Improving the electrochemical properties of nanosized LiFePO$_4$-based electrode by boron doping

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ABSTRACT

Electrode materials with homogeneous distribution of boron were obtained by heating mixtures of nanosized carbon-coated lithium iron phosphate and BPO$_4$ in 3-9% weight at 700 °C. The materials can be described as nanocomposites containing i) LiFePO$_4$, possibly doped with a low amount of boron, ii) FePO$_4$ and iii) an amorphous layer based on Li$_4$P$_2$O$_7$-derived material that surrounds the phosphate particles. The thermal treatment with BPO$_4$ also triggered changes in the carbon coating graphitic order. Galvanostatic and voltammetric studies in lithium half-cells showed smaller polarisation, higher capacity and better cycle life for the boron-doped composites. For instance, one of the solids, called B$_6$-LiFePO$_4$, provided close to 150 and 140 mAhg^{-1} (87% and 81% of theoretical capacity, respectively) under C/2.5 and C regimes after several cycles. Improved specific surface area, carbon graphitization, conductivity and lithium ion diffusivity in the boron-doped phospholivine network account for this excellent rate performance. The properties of an amorphous layer surrounding the phosphate particles also account for such higher performance.

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1. Introduction

Since Goodenough et al. pointed out LiFePO$_4$ as an attractive material for lithium batteries [1–9], this phospholivine has been widely investigated as promising cathode material to replace LiCoO$_2$. This phosphate is cheap, abundant, environmental friendly and shows adequate gravimetric capacity and capacity retention upon cycling. However LiFePO$_4$ shows two major drawbacks: its intrinsic conductivity is very small (10^{-10} S·cm^{-1}) [10] and lithium diffusion is slow in the network ($D_{Li+} \approx 10^{-14}$ cm^{2}s^{-1}) [7–9]. The decrease of particle size can effectively reduce the lithium path and moderate the effects of the slow lithium kinetics, whereas a carbon film surrounding the LiFePO$_4$ particles effectively improves the composite material conductivity [4–9].

Following the discovery of this lithium ion electrode, a great effort was devoted by the scientific community to understand the role played by doping with metallic ions on its electrochemical performance. In a pioneering work, Fisher et al. [11] determined the solution energy for the substitution of a few main groups or first row transition metals for either lithium ions in the octahedral M1 positions or iron ions in the M2 sites. Seemingly, apart from ions as Co^{2+}, Ni^{2+} and Mn^{2+}, whose LiMPO$_4$ phospholivine structures are well known, the true doping and the exact location of a great number of *aleo* ions are still under discussion. For instance, the controversial paper by Chung et al. [12] claimed that Mg^{2+}, Al^{3+}, Ti^{4+}, Zr^{4+}, Nb^{5+} or W^{6+} ions do replace lithium ions, inducing a net cation deficiency and enhancing the phosphate electronic conductivity. However, Ellis et al. [13] later proved that the origin of the huge conductivities shown by these modified phosphates was the occurrence of highly conductive metal phosphides connecting the LiFePO$_4$ particles.

An examination of the recent literature indicates that even when doping is supposed to take place, the exact location of the ions can still be controversial. For instance, some authors indicate that, depending on the ion size, Mg^{2+} replaces lithium in the M1 sites [14]. Thus, in order to guarantee the crystal electroneutrality, Li$_3$PO$_4$ or iron phase segregation should take place. However, neither of these segregated phases have been observed. By contrast, the observed enhancement of the lithium diffusion could be explained by a cell volume increase due to the possible

substitution of Mg^{2+} for Fe^{2+} in the M2 sites. This is consistent with the fact that solution energy of Mg^{2+} ions is 3 eV higher in the lithium sites than it is in the iron sites [15,16]. Moreover, at least three trivalent ions have been used as "doping" agents in the phospholivine, namely Al^{3+} [17], Cr^{3+} [18] and V^{3+} [19]. Seemingly, the first two prefer to occupy the M1 sites, whereas the preferred location of the latter is the M2 site. For the three "doped" systems, an increase in the electronic conductivity has been reported. This can be explained, for example, by the presence of cation (mainly lithium) vacancies coupled with neighboring Fe and O ions to form a conducting cluster. A cell volume expansion is also observed and considered to be the origin of increased lithium ion diffusivity in these doped materials. However, Wagemaker et al. [18] indicated that Cr^{3+} ions located in M1 sites act as motion blocking agents and should decrease the lithium ion diffusivity.

In previous work, Franger et al. [20,21] reported the doping of $LiFePO_4$ with B^{3+} in narrow levels (B/Fe mole ratio $\leq$ 0.1). The samples were obtained by mixing freshly precipitated iron(II) hydrated orthophosphate [$Fe_3(PO_4)_2 \cdot 5H_2O$], BPO_4 and Li_3PO_4 in adequate amounts and heating the mixture at 600 °C under argon for 15 min. The materials obtained showed increased capacities in comparison with boron free system. For example, the sample with a $LiFe_{0.95}B_{0.033}PO_4$ composition provided capacities in the 130-140 mAh g^{-1} under rates C/10 (0.05 mA cm^{-2}), C/3 (0.17 mA cm^{-2}), C/2 (0.25 mA cm^{-2}) and C (0.5 mA cm^{-2}) rates. They were 75% higher than the capacities provided by a $LiFePO_4$ obtained through the same procedure but without boron addition. Such increased capacity led the authors to state that an actual doping, lower than about 10%, can be reached by this particular synthesis method. With this doping, the conduction of the charge carriers is significantly increased [20,21]. Furthermore, the materials showed excellent capacity retention. The exceptional characteristics of these boron doped materials urged us to prepare three boron modified materials based on carbon-coated $LiFePO_4$ [22]. For this purpose, we carried out solid state reactions between BPO_4 and $LiFePO_4$/C. The materials obtained were characterized by several techniques and their electrochemical properties in lithium half cells were compared with thermally-treated $LiFePO_4$/C. The boron amount incorporated in the phosphate has an effect on several physicochemical and the electrochemical properties of these solids.

