-order of disorder band of α-Fe ₂ O ₃	[25,28–32]

the olivine structure at about 950, 1000 and 1070 cm⁻¹, a wide band with two maxima at about 990 and 1040 cm⁻¹ is observed (Fig. 7). The new features of the spectrum related to the vibrations of the valency bonds of PO₄ tetrahedra (900–1250 cm⁻¹) fit well the spec-

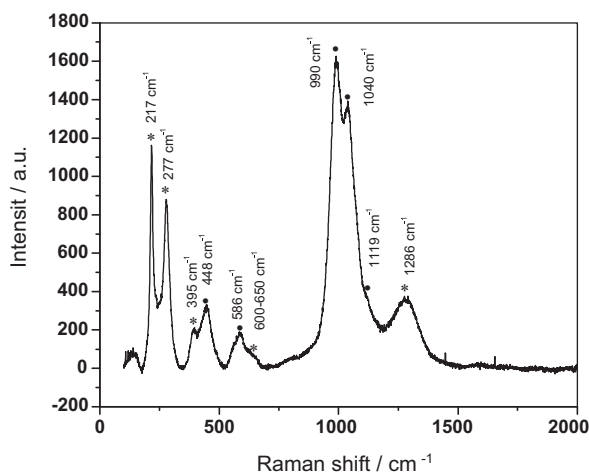


Fig. 7. Raman spectra of the decomposition products of carbon coated LiFePO₄ powder collected in air after the exposure to 633 cm⁻¹ He–Ne laser beam. The bands of γ-Li₃Fe₂(PO₄)₃ are indicated with dots, and the bands of Fe₂O₃ are indicated with asterisks.

tra obtained as a result of the heating of the monoclinic (α-form) of a Li₃Fe₂(PO₄)₃ Nasicon compound up to temperatures higher than 265 °C [21]. The new phase which was formed by this means was defined as the γ-phase of Li₃Fe₂(PO₄)₃ [21,22]. The γ-form of Li₃Fe₂(PO₄)₃ comprises an orthorhombic phase and is characterized by a higher symmetry than the α-form, and correspondingly, by lesser number of peaks [22,23]. The main bands of the Raman spectrum that was obtained for this phase, along with their relative intensities, correspond well with the spectrum of the laser-induced decomposition product of LiFePO₄ (Table 2). The main features of this product are indicated in Fig. 7 with dots. It is interesting that an identical Raman spectrum was recorded from the Ti-doped Li₃Fe₂(PO₄)₃, which differs substantially from the spectrum of the undoped α-form of Li₃Fe₂(PO₄)₃ [24]. This observation is probably the result of the phase transformation of the Ti-doped compound, comparable with that observed during the heating of the monoclinic α-Li₃Fe₂(PO₄)₃.

The second product of the oxidative laser-induced decomposition of LiFePO₄ olivine is α-Fe₂O₃. All the main bands of this compound are readily detectable in the spectrum of the decomposition product and are indicated in Fig. 7 with asterisks. Consequently, the decomposition product comprises the γ-form of Li₃Fe₂(PO₄)₃ mixed with Fe₂O₃ [25–32]. Assignments of the Raman peaks in this spectrum are summarized in Table 2.

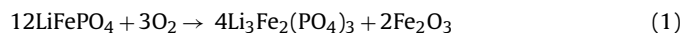
Thus, in contrast to Co²⁺ cations in the olivine structure, Fe²⁺ cations of a LiFePO₄ olivine are readily oxidized by the oxygen in

the air when carbon-coated LiFePO₄ powder is exposed to the laser beam with a moderate power (≤ 1 mW). Such a difference in the behavior of these two olivine powders is not surprising. It is well known that in spite of the same olivine-type structure, the potential of $M^{2+} \rightarrow M^{3+}$ transition vs. Li is much higher for Co than for Fe and comprises 4.8 and 3.5 V, respectively [1,33,34]. In the case of destruction under a laser beam in ambient conditions, $Fe^{2+} \rightarrow Fe^{3+}$ oxidation results in the formation of the γ -form of $Li_3Fe_2(PO_4)_3$ and α -Fe₂O₃, rather than olivine FePO₄. Nonetheless, it is safe to say that LiFePO₄ is much less stable toward oxidation than LiCoPO₄ under the identical conditions. Indeed, a Fe^{2+}/Fe^{3+} standard oxidation potential relative to hydrogen electrode is equal to -0.77 V (3.81 V vs. Li/Li⁺), whereas the Co^{2+}/Co^{3+} redox level is located at a potential of -1.82 V (4.86 V vs. Li/Li⁺). The easy oxidation of LiFePO₄ in air leads to its lower thermal stability, compared to FePO₄ [35]. On the contrary, the crystal structure of completely delithiated CoPO₄ is not stable when in contact with air [36]. The attempts to prepare CoPO₄ by the chemical delithiation of LiCoPO₄ with NO₂PF₆ were not successful [35,37], whereas single phase FePO₄ could be obtained by the oxidation of LiFePO₄ with this reagent [1]. This fact testifies that LiCoPO₄ is also more stable toward oxidation than LiFePO₄.

