Lithium iron phosphates: synthesis and ionic exchange via mechanochemistry

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Over the last few years, iron-based compounds containing polyanions such as $(PO_4)^{3-}$, $(SO_4)^{2-}$ and $(AsO_4)^{3-}$ have been investigated intensively as potential cathode materials for rechargeable lithium ion batteries [1,2].

Indeed, orthorhombic $LiFePO_4$ has a high discharge voltage (3.4 V) and relatively large theoretical capacity of 170 $mAhg^{-1}$ owing to the reversible reaction $LiFePO_4 \Leftrightarrow Li^+ + FePO_4$. Its electrochemical performance is enhanced at moderately elevated temperatures and no evidence of troublesome reactions are observed. The main problem is the poor rate capability. It can be overcome by an electronic conductive particle coating and by synthesizing small particles [3-5].

Two extra lithium ions can be inserted into rhombohedral $Li_3Fe_2(PO_4)_3$ to form $Li_{3+x}Fe_2(PO_4)_3$ at 2.8 V. The $Li_3Fe_2(PO_4)_3$ discharge curves and the effective discharge capacity depend on the synthesis route and subsequent treatment. It was found that after grinding, two plateaus at 2.8 and 2.65 V, corresponding to ca. 1.5-1.6 inserted lithium ions, are observed instead of only one plateau at 2.8 V and ca. 1.1 inserted lithium ions for untreated samples [6]. In both cases, the preparation of small size particles of lithium iron phosphates is highlighted.

Recently, mechanochemical processing has been applied by the authors for the synthesis of different oxide cathode materials [7]. It involves mechanical activation of solid state reactions either directly during milling or under subsequent heat treatment at lower temperatures, as compared to ceramic method, and leads to preparation of highly dispersed materials. Besides synthetic reactions, mechanical activation enables other types of reactions, including ionic exchange.

$LiFePO_4$. Orthorhombic $LiFePO_4$ with an ordered olivine structure is usually prepared by multistage ceramic method at 800°C in inert atmosphere. In our study, $LiFePO_4$ was prepared by short-term mechanical activation of the mixture of $FeC_2O_4 \cdot H_2O$, $NH_4H_2PO_4$ and LiOH or Li_2CO_3 in a highly energetic planetary activator AGO-2 (660 rpm) followed by heat treatment for 1-4 h at temperatures ranging from 400 to 800°C in Ar atmosphere. Figure 1 shows that all samples synthesized via mechanochemical route were single phase $LiFePO_4$ with an ordered olivine structure indexed by orthorombic *Pnmb* and high specific surface area (ca. 3-6 m^2/g). No Fe^{3+} containing compounds formed as impurity. On the contrary, no noticeable formation of $LiFePO_4$ occurs in nonactivated mixtures at 400°C while the samples heated at 600°C are characterized by phase inhomogeneity.

$Li_3Fe_2(PO_4)_3$. Rhombohedral $Li_3Fe_2(PO_4)_3$ can be prepared from monoclinic $Na_3Fe_2(PO_4)_3$ by ionic exchange in a $LiNO_3$ melt or in a concentrated aqueous solution. In the present study, mechanical activation of mixtures of Fe_2O_3 and $NH_4H_2PO_4$ with lithium or sodium hydroxides or carbonates was performed to accelerate solid state interaction under subsequent heat treatment at 800°C. According to X-ray analysis, homogeneous monoclinic $Li_3Fe_2(PO_4)_3$ and $Na_3Fe_2(PO_4)_3$ were obtained after 2-4 h. To prepare electrochemically active R-$Li_3Fe_2(PO_4)_3$, mechanochemical solid state ionic exchange reaction with as-prepared $Na_3Fe_2(PO_4)_3$ was realized using solid $LiNO_3$. The product was washed with water to remove $NaNO_3$ and dried at 100°C (Fig. 2). The as-prepared R-$Li_3Fe_2(PO_4)_3$ was characterized by high dispersion.

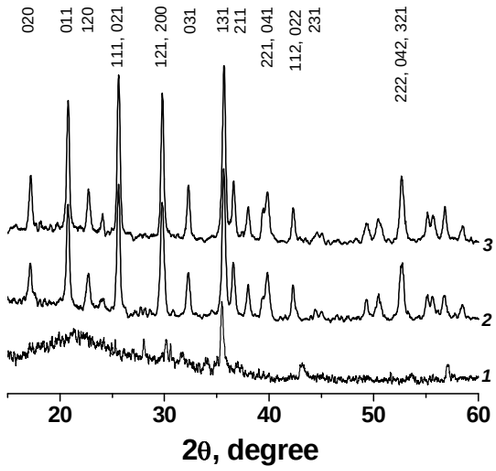

Fig. 1. X-ray patterns of $LiFePO_4$ *prepared from nonactivated (1) and activated (2,3) mixtures heated at 400℃ (1,2) and 600℃ (3).*

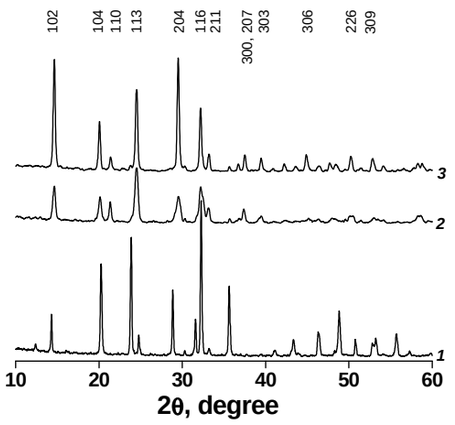

Fig. 2. X-ray patterns of $Na_3Fe_2(PO_4)_3$ *prepared under mechanothermal route (1) and R-*$Li_3Fe_2(PO_4)_3$ *obtained under solid state mechanochemical (2) and solution (3) ionic exchange with* $LiNO_3$.

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