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Mixed lithium phosphates as cathode materials for Li-Ion cells

N. Penazzi[a], M. Arrabito[a], M. Piana[a], S. Bodoardo[a,*], S. Panero[b], I. Amadei[b]

[a]*Department Chemical Engineering and Materials Science, Polytechnic of Turin, c.so Duca Abruzzi 24, 10129 Turin, Italy*
[b]*Department Chemistry, "La Sapienza", University of Rome. Rome, Italy*

Abstract

$LiFe_xCo_{(1-x)}PO_4$ ($x=0.2$, 0.5, 0.8,1) solid solutions have been prepared by solid state reaction method to sevatudy the electrochemical performance of these olivine structure compounds as cathode material for lithium-ion batteries. SEM observations, X-ray powder diffraction (XRPD) profiles and Rietveld refinement have been carried out to investigate the structural characteristics and morphology of the samples. During the preparations citric acid was added to the reactants to improve the electronic conductivity of the cathode. The results showed that when present in small amounts, Co exerts a beneficial effect mainly at the first cycles where the additive is not effective. At higher Co levels this positive effect seems to cease, probably is still present but hidden by the progressive electrolyte degradation that causes a decay of the electrochemical performance.

Keywords: Batteries; Lithium insertion; Microstructure-final; Powders solid state reaction; Transition metal oxides

1. Introduction

The development of an electrochemical power sources system based on the insertion and removal of lithium ions into and from host compounds at both electrodes, the so called li-ion cell, started in the 1970s.[1] Since then an enormous amount of experimental research has been developed.

Considering the positive electrode, most of the work has been devoted to finding materials whose crystalline structure allowed easy diffusion of Li^+ ions to improve capacity and rate capability.

The mineral triphylite, having the formula $LiFePO_4$ and showing an ordered olivine structure has proved to be one of the most promising among the polyanionic compounds tested over recent years.[2–9]

The Fe(III)/Fe(II) couple open circuit potential is 3.5 V/Li that assures a good energy density and yet is sufficiently low to prevent interference with the electrolyte. Its behaviour during charge is based on the transformation of triphylite to the new phase, heterosite $FePO_4$, with the extraction of 1 Li^+ ion per formula unit and contemporary oxidation of Fe from (II) to (III) oxidation state. The corresponding theoretical capacity is 170 mAh/g which is similar to that of cathode materials currently in use.

Since the first investigations on $LiFePO_4$, it was found to be difficult to obtain the theoretical capacity and that a reversible capacity loss is present throughout the charge–discharge cycles, increasing with the current density.[2,9] This capacity loss phenomenon has been related to the limited area of the interface between $LiFePO_4/FePO_4$ phases where the extraction–insertion takes place. According to Andersson and Thomas[4] the factor limiting the full conversion of $LiFePO_4$ to $FePO_4$ is based on the combination of low Li ion diffusion rate and low electronic conductivity.

In our previous studies we have obtained good results in improving the electrochemical features of $LiFePO_4$ by using in the solid state synthesis procedure an annealing temperature of 600 °C and an Ar/H_2 gas mixture during the annealing stage and adding, along with the precursors, ascorbic acid as a conductivity aiding compound.[10,11]

Previous investigations on $LiCoPO_4$, a compound having the same structural characteristics as triphylite put in evidence, according to,[8] that such material exhibited a charge–discharge potential higher than 4.5 $V/Li^+/Li$ and a higher capacity than $LiFePO_4$ at high charge–discharge rates. Such a high value of the potential is nonetheless harmful to the stability of most actual electrolytes. Thinking that the coexistence of Co and Fe in the structure could help make the kinetic of the charge discharge process more rapid so enhancing

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* Corresponding author. Tel.: +39-011-564-46-41; fax: +39-011-564-46-99.

E-mail address: bodoardo@athena.polito.it (S. Bodoardo).

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charging efficiency, we prepared and characterized a series of mixed transition metal phosphates having general formula $LiFe_xCo_{(1-x)}PO_4$ ($1 \geqslant \times \geqslant 0.2$) and are presenting the results in this paper.

