

MORPHOLOGICAL, STRUCTURAL AND ELECTROCHEMICAL PROPERTIES OF LITHIUM IRON PHOSPHATES SYNTHESIZED BY SPRAY PYROLYSIS

L.S. Gómez¹, I. de Meaza², M.I. Martín¹, M. Bengoechea², I. Cantero³,
M.E. Rabanal^{1*}

¹Universidad Carlos III de Madrid and IAAB, Avda. de la Universidad, 30, 28911
Leganés, Madrid, España

²Dpto. Energía, CIDETEC, Pº Miramon 196, Parque Tecnológico de San Sebastián,
20009 Donostia-San Sebastián, España

³Dpto. I+D+i Nuevas Tecnologías, CEGASA, Artapadura, 11, 01013 Vitoria-Gasteiz,
España

* Tel.: +34916249914; fax: +34916249430; e-mail: mariaeugenia.rabanal@uc3m.es

Abstract

In the field of materials for Lithium ion batteries, the lithium iron phosphate LiFePO_4 has been proven for use as a positive electrode due to its good resistance to thermal degradation and overcharge, safety and low cost. The use of nanostructured materials would improve its efficiency. This work shows the results of the synthesis of nanostructured materials with functional properties for Lithium batteries through aerosol techniques. The Spray Pyrolysis method allows synthesizing nanostructured particles with spherical geometry, not agglomerates, with narrow distribution of particle size and homogeneous composition in respect to a precursor solution. Experimental techniques were focused on the morphological (SEM and TEM), structural (XRD and HRTEM-SAED), chemical (EDS) and electrochemical characterization.

Keywords: Spray Pyrolysis; Lithium Ion Batteries; Nanostructured Materials; Cyclic Voltammetries; Electrochemical Properties

1. INTRODUCTION

Considerable effort has been expended in the last few years on the development of rechargeable batteries to meet demands for the powering of portable electronic devices such as cellular phones or laptop computers and more recently for hybrid electric vehicles (HEV). Lithium secondary batteries have satisfied the requirements to a greater degree than other rechargeable battery systems. Lithium metal phosphates belong to the new emergent-class cathode materials to be used as positive electrode in the next generation of Li-ion batteries. These phosphates mostly appear as two crystalline phases, the $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ NASICON-type structure with orthorhombic or rhombohedral symmetry [1] and the LiFePO_4 olivine-type structure with orthorhombic symmetry, called triphylite [2]. The NASICON-like structure was first studied as solid electrolyte [3]; however, the presence of iron makes it also interesting as cathodic material [4]. In respect to the Olivine phosphates LiFePO_4 (triphylite), their excellent electrochemical properties have yielded a cathodic material reference for the new generation of Li-ion batteries due to its high theoretical capability (170 mAhg^{-1}) for Li intercalation, good cycle stability, adequate resistance to thermal degradation and overcharge [5]. Electrochemical results show that the $\text{Fe}^{3+}/\text{Fe}^{2+}$ level lies at higher voltage versus Lithium [6] in the ordered Olivine-type structure than in the Nasicon-like framework, exhibiting a flat discharge voltage of around 3.45 V [5] while the Nasicon $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ presents a double plateau at 2.8 and 2.65 V [2]. In spite of these attractive features, LiFePO_4 requires further modifications to overcome limitations such as poor electronic conductivity and slow lithium-ion diffusion. In the past few years,

conductivity has been enhanced appreciably by coating particles with electrically conductive materials like carbon [7]. Minimizing the particle size of LiFePO_4 to provide more surface area has also been investigated as a means to enhance lithium-ion diffusion [8,9]. The use of Spray Pyrolysis (SP) method allows to prepare nanostructured particles, for which Li^+ ion diffusion lengths are shortened and ohmic drop reduced, giving rise to enhanced electrochemical properties (higher capacities at high rate/ intensity). By means of SP, it is possible to synthesize spherical, not agglomerated nanoparticles, with compositional homogeneity with respect to the precursor solution. This solution is subjected to ultrasonic vibration in a frequency generator device obtaining fine aerosol drops with stoichiometric composition. The fine aerosol is transported by means of a carrier gas (air, N_2 , Ar, ...), into a tubular furnace with a specific temperature. Into the furnace, processes of dehydration, decomposition, diffusion and reaction are carried out at the same time to produce nanoparticles with controlled size, morphology, composition and free of aggregates [10-14]. The efficiency of this SP method has been successfully proven in the synthesis of different materials with functional properties [15,16].

