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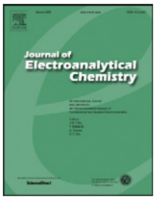

Reaction mechanism and morphology of the $LiFePO_4$ materials synthesized by chemical solution deposition and solid-state reaction☆

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ABSTRACT

The mechanism of a low temperature wet chemical route for synthesis of $LiFePO_4$ cathode material for Li-ion batteries is presented. Using inorganic salts as precursors and diethylene glycol (DEG) as reaction media, nanosize $LiFePO_4$ powder is obtained. The controversially discussed role of the polyol on this reaction has been clarified by in-situ FT-IR analysis of the gaseous reaction products and a full analysis of solid products. It is observed that DEG does not act as reducing agent for iron(II) salts, nor is it oxidized during the synthesis of $LiFePO_4$. Generally, polyols are used to reduce the oxides and hydroxides into their corresponding metals. The nucleation of Li^+, PO_4^{3-} and Fe^{2+}-ions in the DEG solvent starts at temperatures 110 °C, 130 °C and 170 °C, respectively. $LiFePO_4$ precipitation from Li-carbonate, Fe(II)-oxalate dihydrate and ammonium dihydrogenphosphate as precursors is driven by thermal decomposition of the salts, intermediate formation and dehydration of amino-ethoxy-ethane, yielding 1,4-dioxane as volatile by-product. With the help of in-situ investigations reaction time and temperature could be minimized. Furthermore, the effect of the concentrations of Li^+, Fe^{2+} and PO_4^{3-} ionic moieties on the morphology of $LiFePO_4$ materials obtained by chemical solution deposition and solid state reaction are studied with the help of FT-IR analysis. $LiFePO_4$ platelets morphology exhibited better discharge capacity than $LiFePO_4$ agglomerate morphology. The solid product is characterized by X-ray diffraction, scanning electron microscopy and differential thermogravimetry combined with mass spectrometry and FT-IR.

1. Introduction

For energy storage in batteries costs and energy efficiency is required for each component of the battery, in particular also for the synthesis of electrode materials. As one of the most promising cathode materials for rechargeable Li-ion batteries $LiFePO_4$ has been suggested, because of its high thermal stability, high reversible specific capacity, low raw material cost and low toxicity [1]. For full utilization of $LiFePO_4$ as battery cathode material (theoretical capacity 170 mAh/g, open circuit voltage 3.4 V vs. Li/Li^+) improvement of Li-ion diffusivity and of electrical conductivity is necessary [2]. Whereas conductivity improvement can be achieved by carbonaceous or metallic additives [3,4], improved diffusivity requires particle size reduction [5–8], thus nano-powders have become important for enabling short diffusion and charge transport paths [9].

Solid state synthesis of olivine $LiFePO_4$ from carbonate, oxalate and different ammonium salts as precursors is known [6,10,11], but such syntheses are quite energy intensive. Some of the drawbacks of the existing processes for nano-olivine powders are ball milling of the solids prior to reaction, decomposition at high temperature (~350 °C), slow reaction kinetics and the need for prolonged post-heating and sintering at temperature of 600–800 °C. But the main drawback in such types of synthesis is that the reaction can not be controlled during the synthesis to achieve nanostructured material with preferred morphology of materials. Morphology and particle size play a decisive role to improve the lithium diffusion [2]. Based on theoretical models, Islam et al. have assumed two different types of crystal morphology for $LiFePO_4$. According to these models, equilibrium morphology is possible if the concentration of ionic moieties (Li^+, Fe^{2+} and PO_4^{3-}) is very similar at the surfaces and growth morphology dominates by attachment energies. The crystal grows in (010) direction when the concentration of Li^+ ions is higher than concentration of Fe^{2+} in the reaction mixture [12]. Therefore, a deep knowledge about the thermal decomposition of the precursor salts in the presence of reactive solvents is essential to describe the morphology of $LiFePO_4$ materials. Proprietary polyol methods are

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claimed to yield pure Li-metal phosphates, but the role of different precursors as well as additives is not clear [7,13,14].

The goal of this work is a polyol synthesis of nanocrystalline, phase pure $LiFePO_4$ material with preferred morphology at the lowest possible temperature and time, and without prolonged thermal post-treatment. Furthermore, the reaction mechanisms and morphology of $LiFePO_4$ materials synthesized by chemical solution deposition and solid state reaction are compared.

Poly-alcohols are frequently used as reactive solvents to obtain nanosized metal powders in the so called "polyol process", which is driven by reduction of oxides and hydroxides to the corresponding metals and oxidation of the polyol [15]. From thermodynamic calculations participation of the polyol as a reducing agent and a reaction mechanism based on oxidation of the polyol is supported, as shown in Eq. (1) for ethylene glycol as a solvent [15].

$$\mathrm{HO-CH_2-CH_2-OH} + \frac{5}{x}\mathrm{MO}_{x(s)} \rightarrow \frac{5}{x}\mathrm{M}^{o}_{(s)} + 2\mathrm{CO}_{2(g)} + 3\mathrm{H_2O}_{(g)} \quad (1)$$

Furthermore, it is assumed that the poly-alcohol acts as complex forming agent, which controls nucleation, growth and agglomeration of powder particles [16]. However, for ethylene glycol and iron oxides the calculation according to Eq. (1) indicates no reduction of the oxide to metal up to 850 °C, but reduction of iron-hydroxide at temperatures as low as 200 °C [15]. The strong influence of hydroxyl ions is related to the decrease of the reduction potential of glycols at high pH and an enhancement of the reaction rate due to formation of a volatile acetaldehyde [17]. Concomitantly, the oxidation state of iron in the powders obtained is also influenced by the addition of hydroxide [17]. Besides changes in the red-ox potential by hydroxyl ions, the reducing properties of glycols are also influenced by the water content. When water is constantly removed from the reaction mixture by distillation, the oxidation of glycols and the reduction of metal salts is facilitated, because de-hydration occurs prior to oxidation [18]. Therefore, absence of water and hydroxyl-groups as well as a decreased and carefully controlled reaction temperature are required to avoid formation of metallic iron upon a polyol synthesis of a phase pure Fe(II)-salt.