2. Experimental

2.1. Synthesis

Solid State Reaction was the method used to prepare the phospho-olivine compounds. The precursors were Li_2CO_3 (Aldrich > 99% purity), $(NH_4)H_2PO_4$ (Analyticals Carlo Erba, 98%), $Fe(COO)_2{*}2H_2O$ (Carlo Erba, 99%), $Co(CH_3COO)_2{*}4H_2O$ (Carlo Erba, 99%).

The precursors were weighed, according to the stoichiometric ratio, mixed and ground by a planetary ball mixer. The powders, after pre-treating at 325 °C in inert atmosphere for 8 h, were pressed in pellets and annealed at 600 °C for 18 h. The annealing treatment was carried out in inert atmosphere too (high purity Ar).

In order to improve the electrochemical performances citric acid was added during the synthesis.

2.2. X-ray diffraction

The diffraction data of the samples have been collected using the Philips X'pert-MPD powder diffractometer, equipped with Cu $K\alpha$ radiation (V = 40 kV, I = 30 mA) and a curved graphite secondary monochromator. The data collections obtained have been analysed with GSAS [A.C. Larson, R.B. Von Dreele, Los Alamos National Laboratory Report, LAUR 86-748 (2000)], a software package for the structural refinement from diffraction data.

The starting structures of the refinements were the $LiFePO_4$ structure from single crystal data[12] in the case of the samples richer in Fe and the single crystal structure of $LiCoPO_4$[13] in the case of $LiFe_{0.2}Co_{0.8}PO_4$. In order to obtain the structure of the samples, lattice parameters, sample displacement, Pseudo-Voigt profile factors and atomic coordinates have been refined, besides the scale factor and the background intensity.

The samples have been subjected to scanning electron microscope to analyse the morphological and particle size, using the Philips SEM 515.

2.3. Electrochemical measurements

The electrodes for the electrochemical measurements were prepared in the same way as described in Ref. 10. The amount of acetylene black (Super P, MMM Belgium) added as electronic conductor during the preparation of the electrodes which in this case was 5 wt%. The liquid electrolyte used was 1M $LiPF_6$ solution in ethylene carbonate (EC)- propylene carbonate (PC) mixture.

The galvanostatic cycling tests were carried out at room temperature using a Maccor Battery Cycler, and consisted in galvanostatic charge-discharge cycles at C/10 and C/5 rate. Linear scanning voltammetries have been carried out by a PARR 273 instrument. The scan rate was 0.1 mV/sec and the potential range chosen was between 2.9-4 V/Li (2.9–5 V/Li in the case of the compounds containing cobalt).

3. Results and discussion

3.1. Structural results

The X-ray diffraction profiles showed that all the samples synthesized were well crystallised phases. Observations at the scanning electron microscope revealed the presence of micrometric size grains.

The structural refinement of the terms of the solid solution $LiFe_xCo_{(1-x)}PO_4$ (in the range $0.8 \geqslant (1-x) \geqslant 0$). allowed us to show the variation of the lattice parameters, Table 1 with $Co_{(1-x)}$ content.

The lattice parameters *a* and *b* decrease in a similar way, with increasing of $Co_{(1-x)}$ content in the solid solution; on the contrary the variation of *c* is not monotonous, showing a minimum in correspondence of the $(1-x) = 0.2$ value and increasing for higher $(1-x)$ values. Such variation is anyway about one order of magnitude smaller than the *a* and *b* ones. The lattice volume, therefore, follows the trend of *a* and *b*.

The reason of the decreasing lattice parameters is in the ionic radius of Co^{2+} being smaller than Fe^{2+}. This is also confirmed by the decreasing trend of the M–O distances (here not reported for sake of brevity).

