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Gel-combustion synthesis of $LiFePO_4$/C composite with improved capacity retention in aerated aqueous electrolyte solution

Milica Vujković[a], Ivana Stojković[a], Nikola Cvjetićanin[a], Slavko Mentus[a,b,*,1]

[a] University of Belgrade, Faculty of Physical Chemistry, P.O. Box 137, Studentski trg 12-16, 11158 Belgrade, Serbia
[b] The Serbian Academy of Sciences and Arts, Kenz Mihajlova 35, 11158 Belgrade, Serbia

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ABSTRACT

The $LiFePO_4$/C composite containing 13.4 wt.% of carbon was synthesized by combustion of a metal salt–(glycine + malonic acid) gel, followed by an isothermal heat-treatment of combustion product at 750 °C in reducing atmosphere. By a brief test in 1 M $LiClO_4$–propylene carbonate solution at a rate of C/10, the discharge capacity was proven to be equal to the theoretical one. In aqueous $LiNO_3$ solution equilibrated with air, at a rate C/3, initial discharge capacity of 106 mAh g^{-1} was measured, being among the highest ones observed for various Li-ion intercalation materials in aqueous solutions. In addition, significant prolongation of cycle life was achieved, illustrated by the fact that upon 120 charging/discharging cycles at various rates, the capacity remained as high as 80% of initial value. The chemical diffusion coefficient of lithium in this composite was measured by cyclic voltammetry. The obtained values were compared to the existing literature data, and the reasons of high scatter of reported values were considered.

1. Introduction

Thanks to its high theoretical Coulombic capacity (170 mAh g^{-1}) and environmental friendliness, $LiFePO_4$ olivine became a desirable cathodic material of Li-ion batteries [1,2], competitive to other commercially used cathodic materials ($LiMnO_4$, $LiCoO_2$). As evidenced in non-aqueous electrolyte solutions, a small volume change (6.81%) that accompanies the phase transition $LiFePO_4 \rightleftarrows FePO_4$ enables Li^+ ion insertion/deinsertion reactions to be quite reversible [1–3]. The problem of low rate capability, caused by low electronic conductivity [4,5], was shown to be solvable to some extent by reduction of mean particle size [6]. Further improvements in both conductivity and electrochemical performances were achieved by forming composite $LiFePO_4$/C, where in situ produced carbon served as an electronically conducting constituent [5,7–27]. Ordinarily, both in situ formed carbon and carbon black additive, became unavoidable constituent of the $LiFePO_4$-based electrode materials [28–37]. Zhao et al. [27] reported that Fe_2P may arise as an undesirable product during the synthesis of $LiFePO_4$/C composite under reducing conditions, however, other authors found later that this compound may contribute positively to the electronic conductivity and improve the electrochemical performance of the composite [28–30]. Severe improvement in rate capability and capacity retention was achieved by partial replacement of iron by metals supervalent relative to lithium [31–37]. Thus one may conclude that the main aspects of practical applicability of $LiFePO_4$ in Li-ion batteries with organic electrolytes were successively resolved.

After the pioneering studies by Li and Dahn [38,39], rechargeable Li-ion batteries with aqueous electrolytes (ARLB) attracted considerable attention [40–50]. The first versions of ARLB's, suffered of very low Coulombic utilization and significantly more pronounced capacity fade relative to the batteries with organic electrolyte, regardless on the type of electrode materials [43]. For the first time, $LiFePO_4$ was considered as a cathode material in ARLB's by Manickam et al. in 2006 [44]. He et al. [46], in an aqueous 0.5 M Li_2SO_4 solution, found that $LiFePO_4$ displayed both a surprisingly high initial capacity of 140 mAh g^{-1} at a rate 1 C and recognizable voltage plateau at a rate as high as 20 C, which was superior relative to the other electrode materials in ARLB's. Recently, the same authors reported a high capacity decay in aerated electrolyte solution, amounting to 37% after only 10 cycles [48]. In the same study, they demonstrated qualitatively by a brief cyclovoltammetric test, that a carbon layer deposited from a vapor phase over $LiFePO_4$ particles, suppressed the capacity fade [48].