In this paper, we report the synthesis of nanoparticles of lithium iron phosphates and their electrochemical properties towards lithium using ultrasonic spray pyrolysis method. Nanostructured particles -“as-prepared”- with spherical geometry, not agglomerates, with narrow distribution of particle size have been synthesized. Thermal treatments modify the morphologic aspect in the particle surface. Foam aspect and no spherical morphology can be distinguished.

2. EXPERIMENTAL

Homogeneous precursor aqueous solutions with 0.01M concentration, having Li^+ , Fe^{2+} and $[\text{PO}_4]^{3-}$ ions mixed on a molecular level were prepared from LiNO_3 , $\text{Fe}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$, as precursors with addition of nitric acid ($\text{pH} = 1.5$). The solutions were atomized into fine droplets using an aerosol ultrasonic generator RBI, France, with three piezoelectric transducers operating at 2.1 MHz using argon as carrier gas ($Q_g = 1.5 \text{ l/min}$). The droplets are carried to a tubular flow reactor (length=1.5m) and thermally decomposed at temperatures of 400°C, 500°C and 700°C respectively as schematized in Figure 1. The powders were additionally heated at 600-800 °C/6h, in an argon atmosphere, in order to reach the target triphylite phase.

The characterization was focused on morphologic, chemical, structural and electrochemical analysis. X ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), high resolution electron microscopy (HRTEM) and selected area electron diffraction (SAED) were used. Crystallographic phases were determined by combining the XRD and the electron diffraction-HRTEM techniques, using the Morniroli procedure [17]; HRTEM images were performed using the digital micrograph™ program.

XRD patterns were recorded with $\text{CuK}\alpha$ radiation in an X'Pert Philips automatic diffractometer. The 2θ range analyzed was 10° to 80° with a scan step of 0.02° and a counting time of 10 s for each step. The working conditions were 40 kV and 40 mA. A Philips XL 30 SEM equipped with secondary (SE), backscattered (BSE) and an energy dispersive X-ray (EDAX) detector was employed to study the microstructure and chemical composition of the material. TEM samples were prepared by ultrasonic dispersion of a small powder portion in acetone and then this suspension disposed on a carbon coated copper grid with 3mm diameter. A TEM JEOL JEM 4000 EX operated at 400 kV with a resolution of 1.8 \AA was employed.

A potentiodynamic analysis was carried out using cyclic voltammetry. Electrochemical tests were performed on 2-electrode Swagelok hermetic cells assembled in a LabMaster (MBraun) glove box, using metallic Lithium as counter and reference electrode, and 1 M of LiPF₆ in EC/DMC as electrolyte. The electrode pellet was constituted by active material (61%), acetylene black (30%) to contribute to the electric conductivity and a binder (PVDF) (9%) to ensure mechanical stability. A Biologic MPG multichannel potentiostat-galvanostat system was used, applying a potential gradient of 0.1 mVs⁻¹ in a 1.5 to 4 V window vs. Li/Li⁺. To identify the presence of Fe(II) and/or Fe(III), two cells were prepared for each sample to start with the oxidation in one of them and by reduction in the other.

3. RESULTS

Morphologic analyses were carried out in the “*as prepared*” materials and samples with thermal post-treatment using scanning and transmission electron microscopy techniques.

Figure 2 shows two images obtained by scanning electron microscopy (a) and transmission electron microscopy (b) of samples synthesized at 500°C. The general aspect indicates spherical disaggregates with particle size between 200-400 nm (a). The TEM image (b) shows three particles with diameters between 250-350 nm. The contrast allows the identification of primary particles ranging between 15-30 nm.

Thermal treatments modify the morphology of the particle surface. Foam-like aspect and no spherical morphology can be distinguished by SEM as shown in Figure 3. Particle size is increased with the thermal treatment at 600°C/6h in all systems.

