

Phospho-olivines as cathode materials for lithium ion battery: trends on microwave synthesis

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Abstract. In recently years, scientific research has been focused on finding new sources of efficient energy storage and lithium batteries are one of the most outstanding alternatives. Nowadays, investigation on cathode materials constitute one of the key factors of lithium rechargeable batteries studies. Recently, oxides with olivine structures has triggered the battery field, due to its excellent electrochemical properties, crystal stability, energy density, power capacity and are not expensive. However, the demand and development of more enhanced cathode materials can be achieved by the use of sophisticated synthetic methods. The purpose of this article is to provide a perspective to the materials community on the opportunities and limitations of nanostructured materials by highlighting examples in synthesis, fundamental studies and applications on microwave synthesis as novel route to obtain high voltage phospho-olivines.

1. Introduction

Since their commercialization in the early 1990's by Sony[®], Li-ion batteries (LIB) are considered an important element inside the so-called "modern electricity-based society". So far, LIB constituted the most appropriate method of energy storage: they show long cycle life, wide range of operating temperatures, high energy density, low cost and safety [1]. LIB have prompted the progress of electronic devices commercialization (mobile phones, laptops, tablets), internal combustion engines (ICE), electric vehicles (EVs) and support the storage of energy produced by renewable energy sources (RES) [2]. In currently LIB technology, the electrochemical performance (cell voltage, capacity, Li⁺ transportation rate) is determined mainly by the cathode material and this justifies the intense research in this field [3]. Since report of electrochemical activity of LiMPO₄ (*M*=Fe, Mn) by Goodenough [4], lithium transition metals phosphates with ordered olivine structure (Phospho-olivines) has emerged as a promising cathode material due to its excellent electrochemical properties, good thermal stability, low cost and environmentally friendly [5]. Crystalline LiMPO₄, has an orthorhombic unit cell (D_{2h}^{16} -space group *Pmnb*), where oxygen ions form strong covalent bonds with P⁵⁺ to form PO₄³⁻ tetrahedral units stabilizing the entire network assuring a stable operation and high temperatures; present the so-called "inductive effect" due to the P_{tet}-O-M_{oct} linkage allowing an interaction that tunes the M³⁺/M²⁺ redox energy to useful levels (3.4 to 5.0 V) and present high theoretical capacity (up to 170 mAh/g) that provides high energy density compared with other cathode materials such as spinel-oxides or layered oxides [6,7]. The insertion and extraction of Li⁺ ions into



the stable crystal lattice of the electrode is the key factor inside LIB operation. One of the main causes of poor performance of the battery is the instability of electrode materials, due to the existence of secondary phases, inhomogeneity in the compound formation, stoichiometry, crystal structure and morphology of the active material [8]. These factors are closely related and the selection of an appropriate synthesis route is the key factor to enhance the battery working. Following the report of Higuchi [9], microwave-assisted route is considered a novel processing technique to obtain nanoscale cathode materials with excellent electrochemical properties. The purpose of this article is not provide a comprehensive review; rather, this paper offers a perspective to the materials community on the microwave (mw) synthesis by highlighting examples and propose some promising developmental directions on assisted-microwave route for the synthesis of phospho-olivines for LIB cathode-materials.