Inspired by the recent discoveries about excellent rate capability [46] but short cycle life [48] of $LiFePO_4$ in aerated aqueous solution, we attempted to prolong the cycle life by means of protecting carbon layer over the $LiFePO_4$ particles. Therefore we

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* Corresponding author at: University of Belgrade, Faculty of Physical Chemistry, P.O. Box 137, Studentski trg 12-16, 11158 Belgrade, Serbia. Tel.: +381 11 2187 133; fax: +381 11 2187 133.
E-mail address: slavko@ffh.bg.ac.rs (S. Mentus).

[1] ISE member.

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synthesized $LiFePO_4$/C composite by a fast and simple glycine-nitrate gel-combustion technique. This method, although simpler than a classic solid state reaction method combined with ball milling [44,48], was rarely used for $LiFePO_4$ synthesis [19,27]. It yielded a porous, foamy $LiFePO_4$/C composite, easily accessible to the electrolyte. Upon the fair charging/discharging performance was confirmed by a brief test in organic electrolyte, we examined in detail the electrochemical behavior of this material in aqueous electrolyte, by cyclic voltammetry, complex impedance and cyclic galvanostatic charging/discharging methods. In comparison to pure $LiFePO_4$ studied in Ref. [48], this composite displayed markedly longer cycle life in aerated aqueous solutions. The chemical diffusion coefficient of lithium was also determined, and the reasons of its remarkable scatter in the existing literature were considered.

2. Experimental

The $LiFePO_4$/C composite was synthesized using lithium nitrate, ammonium dihydrogen phosphate (Merck) and iron (II) oxalate dihydrate (synthesized according to the procedure described elsewhere [51]) as raw materials. Our group acquired the experience in this synthesis technique on the examples of spinels $LiMn_2O_4$ [52] and $LiCr_{0.15}Mn_{1.85}O_4$ [53], where glycine served as both fuel and complexing/gelling agent to the metal ions. A stoichiometric amount of each material was dissolved in deionized water and mixed at 80 °C using a magnetic stirrer. Then, first glycine was added into the reaction mixture to provide the mole ratio of glycine: nitrate of 2:1, and additionally, malonic acid (Merck) was added in an amount of 60 wt.% of the expected mass of $LiFePO_4$. The role of malonic acid was to decelerate combustion and provide controllable excess of carbon [14]. After removing majority of water by evaporation, the gelled precursor was heated to initiate the auto-combustion, resulting in a flocculent product. The combustion product was heated in a quartz tube furnace first at 400 °C for 3 h in Ar stream, and then at 750 °C for 6 h, under a stream of 5 vol.% H_2 in Ar. This treatment consolidated the olivine structure and enabled to complete the carbonization of residual organic matter.

The VO_2 powder prepared by hydrothermal method was used as an active component of the counter electrode in the galvanostatic experiments in aqueous electrolyte solution. The details of the synthesis and electrochemical behavior of VO_2 are described elsewhere [54,55]. The considerable stoichiometric excess of VO_2 was used, to provide that the $LiFePO_4$/C composite only presents the main resistive element, i.e., determines the behavior of the assembled cell on the whole.

The XRD experiment was performed using Philips 1050 diffractometer. The Cu $K\alpha_{1,2}$ radiation in 15–70° 2θ range, with 0.05 °C step and 2 s exposition time was used.

The carbon content in the composite was determined by its combustion in the flowing air atmosphere, by means of thermobalance TA SDT Model 2090, at a heating rate of 10 °C min^{-1}.

The morphology of the synthesized compounds was observed using the scanning electron microscope JSM-6610LV.

For electrochemical investigations, the working electrode was made from $LiFePO_4$/C composite (75%), carbon black-Vulcan XC 72 (Cabot Corp.) (20%), poly(vinylidene fluoride) (PVDF) binder (5%) and a N-methyl-2-pyrrolidone solvent. The resulting suspension was homogenized in an ultrasonic bath and deposited on electronically conducting support. The electrode was dried at 120 °C for 4 h. Somewhat modified weight ratio, 85:10:5, and the same drying procedure, were used to prepare VO_2 electrode.