XRD results show three phases in the three evaluated experimental conditions as shown in Figure 4. Both in the “*as prepared*” samples at 500°C and after thermal treatment at 600°C/6h, an orthorhombic NASICON like structure with composition

$\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ (jcpds= 43-0526, $a= 8.827\text{\AA}$, $b= 12.3929\text{\AA}$, $c=8.818\text{\AA}$) is identified associated to Fe_2O_3 (jcpds = 24-0072, $a = 5.038\text{\AA}$, $c = 13.73\text{\AA}$, SG = 148), and a small contamination of SiO_2 from the quartz tube is present. With the thermal treatment at $800^\circ\text{C}/6\text{h}$, the triphylite phase LiFePO_4 (jcpds = 40-1499, $a = 6.002\text{\AA}$, $b = 10.32\text{\AA}$, $c = 4.68\text{\AA}$ GE = 62) begins to appear as shoulders associated to the $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ phase and Fe_2O_3 is still present. The position of triphylite, Nasicon and Fe_2O_3 reflections are indicated in the figure.

Due to the amorphous aspect of the “*as prepared*” samples HRTEM images were impossible to obtain. However, as a result of a better atomic order in the nanostructured particles, lattice images can be observed for samples after a thermal treatment at $800^\circ\text{C}/6\text{h}$.

High resolution TEM observations allow identifying the triphylite phase in the samples subjected to thermal treatment at $800^\circ\text{C}/6\text{h}$ as shown in Figure 5. In the image lattice, the interatomic distances corresponding to the (121) and (101) planes of the triphylite phase are resolved. The Fourier transformed (*fft*) (as inset) shows the orientation along the [111] zone axis.

Semiquantitative EDS microanalysis by SEM was carried out to determine the chemical composition in the synthesized samples. The detector is sensitive to the elements in which $Z > 4$, excluding the Lithium atoms detection. Fe, P and O atomic percentages were evaluated in all samples (“*as prepared*” and heated samples). In “*as prepared*” samples (500°C), experimental values were Fe: 18 ± 1 , P: 19 ± 2 , O: 62 ± 1 at%, which are in good agreement with the chemical composition equivalent to $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ and Fe_2O_3 . Values obtained for samples treated at 800°C are Fe: 35 ± 2 at%, P: 30 ± 2 .at% and O: 37 ± 3 at% indicating the coexistence of three phases: LiFePO_4 , $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ and Fe_2O_3 . Small differences could be explained by the low sensibility in the EDS device

for the oxygen detection. Spot analysis shows an increase in Fe content due to the association of LiFePO_4 or $\text{Li}_3\text{Fe}_2(\text{PO}_4)_2$ with Fe_2O_3 .

Voltammetry studies were carried out on the two compositional extremes of the studied samples: one “*as prepared*” sample synthesized at 500°C and one sample subjected to thermal treatment at 800°C/6h from a sample synthesized at 700°C.

Figure 6 shows the cyclic voltammetry experiments carried out on the “*as prepared*” sample synthesized at 500°C. Figures correspond to the oxidation up to 4V vs. Li/Li^+ from the initial OCV (3.2 V, open circuit potential) (a) and the initial reduction down to 1.5 V from OCV (b). There is no evidence of Fe(II) due to the absence of signal in the first oxidation (broken line in Fig. 6a), although in the reduction (negative intensities) a broad signal around 2.6 V corresponding to the $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ reaction can be observed. The potential of this quasi-reversible process that can be observed in both voltammetries (from 2nd cycle on, 2.6 V in reduction, 2.9-3 V in oxidation) is significantly lower than the reported values for the olivine LiFePO_4 (3.5 V) [4] and corresponds to the Fe (III) from the nasicon type $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ identified by XRD that shows electrochemical activity towards Lithium intercalation [4]. Only a weak signal of the iron oxidation around 3.6 V can be observed, probably related to noncrystallized LiFePO_4 . Small signals around 1.6-1.8 V in reduction might correspond to iron (III) oxides, like the Fe_2O_3 identified by XRD.