It is therefore concluded that one should carefully control the power of the laser beam when using Raman spectroscopy to analyze a LiFePO₄ olivine under ambient conditions, as an excess of the limiting power of the excitation laser could lead to the destruction of the sample and a misinterpretation of the spectra. An analysis of the current literature supports the fact that in many cases the wrong interpretation of the Raman spectra of LiFePO₄ olivine occurs, obviously due to the uncontrolled use of the high power laser beam. For example, in [38] Raman spectra of LiFePO₄ nanoparticles synthesized by different ways are presented. Instead of spectra of an olivine with its most pronounced band at about 950 cm⁻¹ (ν_1), one can observe two peaks of approximately equal intensity at about 1000 and 1035 cm⁻¹ that are obviously related to the γ -form of $Li_3Fe_2(PO_4)_3$, and resulted from the decomposition of the olivine structure due to exposure of the sample to a laser beam with too high power. In another work [39] devoted to the preparation of LiFePO₄ cathode material by dispersing nanometer-sized particles of LiFePO₄ into a nanoporous carbon matrix, the Raman spectrum of the synthesized material contains the same two bands (1000 and 1035 cm⁻¹) when the characteristic olivine peak at 950 cm⁻¹ is absent. The same mistake is observed in the data devoted to the changes that are observed in the spectrum of the LiFePO₄ olivine at the various stages of the charge–discharge process during Li intercalation [40]. Pristine and fully discharged materials again contain two bands of γ - $Li_3Fe_2(PO_4)_3$ instead of the olivine peaks. In these works, the other characterization methods suggest the olivine structure of the analyzed samples. Consequently, transformed Raman spectra in all these cases are the result of the incorrect use of Raman spectroscopy.

The second component, which is determined at the point of the sample, exposed to the laser beam, is α -Fe₂O₃. As is clearly seen in Fig. 6a, in the Raman spectrum of carbon-coated LiFePO₄ (black line) two bands at about 217 and 277 cm⁻¹ are present. These bands relate to A_{1g} and E_g vibrations in α -Fe₂O₃ [25–32]. Fe₂O₃ is often present in LiFePO₄ powders as a contaminant as a result of Fe²⁺ ion oxidation processes during the synthesis of the olivine [41,42]. In addition, Fe₂O₃ is obviously a product of the decomposition of the LiFePO₄ olivine in air under exposure to the laser beam (Fig. 7 and Table 2). Xia et al., with the use of Raman spectroscopy, showed that the exposure of LiFePO₄ in hot air leads to the formation of α -Fe₂O₃, lithium and iron phosphates on the surface of the samples [43]. The same mechanism of LiFePO₄ oxidation during heat treatment in air was proved by the combination of temperature-controlled X-ray diffraction, thermogravimetric analysis, Mössbauer and NMR

spectroscopies [44]. The formation of hematite under laser irradiation during micro-Raman analysis of several kinds of LiFePO₄ olivine powders was observed as well [16]. Therefore, according to the spectrum obtained (Fig. 7), the following scheme of LiFePO₄ decomposition during Raman spectra acquisition may be proposed:



A phenomenon of the very fast and full removal of the carbon coating layer from the surface of LiFePO₄ carbon-coated nanoparticles leads to another kind of misinterpretation of the Raman spectra of these materials. After carbon gasification one can observe the disclosure of a wide band at about 1280–1300 cm⁻¹ (Fig. 5) related to second-order of disorder band of α -Fe₂O₃ (2LO). The disorder band (LO) at about 646 cm⁻¹ appears due to the presence of point defects of α -Fe₂O₃ [25,28–32]. The second-order band of this vibration is located in the frequency region of amorphous carbon and is sometimes mistaken for the carbon D-band [45,46]. For example, in the Raman spectra of the LiFePO₄-C composite films deposited with the use of a pulse laser deposition technique [46], the authors observed a fairly intensive wide band at 1309 cm⁻¹, whereas the carbon G-band was absent or poorly detectable, as shown in Figs. 6 and 7. We believe, however, that this band is related to α -Fe₂O₃, as the rest of its bands are clearly seen in the spectrum, along with the absence of the main olivine peaks. Thus, the conclusion of the authors that the poor conductivity of the film is explained by the absence of the conducting form of carbon, due to the absence of the G-band (sp²-bonding) and the presence of only a non-conductive form of carbon due to the presence of the D band signal (sp³-bonding), appears incorrect.