2. Microwave assisted-solid state synthesis

Microwave processing method is based on a self-heating process that occurs by the absorption of electromagnetic energy; due to the use of dielectric microwave (which reduce the thermal gradients inside the reactor), a very fast and uniform heating of the total volume of reactants is obtained within a short time, resulting in very homogenous reaction conditions. Moreover, it allows the possibility to synthesized cathode materials at temperatures lower than those required in solid state synthesis using an oven [10]. The first attempts of direct microwave synthesis evolved from preliminary steps of mixing precursors, pelletizing and the use of domestic microwave ovens; in the case of LiFePO_4 a capacity value of 125 mAh/g was reported [9] and then improved until 161mAh/g at C/10 mixing stoichiometric amounts of Li_3PO_4 and $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ in a ball-milling jar with 5 wt.% acetylene black, pressed in a pellet and then irradiated for several minutes (2-5) at 750 W [11]. Recently reports shows alternative procedure using $\text{FePO}_4 \cdot 4\text{H}_2\text{O}$ and Li_2CO_3 mixed with glucose and milling in ball-mill for 5 min at 400 rpm. Mixture is transferred in a crucible and alternatively heated at a procedure of 20 seconds with 10 seconds pause for 4 times at 1000W and 2.45 GHz without use of inert gas; the reported capacity reach 162 mAh/g at C/10 which is one of the highest discharge specific capacity reported so far [12]. The use of carbonaceous substance (such as acetylene and glucose) is a good strategy to include in mw synthesis. The carbon source acts as a room temperature susceptor that reaches a critical temperature to couple with the mw radiation; besides, carbon supplies thermal energy by heat transfer by surrounding and immersing the sample in both thermal and electric fields [8] and finally, carbon covers the precursor particles and create a layer around them to facilitate the transport of electrons between the current collector and the particle surface [13].

On the other hand, reports on formation of LiCoPO_4/C nanocomposites, mixing CH_3COOLi , $(\text{CH}_3\text{COO})_2\text{Co}$, $(\text{NH}_4)_2\text{HPO}_4$ with acetylene black in alcohol media, followed by decomposition under Ar atmosphere for 2 h at 350°C and mw irradiation (2.45 GHz, 700W) for 11 min; shows particle sizes of 150 nm and capacities of 144 mAh/g at C/10 [14]. Develop of nanosized electrode materials is an essential strategy to achieve short diffusion path lengths from the particle-core to the surface, faster ion diffusion and higher rate capability in LIB's [15]. Synthesis of LiMnPO_4 nanocrystallites deposited in nanopores of porous carbon was made using mw irradiation process. Here, LiH_2PO_4 and $\text{Mn}(\text{COOCH}_3)_2 \cdot 4\text{H}_2\text{O}$ were dissolved with a Li/Mn/P molar ratio of 1/1/1 in diethylene glycol and mixed with porous carbon with an average pore diameter of 110 nm (PC110) afterward, subjected to a mw irradiation (2.45 GHz, 400 W) for 5 and 8 min at 200 °C and 250 °C respectively and finally dried at 110 °C in air for 12 h. . Although capacity of the samples is not high so far ($\approx 104 \text{ mAg/h}$ at C/10), the formation LiMnPO_4 nanocrystallites-embedded porous carbons exhibited a retention capacity of 87% at 0.5 C against 0.1 C, which was comparable to that reported for $\text{LiMnPO}_4\text{-C}$ coated [16].

3. Microwave assisted-solvo/hydrothermal synthesis

The requirement of uniformity conditions during the mw irradiation is fundamental to assure good electrochemical activity in the final material. The use of an adequate hydro/solvothermal settings, facilitates the synthesis of polyanionic compounds with well controlled morphology and fine crystal particles; tuned by factors such as temperature, pH, concentration of species and kinetic parameters (speed stirring) [17]. Murugan [18], present a combination of mw and solvothermal process using as starting materials LiOH and $(\text{CH}_3\text{COO})_2\text{Fe}$ solved in tetraethyleneglycol (TEG) and mixed with H_3PO_4 . The homogenous gel is placed in an Anton Paar microwave synthesis system (2.45 GHz, 400 W) machine and heated for 5 min at 300 °C. In addition, produced LiFePO_4 particles were coated with *p*-toluene sulfonic acid (*p*-TSA) doped poly(3,4-ethylenedioxythiophene) (PEDOT) in ethanol. TEM analysis reveals well-defined crystalline nanorod morphology of 25 ± 6 nm and a length of up to 100 nm. This material exhibits high discharge capacity (166 mAh/g) at C/10. PEDOT is used due to its redox behavior (over a wide range of potentials), relative high environmental and thermal stability and high electronic conductivity in its doped state compared to other commonly available conducting polymers. A key factor in hybrid mw-solvothermal synthesis is the use of an organic solvent; indeed polyalcohols (ethylene glycol, tetraethylene glycol) acts first as a solvent in the process and then as a stabilizer to allow limit the particle growth and prohibiting agglomeration [19]. Versatility of the method includes recent contributions on synthesis of doped samples. Goodenough [20] use mw-solvothermal method to produce $\text{LiFe}_{1-3x/2}\text{V}_{x-x/2}\text{PO}_4$ ($x \leq 0.2$) doped samples by mixing LiOH.H₂O, H_3PO_4 , $(\text{CH}_3\text{COO})_2\text{Fe}$ in TEG and adding $\text{OV}(\text{OCH}(\text{CH}_3)_2)_3$ at 300 °C for 30 mins. First charge–discharge curves of the samples shown values around 160 mAh/g in the range of 3.8–4.5 V. This synthetic approach demonstrated a maximum V doping of 10% without the formation of impurity; in fact, the method avoid to use conventional high-temperature routes. Finally, formation of vacancies on Fe site provide an additional conduction pathway for Li^+ ions to transfer between neighbouring 1D conduction channels along the crystallographic b axis.

