



Microwave assisted synthesis, characterization and electrochemical performance of LiVPO_4F cathode material

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ABSTRACT

High-voltage cathode material, lithium vanadium fluorophosphate LiVPO_4F , has been for the first time synthesized by a rapid two-step method based on microwave-assisted carbothermal reduction (CTR) and characterized with the use of scanning electron microscopy (SEM), X-ray diffraction and DTA/TG thermal analysis. Its electrochemical performance has been examined by galvanostatic charge-discharge cycling. Calculated lattice parameters of the obtained LiVPO_4F compound were in accordance with literature. Its thermal stability up to $550\text{ }^\circ\text{C}$ was confirmed. Charge-discharge cycling of LiVPO_4F in the voltage range between 3.0 V and 4.4 V at a current rate of $7.75\text{ mA}\cdot\text{g}^{-1}$ (C/20) after 5 cycles showed a charge capacity of $90\text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ and a discharge capacity of $58\text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$. For a current rate of $15.5\text{ mA}\cdot\text{g}^{-1}$ (C/10) after 10 cycles charge capacity achieved the value of $60\text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ whereas the discharge capacity was of $52\text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$. The discharge plateau was at 4.18 V. The presented results suggest that LiVPO_4F cathode material can be synthesized by the simplified two-step microwave-assisted reduction method. Although it needs to be further optimized, the method is simpler, faster and cheaper as compared to other preparation routes.

1. Introduction

The market of electronic devices and electric vehicles exhibits ever growing need for better performing and safer rechargeable batteries. Lithium-ion batteries have already dominated the area of portable electronics, but its development towards new large-scale applications is inhibited by the lack of appropriate cathode materials which could deliver high power and energy density. A range of new materials has been proposed to replace commonly used LiCoO_2 . In particular favorite-structured fluorophosphates LiMPO_4F , $\text{Li}_2\text{MPO}_4\text{F}$ ($M = \text{Fe, Mn, Co, Ti}$ etc.) and fluorosulphates LiMSO_4F ($M = \text{Fe, Ni, Co, Mn, etc.}$) receive increasing research attention due to their interesting properties.

In particular LiVPO_4F proposed by Barker et al. [1] is considered as an attractive “4V-class” cathode for lithium-ion batteries. This comes from its high theoretical capacity of $155\text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ from $\text{V}^{3+}/\text{V}^{4+}$ redox couple, an improved voltage profile and a higher discharge voltage of 4.2 V vs Li^+/Li^0 in comparison to the commonly used LiCoO_2 .

Additionally, it is reported that LiVPO_4F exhibits an excellent lattice stability upon repeated Li^+ extraction/insertion reactions due to the presence of stable V–F bonds [2], [3], [4] in the crystal structure. Additionally, it shows good thermal stability, comparable with olivine LiFePO_4 [5]. Although favorite LiVPO_4F exhibits promising electrochemical properties, some issues need further research and

optimization. Similarly to the most of the phosphate-based materials electronic transport in favorite LiVPO_4F lattice is expected to be inferior when compared to conventional oxide cathode materials [6].

A number of experimental methods have been developed in order to obtain LiVPO_4F , e.g. two-step [7], one-step solid state reaction [18] or sol-gel method [8]. As these approaches have their drawbacks: complexity, considerable time- and energy consumption, in this study we decided to explore a novel preparation route, the carbothermal reduction (CTR) stimulated by microwave radiation heating.

Apart from telecommunication and food heating, microwaves are used in many technological processes, such as melting, sintering, drying, carbothermal reduction of oxides etc. [9]. Microwave stimulated heating consists of inducing molecular motion by migration of ionic species and/or rotation of bipolar species. It offers certain advantages over conventional heating routes such as: non-contact, rapid heating and quick start-up and stopping [10].

But the main benefit from using microwave energy instead of conventional heating is the fact that it transforms into heat in the bulk. That results in significant energy savings and reduction of preparation time, which is particularly important for mass production. Compared to solid state reaction, the microwave preparation route allows to make the material with proper crystal structure within minutes of synthesis, what is more, no protective or reducing atmosphere (e.g. Ar, H_2 flux) is

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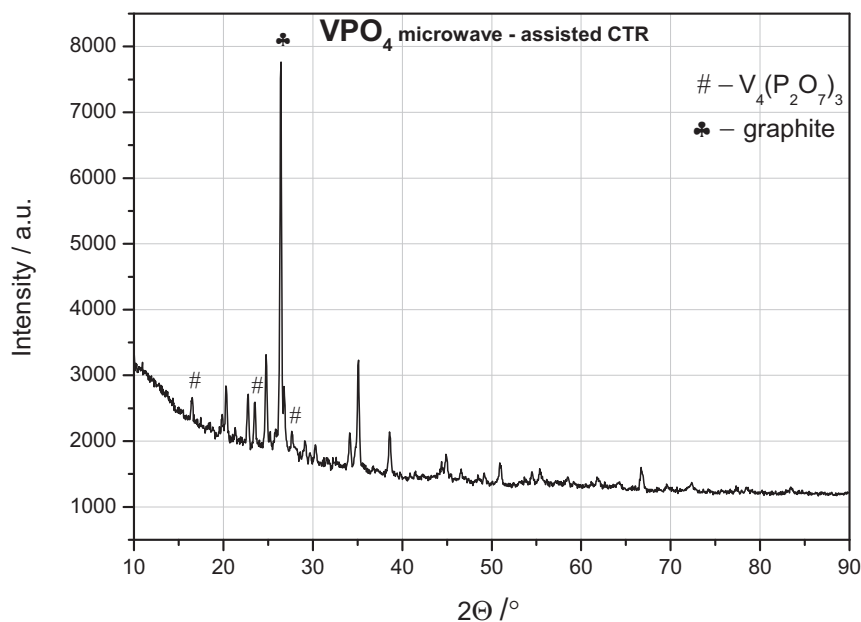