The non-aqueous electrolyte was 1 M $LiClO_4$ (Lithium Corporation of America) dissolved in propylene carbonate (PC) (Fluka). Before than dissolved, $LiClO_4$ was dried over night at 140 °C under vacuum.

The aqueous electrolyte solution was saturated $LiNO_3$ solution.

The cyclic voltammetry and complex impedance experiments were carried out only for aqueous electrolyte solutions, by means of the device Gamry PCI4/300 Potentiostat/Galvanostat. The three electrode cell consisted of a working electrode, a wide platinum foil as a counter electrode, and a saturated calomel electrode (SCE) as a reference one. The experiments were carried out in air atmosphere. The impedance was measured in open-circuit conditions, at various stages of charging and discharging, within the frequency range $10^{-2}-10^{5}$ Hz, with 7 points per decade.

Galvanostatic charging/discharging experiments were carried out in a two-electrode arrangement, by means of the battery testing device Arbin BT-2042, with two-terminal connectors only.

In the galvanostatic tests in non-aqueous solution, working electrode was a $2 \times 2\,cm^2$ platinum foil carrying 2.3 mg of composite electrode material (1.5 mg of olivine), while counter electrode was a $2 \times 2\,cm^2$ lithium foil. The cell was assembled in an argon-filled glove box and cycled galvanostatically within a voltage range 2.1–4.2 V.

The galvanostatic tests in the aqueous electrolyte solution were carried out in a two-electrode arrangement, involving 3 mg of cathodic material, as a working electrode, and VO_2 in a multiple stoichiometric excess, as a counter electrode. According to its reversible potential of lithiation/delithiation reaction [55], VO_2 performed as an anode in this cell. The 4 cm^2 stainless steel plates were used as the current collectors for both positive and negative electrode. The cell was assembled in room atmosphere, and cycled within the voltage window between 0.01 and 1.4 V.

3. Result and discussion

3.1. The XRD, SEM and TG analysis of the $LiFePO_4$/C composite

Fig. 1 shows the XRD patterns of the composite $LiFePO_4$/C prepared according to the procedure described in the Experimental Section. As visible, the diffractogram agrees completely with the one of pure $LiFePO_4$ olivine, found in the JCPDS card No. 725-19. The narrow diffraction lines indicate complete crystallization and relatively large particle dimensions. On the basis of absence of diffraction lines of carbon, we may conclude that the carbonized product was amorphous one.

Fig. 2 shows the SEM images of the $LiFePO_4$/C composite at two different magnifications. The flaky agglomerates, Fig. 2 left, with apparently smooth surface and low tap density, are due to a partial liquefaction and evolution of gas bubbles during gel-combustion procedure. These agglomerates consist of small $LiFePO_4$/C

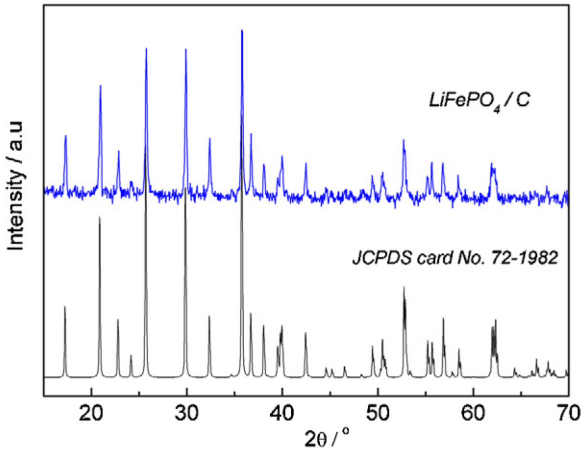

Fig. 1. XRD patterns of $LiFePO_4$/C composite in comparison to standard crystallographic data.