Thus, from the above description of the peculiarities of Raman spectra of both carbon-coated olivine powders, obtained at a laser power higher than ~ 1 mW, it appears that for LiFePO₄ powder two parallel processes occur, namely, $Fe^{2+} \rightarrow Fe^{3+}$ oxidation with the formation of $Li_3Fe_2(PO_4)_3$ and Fe₂O₃ compounds and carbon gasification by oxygen, and for the LiCoPO₄ sample only the last process of the carbon removal is observed.

Fig. 6b presents the Raman spectra of LiFePO₄ carbon-coated olivine powder collected as a function of power in inert atmosphere. In these conditions, the olivine structure of the sample is stable up to a laser power of 4.3 mW. However, after prolonged exposure it undergoes transformation with the formation of the same products as for the process occurring in air (Fig. 6a). In the inert atmosphere the only source of oxygen for the oxidation of Fe²⁺ is the own olivine structure and, to a small extent, the oxygen-containing surface groups of the carbon layer. In such conditions the process requires much higher energy. One can see that during the prolonged exposure of the LiFePO₄-C sample to the laser beam with energy of 4.3 mW in the inert medium, carbon gasification stops while the olivine structure continues to degrade.

The exposure of LiCoPO₄-C nano-powder to a laser beam with maximal power (4.3 mW) under inert conditions reveals the stability of the olivine structure for at least 6 h.

The oxidative removal of the carbon layer in air under the laser beam occurs much more easily for LiFePO₄-C nano-powder than for LiCoPO₄-C nano-powder. This difference may stem from the different catalytic properties of Co and Fe compounds that are in contact with the carbon-coating layer. It is known that both Co [19,20] and Fe [47,48] cations may act as the catalysts of carbon gasification. We defined the temperature for the oxidative removal of carbon for these two powders with the use of TGA-mass spectrometry analysis in air. In this experiment, the possible photo catalysis of the excitation laser beam was excluded. The results are shown in Fig. 8a. It is clearly seen that the total weight of the LiFePO₄-C sample increases as a result of heating the powder in a dry air atmosphere. However, for the LiCoPO₄-C powder, a decrease in the sample weight is observed. These observations are in agreement with our Raman

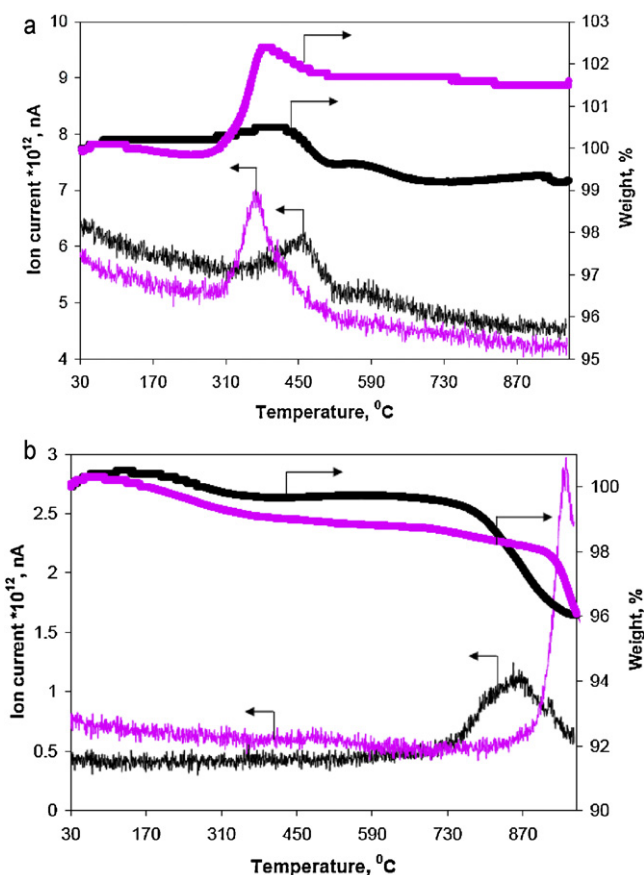
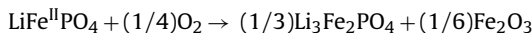


