Erratum to: Impedance spectroscopy study on the ionic conductivity processes of the novel LiFeVO_4 phase

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Erratum to: Ionics

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In the paper of Ref. [1], we presented results of studies detailing the electrical properties of a vanadate phase then believed to be a novel compound with the chemical formula LiFeVO_4 . Since the time of that publication, we have endeavored to probe further into the properties of this material to elucidate the relationships between its structural and electrical properties. This erratum presents recent results that put in doubt the nature of the phase produced and reported in [1]. Our finding is that the primary phase could not be LiFeVO_4 as first believed, but instead a LiVO_3 and $\alpha\text{-Fe}_2\text{O}_3$ composite. At the time our work was submitted to Ionics there were only two reports claiming the existence of a novel compound with the chemical formula LiFeVO_4 [2, 3]. At that time we were studying the conductivity processes in a whole series of LiMVO_4 ($\text{M}=\text{Ni, Co, Zn, Mn, Mg}$) and therefore we found it intriguing to further investigate the conductivity properties of a novel vanadate. As we mention in [1] “*Impedance spectroscopy study of the compound LiFeVO_4 has been performed in [11, Ref. 2 of this erratum] and the equivalent*

circuits of the compound have been given at 25, 50, 75, 100, 125 and 250°C. In that paper a study of the variation of impedance versus temperature at 50, 100, 125 and 250°C is presented. In our present work an impedance spectroscopy study of the novel compound LiFeVO_4 is presented based on a different methodology and perspective than that reported in [11].” Additionally we expanded the temperature range up to 500°C. In Ref. [2] a detailed description of the reaction processes and of the characterization (though preliminary) of the reaction product were presented. In the case of the discovery of a new phase it is common that a provisional structural characterization is provided and in a follow-up work of the same or other authors the actual structural description is given. Based on that we repeated the reaction described in [2] and found that the XRD pattern of our product was identical to that given in [2] unfortunately disregarding the obvious fact that the latter is smoothed. However, we stated in [1] “*The main diffraction peaks in Fig. 2 completely coincide with the XRD pattern given in Ref. [11] (in a 20–80° interval) and could be indexed according to that preliminary study in the orthorhombic system, see Fig. 2. In our pattern there are some small peaks which cannot be seen in the smoothed pattern provided in [11,13]. Nevertheless, there is not another source of information in literature for the XRD study of LiFeVO_4* ”. It turns out that there was a simple reason for the existence of these unidentified peaks.

Recently, we realized that the XRD pattern of our product can be also indexed considering a two phase system consisting of LiVO_3 and $\alpha\text{-Fe}_2\text{O}_3$ [4]. Therefore, we performed a Rietveld analysis on the same X-ray diffraction pattern which has been reported in [1]. Thus, that XRD pattern was treated as a mixture of two phases, $\alpha\text{-Fe}_2\text{O}_3$ and LiVO_3 . For the latter the structure model described by Muller et al. [5] was

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Fig. 1 XRD spectrum refined by the Rietveld method. (+) experimental points, the continuous line corresponds to the calculated spectrum, triangles at the bottom indicate the position of Bragg peaks for α - Fe_2O_3 (above, fewer peaks due to higher symmetry) and vertical bars at the bottom LiVO_3 (below). The continuous line at the bottom is the difference between the experimental intensity values and the calculated one

used. Rietveld analysis was carried out to fit the data with the program GSAS [6, 7] and extract the crystallographic and compositional parameters of the two phases, Fig. 1. The α - Fe_2O_3 phase is crystallized in R $\bar{3}$ 2/c space group (No 167) and the crystallographic parameters which were derived from the fit were $a=b=5.03\text{ \AA}$, $c=13.74\text{ \AA}$ and cell volume $301.414\text{ \AA}^3$. The LiVO_3 phase is described by the C 1 2/c 1 space group (No 15) and the crystallographic parameters were found to be $a=10.15\text{ \AA}$, $b=8.42\text{ \AA}$, $c=5.88\text{ \AA}$, $\beta=110.46^\circ$ and cell volume $470.911\text{ \AA}^3$, in agreement with the literature.

The reduced chi-square value of the fit was 3.593. It turned out that the material was indeed composed by the two phases described above with 43.7 wt.% Fe_2O_3 and

56.3 wt.% LiVO_3 . The theoretical values for the composition of the sample are 43 and 57 wt.% by taking into account the chemical reaction

practically identical with our results. It is profound that crystallographically the material should be described as a mixture of the trigonal α - Fe_2O_3 (R-3c SG) and the monoclinic LiVO_3 (C2/c SG) phases. In the meantime two publications have re-examined the synthesis of LiFeVO_4 confirming that under the reaction conditions used in our paper a mixture of α - Fe_2O_3 and LiVO_3 is obtained [8, 9]. Therefore, our results of Ref. 1 on the ionic conductivity behaviour of this system should be considered as the electrical properties of α - Fe_2O_3 / LiVO_3 composite and not of “ LiFeVO_4 ”.

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