Fig. 1. Observed XRD plot obtained for VPO_4 . Impurity lines for residual graphite and $V_4(P_2O_7)_3$ are marked.

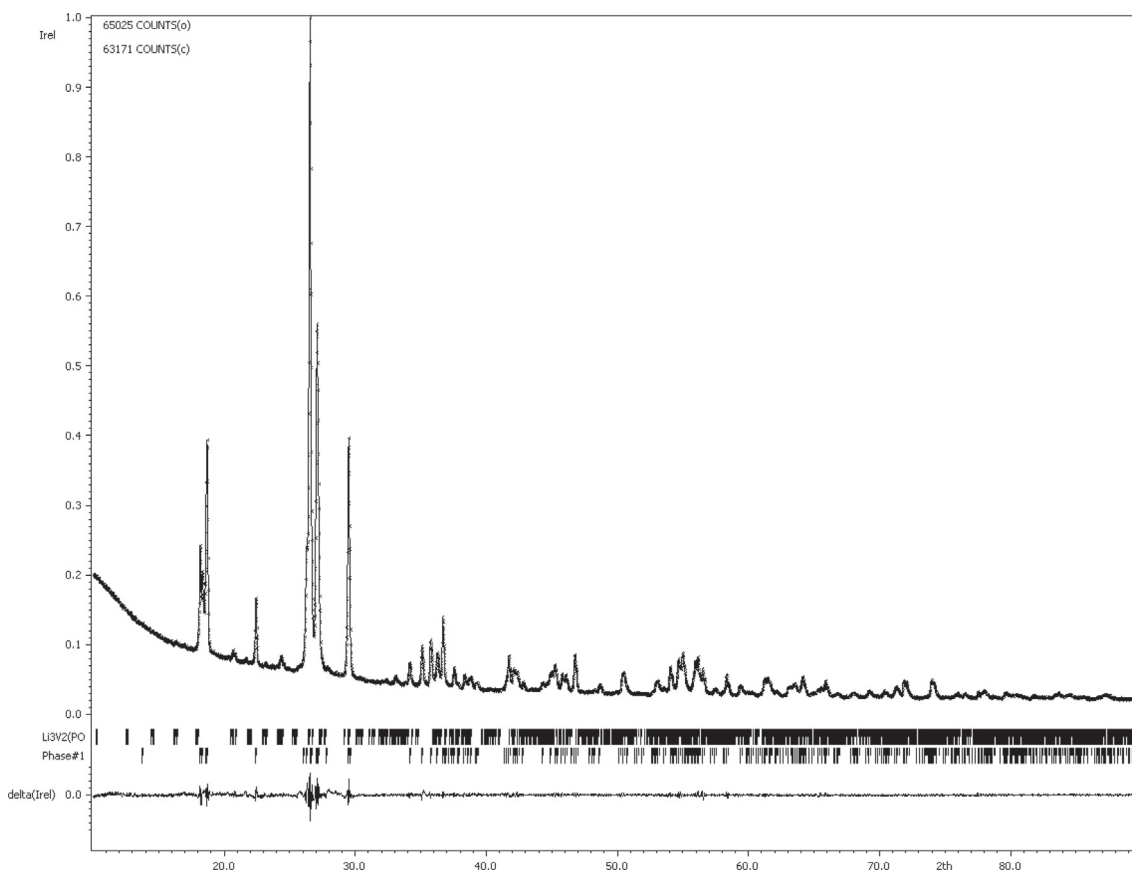


Fig. 2. Observed, calculated and difference plots for $LiVPO_4F$ from Rietveld refinement (for unit cell parameters see text).

needed. According to Standish et al. [11] microwave assisted carbothermic reduction of metal oxides could save from 15% to 50% of capital and operating costs compared to conventional operation. Even the materials that are poor microwave absorbers, can be heated when facilitator (magnetite, silicon carbide or carbon) is used. Microwave energy first heats the facilitator, which subsequently heats the target material [12]. One of the best microwave absorbers is carbon – it heats

up to 1000 °C in 10 s.

It should be emphasized that the microwave assisted carbothermic reduction was already successfully applied to obtain several electrochemically active solids, such as $LiFePO_4$ [13] or $Li_3V_2(PO_4)_3$ [14], but as far as we know, there is no evidence of applying this method to prepare $LiVPO_4F$. In this context, our approach could be considered as a novel preparation route of this specific compound.

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