In the previous work devoted to the study of the polyol reaction mechanism with iron-salts, Fe-acetate and Fe-acetylacetonate were used as precursors [19–21]. The decomposition products of such precursors are identical with by-products of poly-alcohol oxidation. Reaction mechanism studies with these precursor salts are ambiguous, because reaction by-products can not unequivocally be assigned to salt or solvent decomposition.

In order to avoid such uncertainty in the work reported here, Fe-oxalate is employed as iron-source, together with Li-carbonate and ammonium phosphate. In addition, water-free DEG was used to insure the absence of Fe-hydroxides as intermediates and for disabling competition between reduction and hydrolysis [22]. Only water liberated from hydrated salts is present in the reaction mixture. Furthermore, the pH of the reaction mixture was not changed by adding additional base, to account for the controversially discussed role of the glycol with respect to the choice of pH [23].

The sequence of decomposition reaction of all salts in DEG solvent was investigated by on-line IR-spectroscopy of the evolved gas phase during $LiFePO_4$ synthesis in a batch reactor purged with Argon gas. Trace analysis of all gaseous species in the reaction atmosphere is enabled by utilization of a "long path" gas cell for FT-IR analysis, implemented into the reactor periphery. From this study the minimum reaction temperature for the thermal decomposition of the carbonate, oxalate and ammonium salt in DEG as solvent as well as of DEG itself was obtained. In addition, unequivocal information about reactions between the solvent DEG and the salts or their decomposition products is gained.

For comparison, the sequence of decomposition reaction of all salts (used in chemical solution deposition) in solid state reaction method was investigated by FT-IR and mass-spectroscopy of the gaseous products evolving during the TG/DSC (thermogravimetry and differential scanning calorimetry) analysis.

The presented work is the first report on the mechanism of a low temperature olivine synthesis from oxalate, carbonate and ammonium phosphate salts in DEG solvent as reaction medium.

2. Experimental

As precursor salts iron(II) oxalate dihydrate ($FeC_2O_4 \cdot 2H_2O$, purity >99%, VWR International), lithium carbonate (Li_2CO_3, purity >99%, Merck) and ammonium dihydrogen phosphate ($NH_4H_2PO_4$, purity 99.999%, Sigma Aldrich) are employed in stoichiometric molar ratio (1:1:1). All chemicals were used directly without any further purification. Molecular sieve was used for drying the solvent diethylene-glycol (DEG, purity 99%, Sigma Aldrich). After 48 h contact with the molecular sieve, the water content in DEG measured by Karl-Fisher method was ~700 ppm. All salts are not soluble in DEG at ambient temperature; they are dispersed in the dried DEG. A three-neck round bottom flask equipped with both a refluxing unit and a magnetic stirring unit is used as reactor. The flask is purged with Argon (2 l/h) 30 min prior to heating up and during the whole experiment. The solution is heated to 245 °C, the boiling point of DEG, and than kept under refluxing. Between 120 and 130 °C the salts dissolve and a transparent yellow solution is obtained. Upon refluxing a white precipitate forms. After cooling to room temperature, the precipitate is separated from the solvent by centrifugation (2000 rpm) and washed with acetone a couple of times for removing the polyol residue and other organic compounds. Finally, the precipitate is dried in a vacuum oven at 150 °C for 12 h.

The solid products were characterized by X-ray diffractometry (XRD, Philips X'Pert PW 3040) with CuKα radiation. TG/DSC (thermogravimetry and differential scanning calorimetry) data were obtained with a STA 449 C/4/G Jupiter (NETZSCH) in the temperature range 30–1000 °C, using an alumina crucible under argon atmosphere (40 ml/min) and a heating rate of 5 °C/min. The evolved gaseous products were analysed by FT-IR (Bruker IPS 60V) and mass spectroscopy(NETZSCH, QMS 403C, Aëolos). The morphology and size of particles were examined by scanning electron microscopy (SEM, Leo 1530 Gemini), the SEM samples were coated with approximately 1 nm Platinum.

During the reaction FT-infrared spectra were recorded using a long path gas cell (Bruker Optics, type A 136-QT) equipped with KBr windows, on a Bruker IPS 60 V spectrometer, in the wavenumber range 600–4000 cm^{-1}, at 1 atm pressure. The path length of 8.0 m enables a signal enhancement equal to 40 refection ways. The gas cell of the FT-IR instrument was attached to the outlet of the argon purge gas tubing. High boiling solvents were removed from the gas stream be means of a dry ice cooling trap (−78 °C). The cooling trap also enabled to reduce the water vapour pressure, in order to protect the KBr-windows of the gas cell. The IR-spectrometer chamber was purged with dry Argon for 30 min, prior to measurement.

For comparison, $LiFePO_4$ material was also synthesized by solid state reaction using the same precursor salts. The mixture of precursor salts in the acetone was ball milled for 3 h. To know about the decomposition mechanism, this solid dry mixture was characterized by TG/DSC in the temperature range 30–700 °C, using an alumina crucible under argon atmosphere (40 ml/min) and a heating rate of 5 °C/min. The evolved gaseous products were analysed by FT-IR and MS. Firstly, this solid dry mixture was heated at 350 °C for 10 h to decompose the precursor salts and then annealed at 600 °C for next 10 h to obtain the crystalline $LiFePO_4$.