3.2. Behaviour of the mixed Fe-Co phospho-olivines

Fig. 1 reports some of the second cycle linear scan voltammetries for the various terms $LiFe_xCo_{(1-x)}PO_4$. For $x = 1$ we have the $LiFePO_4$ response to the potential increase and decrease showing, as expected, just a couple of peaks around 3.5 Volts/Li app. The remaining curves are related to the mixed Fe–Co phosphates and

Table 1
Refined lattice parameters and lattice volume of synthesized $LiFe_xCo_{(1-x)}PO_4$ microcrystalline powders, in comparison with those taken from bibliography[5,14] (sigmas in brackets)

$(1-x)$ in $LiFe_xCo_{(1-x)}PO_4$	a/Å	b/Å	c/Å	Volume/Å^3
0 (Ref. [5])	10.332(4)	6.010(5)	4.692(2)	291.4(3)
0	10.3205(7)	6.0049(4)	4.6917(3)	290.76(3)
0.2	10.3156(4)	6.0007(3)	4.69055(23)	290.350(23)
0.5	10.2737(5)	5.9735(3)	4.69357(24)	288.042(24)
0.8	10.2300(5)	5.9441(3)	4.69671(23)	285.599(23)
1 (Ref. 15)	10.2001(6)	5.9199(4)	4.690(2)	283.2(1)

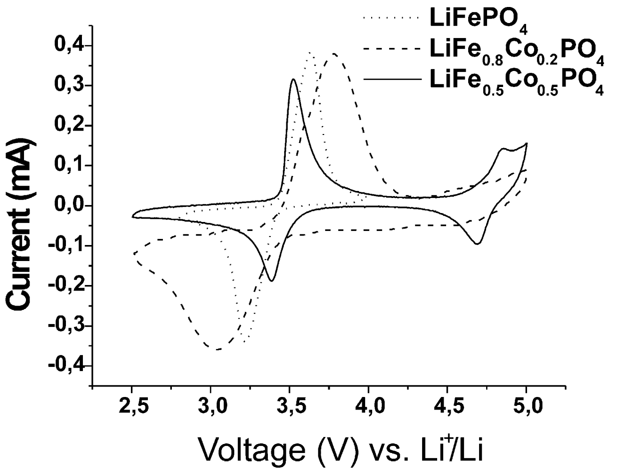

Fig. 1. Second voltammetric cycle for some of the $LiFe_xCo_{(1-x)}PO_4$ samples. Scan rate 0.1 mV/s.

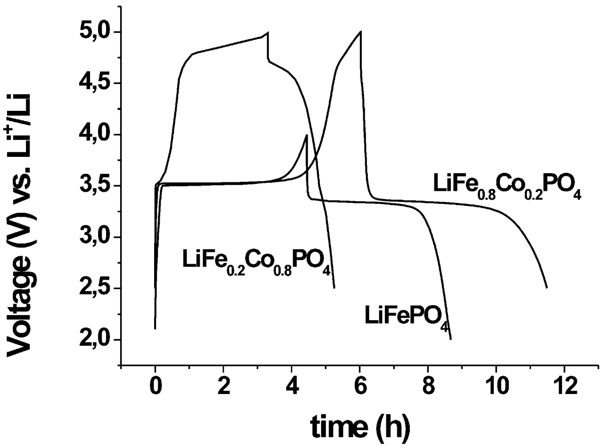

Fig. 3. Voltage profiles for the second galvanostatic charge-discharge cycle at C/10 for $LiFePO_4$ and $LiFe_xCo_{(1-x)}PO_4$ samples having $x=0.8$ and $x=0.2$.

show both the features typical of $LiFePO_4$ and of $LiCoPO_4$ (a couple of peaks centered around 4.8V/Li app.). Qualitatively (the mass of the various samples are slightly different so the peaks' area cannot be considered) the Co couple of peaks always becomes more detectable with the increase of $(1-x)$. This plot puts in evidence also that the presence of Co does not influence the redox behaviour of Fe: the Fe(II)/Fe(III) redox potential is the same for all considered samples. This finding is confirmed by the fact the galvanostatic charge–discharge profiles for the various samples, at 3.5 V step is clearly flat and is not modified (apart from the extension) passing from Fe to Fe–Co phosphate so indicating the Fe redox is in all cases a two phase reaction (Fig. 3 in the followings).