Microwave-hydrothermal have gained reception and made remarkable progress due to increase in kinetic rates of reactions by one or two orders of magnitude, reduce reactions times, offers large scale batch reactions and saves energy [21]. Furthermore, control of the morphology shows an improvement in electrochemical performance as published by Ji [22]. In this study, LiMnPO_4 crystals were obtained using $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, H_3PO_4 , LiOH as starting materials in the stoichiometric ratio 1:1:3. Sodium dodecyl benzene sulfonate (SDBS) and citric acid (H_3cit) were used to affect the morphology of the products and 5 min mw irradiation at 180 °C – 300 °C and 300 W conditions were used. SEM analysis shows the formation of nanoplatelets (150 nm) orientated in the ac plane whose thickness is controlled mainly by the concentration of precursors. The plate-like morphology could be useful for fast charge–discharge performances as it offers short lengths for Li^+ ion insertion/exertion as comment previously. Addition of organic additives to limit the size shown and improve of capacity value from 44.1 to 89.0 mAh/g. On the other hand, the mw-hydrothermal was used in synthesis of high homogeneity LiFePO_4 with elongated parallelepiped shape in the range 0.5–1.0 mm for suitable studies onto the intrinsic defectivity, chiefly the so-called lithium iron *anti-site*, considered one of the most critical issues when envisaging electrochemical applications [23].

4. Microwave assisted-sol-gel synthesis

From the point of view of yields and use of novel strategies such as carbon-nanotubes to increase the conductivity, new mw-sol-gel synthesis offer better characteristics rather than conventional sol-gel method [24]. Gyroscope-like lithium iron phosphate/multiwalled carbon nanotubes composites has been synthesized with initial discharge capacities of 153.3, 149.6, 140.7, 135.3 and 130.1 mAh/g at 0.1, 0.2, 0.5, 0.8 and 1 C rate, respectively. Multi-wall carbon nanotubes (MWCNTs) are considered ideal materials due to hollowfiber structure and ability to be inserted in the centre of LiFePO_4 , thus forming a conductive network, which not only provide pathways for electron transference but also lead to interparticle electronic connection [25]. Not only carbon compounds are suitable to use to

make coating in phospho-olivines. Zhang [26] use mw-sol-gel method to prepare $\text{LiFePO}_4\text{-Li}_4\text{SiO}_4$ cathode material. The Li_4SiO_4 coating prevent the direct contact between LiFePO_4 and the electrolyte solution. The discharge capacity of the uncoated LiFePO_4 decayed with the increase of the discharge rates, whereas Li_4SiO_4 -coated LiFePO_4 shown a very steady cycling behaviour. Moreover, from electrochemical impedance spectroscopy coated cathode exhibits a smaller charge-transfer the resistance (135.1Ω) than that of the uncoated LiFePO_4 cathode (305.6Ω).

5. Conclusion

Microwave processes constitute a powerful tool to synthesize phospho-olivines with a strong reduced power consumption. Microwave assisted process enables us to produce crystalline cathode particles with different shapes and sizes and has the advantage that the solvent used in the synthesis can often be converted into the carbon source upon heating. Finally it is a simple method for mass production at low cost and short time of synthesis.

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