Fig. 8. TGA-MS (CO_2 , $m/z = 44$) response for two carbon coated nano powders, LiCoPO_4 (black) and LiFePO_4 (pink): (a) in dry air and (b) in argon (99.999%). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

measurements. For the $\text{LiCoPO}_4\text{-C}$ sample, carbon removal, accompanied by weight loss, is the only result of both heating in air and exposure to the laser beam. In contrast to this behavior, the heating of the $\text{LiFePO}_4\text{-C}$ sample is accompanied by an increase in the sample weight due to the up-take of oxygen, in the course of the $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ transition. Belharouak et al. [49] obtained the same run of the TGA curve for carbon-coated LiFePO_4 in air. By coupling the TGA and XRD results, they proved the following oxidative mechanisms for LiFePO_4 during the TGA experiment, and which is in line with our Raman observations:



It is seen that in air (Fig. 8a) the evolution of CO_2 from the $\text{LiFePO}_4\text{-C}$ powder is observed at lower temperatures than for $\text{LiCoPO}_4\text{-C}$ powder, probably due to the higher catalytic activity of Fe compounds in the reaction of carbon gasification by oxygen.

The Mössbauer spectrum of $\text{LiFePO}_4\text{-C}$ powder revealed that the content of Fe^{3+} impurity in the sample was equal to 4.5%. From the combination of this result with the result of ICP analysis, one can calculate a weight gain of 2.4% for this sample in the TGA response in the air (Fig. 8a), namely, 4.8% (weight gain due to the uptake of oxygen from the air) – 2.4% (weight loss due to the removal of carbon). Our result of 1.5% of the weight gain may be related to the partial oxidation of Fe^{2+} by the oxygen of the crystal structure of the olivine. This assumption is supported by the result of TGA-mass analysis performed for these samples in pure argon (Fig. 8b) at the same heating rate. In this situation, when the olivine structure is the only source of the oxygen, CO_2 liberation is obviously accompanied by the partial decomposition of the olivines. It is remarkable

that, contrary to the results obtained for the laser-induced decomposition of both carbon coated olivines in an inert atmosphere, the $\text{LiFePO}_4\text{-C}$ sample reveals a higher thermal stability than that of $\text{LiCoPO}_4\text{-C}$ during TGA measurements in argon. The onset of CO_2 formation for the Co-based olivine powder is observed even at about 730°C , while for the $\text{LiFePO}_4\text{-C}$ sample the evolution of CO_2 does not start until 850°C . The opposite tendency in the stability of the two carbon-coated olivine compounds during Raman and TGA measurements in the inert gas suggests that several factors lead to the decomposition of these olivine compounds, namely, temperature, catalytic action of the transition metals and the photo catalytic action of the laser beam. The latter factor, which is absent in the TGA measurements, is obviously responsible for the lower stability of the $\text{LiFePO}_4\text{-C}$ sample as compared to $\text{LiCoPO}_4\text{-C}$ during Raman measurements under inert atmosphere.

4. Conclusions

In this work we have shown some possibilities and limitations of the use of Raman spectroscopy for the analysis of two carbon-coated olivine nano-powders, LiCoPO_4 and LiFePO_4 . We measured the Raman spectra of these materials at different He–Ne laser power and revealed that they possess a different stability toward laser irradiation. Under air we observed the phenomenon of the removal of the carbon coating layer at moderate laser beam power. The olivine structure of $\text{LiCoPO}_4\text{-C}$ powder remains unchanged during prolonged exposure to a laser beam with a power of 4.3 mW. Thus, the removal of the carbon layer makes it possible to analyze the details of the LiCoPO_4 structure in air without interference from carbon.

$\text{LiFePO}_4\text{-C}$ powder, along with carbon layer gasification, undergoes oxidative decomposition by the oxygen with the formation of $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ and Fe_2O_3 , even at a laser power of 1 mW. In an inert atmosphere, the decomposition of a LiFePO_4 olivine structure occurs with the formation of the same oxidation products as in air, but takes place at a higher power of the excitation laser (4.3 mW) and longer exposure. Thus, care should be taken when measuring and interpreting the Raman spectra of LiFePO_4 olivine both in air and in an inert atmosphere.

The $\text{LiCoPO}_4\text{-C}$ sample is stable in inert conditions and under maximal laser power (4.3 mW) for a long time. The opposite tendency was observed for the thermal stability of the two powders under inert atmosphere with the use of TGA-mass spectrometry. LiCoPO_4 seems to be less thermally stable than LiFePO_4 . We attribute the lower stability of LiFePO_4 powder observed during the Raman measurements to a photo-catalytic effect of the laser irradiation on the decomposition rates of the olivine compounds, which is more pronounced when the transition metal in the LiMPO_4 is iron.

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