The specific capacity vs the number of charge–discharge cycles is reported in Fig. 2. In general the trend of the curves is similar: a marked decay of the capacity after the first cycle and a more or less shallow decay afterwards. Nonetheless, while the samples $LiFePO_4$ and $LiFe_{0.8}Co_{0.2}PO_4$ show an initial capacity almost similar to the theoretical, decaying abruptly to half of that value, the samples more rich in Co show capacity values which are insufficient from the very beginning.

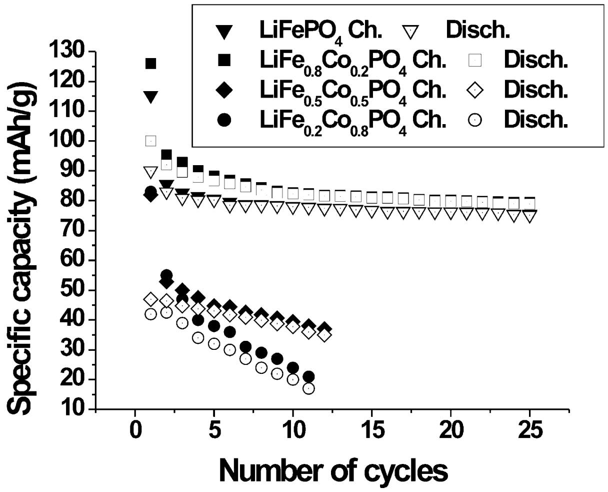

Fig. 2. Charge and discharge specific capacity vs number of cycles for all $LiFe_xCo_{(1-x)}PO_4$ samples. Charge and discharge regime C/5.

The most important result regarding the $LiFe_{0.8}Co_{0.2}PO_4$ curves: they show the same ongoing as the pure Fe sample but are displaced at detectably higher capacity values. As this occurs in particular at the first cycles, it appears that the presence of small quantities of Co help in decreasing the marked capacity loss only at the initial cycles. We think that the limited improvement of capacity in the presence of Co at low levels should be put in relation to the variation of the structural parameters previously described being, of course, the two dimensional motion[15] of Li ions inside the crystalline structure influenced by such modifications. At the actual stage of the investigation, however, it is not possible to be more exhaustive. The rapid decay of capacity at higher levels of Co is not unexpected, being related to the potential value of the Co(II)/Co(III) redox reaction which is higher than the upper limit of the electrolyte stability potential window. This is not a new finding, being the major cause of the unsatisfying performance of $LiCoPO_4$[8] as a positive electrode. The positive effect that seems to cease at higher Co levels (Fig. 2), is probably at least maintained for all $LiFe_xCo_{(1-x)}PO_4$ solid solutions but is hidden by the progressive electrolyte degradation causing a rapid decay of the performance.

Fig. 3 puts in evidence the previous observation: the higher the quantity of Co, the higher the portion of the charge curve at potentials over 4 V/Li. This means that an always more consistent part of the charge period passed at a potential higher than 4 V, making the electrolyte degradation progressively more rapid and preventing any possible beneficial effect of Co.

4. Conclusions

$LiFePO_4$ is a promising cathodic material for Li-ion batteries but is affected by a marked capacity loss. We prepared and investigated the electrochemical behaviour of Fe-Co mixed phosphates having the formula $LiFe_xCo_{(1-x)}PO_4$ to assess if such materials show enhanced performance. Our experimental findings put in evidence that:

- At low Co levels ($LiFe_{0.8}Co_{0.2}PO_4$) the capacity shows a limited but detectable enhancement with respect to $LiFePO_4$. On the contrary, the samples more rich in Co show far lower initial capacity rapidly fading with the number of cycles.
- At the actual stage of our research we have good grounds to think that the better electrochemical performance shown by mixed Fe–Co phosphates is related to the variation of the structural parameters, a statement that must still be more thoroughly investigated.

The samples with higher Co levels show a marked decay in performance because of the rapid degradation of the electrolyte being the cathode maintained for longer at high potential during cobalt(II) oxidation.

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