In Figure 7 the cyclic voltammetries for the sample synthesized at 700°C with a thermal post treatment at 800°C/6h are shown. More signals and better definition are registered in comparison to the “*as prepared*” sample shown in Figure 6. The reversible process with broad signal observed in the “*as prepared*” sample is disclosed in this case as two processes around 2.8 V and 2.94 V in oxidation and in 2.64 V and 2.8 V in reduction in both voltammetries (a and b). Narrow and well defined peaks are the

consequence of a better atomic order in the sample as a result of thermal treatment. The overlap of two peaks is typical of a redox pair in two slightly different environments. This behaviour is observed in materials with two crystallographic positions for the metal that can be distinguished as two peaks in the electrochemical measurements, in this case for the Fe (III) phosphate identified by XRD as $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ NASICON like structure. A quasi-reversible process centred between 3.38V and 3.54V is observed also in the first oxidation process (Figure 7a). These values coincide with the triphylite phase (LiFePO_4) [4] also identified by XRD and HRTEM.

4. CONCLUSIONS

Nanostructured materials, free of aggregates, compositionally homogeneous, hollow with narrow particle size distribution and spherical morphology were synthesized through Spray Pyrolysis technique. As a result of the thermal treatment at 600°C - 800°C /6h, morphologic aspects are modified, obtaining non spherical hollow particles with foam appearance and bigger sizes.

$\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ and Fe_2O_3 have been identified from the XRD results in the “*as prepared*” samples and in the samples subjected to thermal treatment at 600°C /12h. Additionally, the triphylite phase (LiFePO_4) has been detected in small proportion in samples after a thermal treatment at 800°C /6h, as shoulders associated to the $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ phase. High resolution transmission electron microscopy observations confirm the presence of triphylite phase.

Electrochemical analysis confirms the $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ phase with NASICON like structure in the “*as prepared*” samples obtained at 500°C and in the samples synthesized at 700°C with post thermal treatment at 800°C /6h. Also, the appearance of LiFePO_4

phase with olivine like structure as a result of thermal treatment at 800°C/6h is confirmed.

The higher electrochemical signal is registered for the NASICON like structure, both in the “*as prepared*” sample at 500°C and in the one subjected to thermal treatment at 800°C/6h. In the “*as prepared*” samples stress and structural defects contribute to the high cationic disorder, hindering the intercalation and de-intercalation of Lithium, justifying the low signal in the samples. The temperature effect produces better definition in the peaks and an increase of the signal in both phases as a result of better atomic order that allows a higher electrochemical activity.

ACKNOWLEDGMENTS

The authors gratefully appreciate the financial support of the Ministry for Education and Science of Spain in the project “Advanced materials for Lithium batteries through alternative synthesis” (PIROLION project-PROFIT 2007-2008), MAT2007-64486-C07-05 (FEDER) and the Juan de la Cierva program JCI-2005-1892-13 (M.I. Martín). We thank I. Boyano for helpful discussions and A. Lago for experimental aid. The assistance in TEM characterization of the Electron Microscopy and Citometry Center, Universidad Complutense, Madrid, Spain is also kindly acknowledged.

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FIGURE CAPTIONS

Fig. 1: Schematic Spray Pyrolysis synthesis process.

Fig. 2: Images of nanoparticles “*as prepared*” synthesized at 500°C, obtained by SEM (a) and TEM (b).

Fig. 3: SEM images of the sample synthesized at 500°C (a) and a sample synthesized at 400°C (b) after thermal treatment at 600°C/6h.

Fig. 4: Evolution of X-ray diffraction patterns synthesized at 500°C and thermally treated. In the bottom, the position of the Nasicon (Nas), triphylite(Tr) and hematite(Hem) patterns are shown.

Fig. 5: HRTEM image of the sample synthesized at 500°C after a thermal treatment at 800°C/6h showing the interatomic distances of the (121) and (101) of the triphylite phase. In the right corner (as inset) the *fft* along the (001) zone axis is shown.

Fig. 6: Cyclic voltammetries at 0.1 mVs⁻¹ rate in the 1.5 to 4 V vs. Li/Li⁺ range of the “*as prepared*” sample synthesized at 500°C. Sample first oxidized from the initial OCV to 4 V (a) and initial reduction from OCV to 1.5 V (b).

Fig. 7: Cyclic voltammetries at 0.1 mVs⁻¹ of a sample synthesized at 700°C with a post thermal treatment at 800°C/6h. Oxidation up to 4 V vs. Li/Li⁺ from initial OCV (a) and initial reduction down to 1.5 V from OCV (b).

