2. Experimental

Nanosized lithium iron phosphate and BPO_4 (99.995%) were supplied by *Phostech Lithium Canada* and *Aldrich* respectively. The phosphate contains a carbon-coating in order to make it conductive, the carbon/$LiFePO_4$ weight ratio being 2–5%. Three mixtures were prepared by manually grinding the lithium iron phosphate with BPO_4 in the following weight ratios: 97:3, 94:6 and 91:9 ($LiFePO_4$:BPO_4). The mixtures were subsequently heated at 700 °C under a nitrogen flow for 5.5 h. The samples obtained will be hereafter named B_x-$LiFePO_4$ (x = 3, 6, 9). For comparison purposes, a sample was prepared by heating $LiFePO_4$ in absence of BPO_4 (hereafter called B_0-$LiFePO_4$). X-ray diffraction (XRD) patterns were recorded on a Siemens D5000 X-ray diffractometer, using Cu Kα radiation and a graphite monochromator. Rietveld refinements were carried out by using the GSAS software. Transmission electron microscopy (TEM) images were obtained on a JEOL 2010 microscope operating at 200 keV. Scanning electron microscopy (SEM) images were obtained with a Jeol 6300 microscope coupled with an energy dispersive X-ray analyser (EDAX). Textural properties were determined from nitrogen adsorption/desorption isotherms on a Micromeritic ASAP 2020 instrument, using N_2 gas as adsorbate. Raman measurements were carried out with a

Renishowin Vida Microscope, a Renishaw CCD Camera (578x400) detector and with a 785 mm edge laser in Linefocus mode, working in a 100 to 1700 cm^{-1} wavenumber range. The power of the laser beam on the sample used, was 0.1 or 5 mW.

Galvanostatic and potentiostatic measurements were made with two-electrode cells. The electrolyte used was Merck battery electrolyte LP 40, which consists of 1 M $LiPF_6$ in ethylene carbonate (EC) and dimethyl carbonate (DMC) in a 1:1 (w/w) ratio. Lithium disk acted as a negative electrode. Around 5 mg of the electrodic mixture (consisting of B_x-$LiFePO_4$, carbon black and Teflon in a 85:10:5 weight ratio) were pressed on stainless steel grid (0.3 mm thick, φ=12 mm) and acted as a positive electrode. Potentiostatic cycling was carried out on swagelock cells with voltage steps of 10 mV h^{-1}. Coin cell configuration was used for galvanostatic cycling of the Li/$LiPF_6$(EC,DMC)/B_x-$LiFePO_4$ cells under a C/10, C/5 or C/2.5 regime. Electrochemical measurements were controlled via a MacPile II (Biologic, Claix-France). Finally, a TOYO three-electrode cell with lithium wire and lithium foil as reference and counter electrodes, respectively, was used for electrochemical impedance spectroscopy (EIS) measurements. The spectra were recorded with a potentiostat EGG PAR 273 A coupled with a 1255 Solartron Frequency Response Analyzer. Measurements were made over the range 84 kHz–3.4 mHz. The AC signal was 10 mV peak to peak. The equilibrium potential was assumed to be reached when the drift in open-circuit voltage fell below 1 mV h^{-1}. Impedance diagrams were fitted with the software Zplot®, from Scribner Associates.

3. Results and discussion

3.1. Physicochemical characterization

According to Franger et al. [20,21] up to 10% of iron can be substituted by boron ions. In our case, the B_x-$LiFePO_4$ (x = 3, 6, 9) samples contain an atomic boron level of 4.4%, 8.7% and 12.9%, per Fe+B respectively. Only the latter would therefore be out of the presumed doping range [20,21]. However, based on XRD data of the B_x-$LiFePO_4$ samples, it was concluded that none of them contained a single phase. In fact, peaks associated to the heterosite ($FePO_4$) phase were present in addition to the $LiFePO_4$ peaks. The presence of boron seems to enhance the segregation of heterosite on heating. In particular, the heterosite peaks for the B_9-$LiFePO_4$ sample were very intense and a further study on this material was discarded. Moreover, no peaks belonging to BPO_4 (JCPDS 34-132), boron or iron phosphides or carbides were detected in the XRD patterns. However, the nanosized nature and/or poorly crystallization of possibly present metal phosphides [9,23] hinders their detection by XRD. ICP measurements yielded a B/(Fe+B) ratio close to 2% and 6% for B_x-$LiFePO_4$ (x = 3, 6) respectively.

Rietveld analysis of the XRD patterns was applied in order to study the location of boron. Note that this analysis is limited by the low X-ray sensitivity of boron, a light atom. Therefore, the main conclusions of the next discussion must be confirmed by carrying out neutron diffraction studies. Unfortunately, this technique was not available.

Two different approaches, namely (i) M1 or M2 site occupancy and (ii) P replacement, were considered. The unsuitability of the first models, based on chemical and structural considerations, was confirmed by the poor fitting of the XRD pattern (results not shown). A somewhat better fitting (Fig. 1) was obtained with B occupying the P positions. Actually, it is found that in BPO_4, B and P are distributed in the center of tetrahedral units which share their corners. The cell parameters obtained are shown in Table 1. The presence of boron barely changed the unit cell volume (291.17 Å^3) in spite of the differences in the ionic radii [(r(P^{5+}) = 0.17 Å,