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A versatile method of preparation of carbon-rich LiFePO4: A promising cathode material for Li-ion batteries

Elvira M. Bauer [a], Carlo Bellitto [a], Guido Righini [a], Mauro Pasquali [b], Alessandro Dell'Era [b], Pier Paolo Prosini [c,*]

[a] CNR, Istituto di Struttura della Materia, Via Salaria, km. 29.300, c.p. 10, I-00016 Monterotondo Scalo, Roma, Italy
[b] Dipartimento ICMMPM, Facoltà di Ingegneria, Università di Roma "La Sapienza", Roma, Italy
[c] ENEA, Idrocomb, C.R. Casaccia, Via Anguillarese 301, Roma 00060, Italy

Abstract

LiFePO4/C composites were prepared by using organo-phosphonates as a single source of iron, phosphorus and carbon. $Fe[RPO_3] \cdot H_2O$ (R = methyl or phenyl group) was heated in the presence of Li_2CO_3 at high temperature and under nitrogen flux. Elemental carbon is formed on the surface of LiFePO4 particles leaving a carbon coated material. The materials were characterized by elemental analysis, TG/DTA, XRPD and SEM. Coulometric titration showed that some impurities are present in the final products. The material prepared starting from the iron(II) phenyl phosphonate showed higher discharge capacity, specific energy, and specific power. The specific energy evaluated at C/10 rate was about 520 Wh kg^{-1}. The specific power calculated at 3C rate was in excess at 1400 W kg^{-1} while the specific energy was about 63% of the energy delivered at C/10. No capacity fading was observed upon cycling. The performance of LiFePO4 prepared from the iron(II) methyl phosphonate was found to be slightly lower, probably due to the lower carbon content.
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1. Introduction

The number of publications related on LiFePO4 is increasing yearly since Ravet et al. [1] renewed the interest of the electrochemical community on this material. Without any doubt, LiFePO4 is a good candidate to replace lithiated metal oxides as cathode in Li-ion batteries. It should be noted that the cost of the cathode active material is about 40% of the total battery cost [2] and therefore the use of iron instead of cobalt or nickel is very attractive. Ravet et al. [1] showed that it was possible to increase the electrochemical performance of LiFePO4 by adding carbon before material crystallization. Other techniques have been proposed to increase the electronic conductivity: i.e. covering the surface with conducting particles [3] or synthesizing the material in presence of conductive particles [4]. Conductive parti-

cles, formed or added during the synthesis, interfere with the grains coalescence determining grain size reduction. Particle size minimization and intimate carbon contact both have been proved to optimize the electrochemical performance.

In this paper we stress this concept reporting a new synthetic route to prepare LiFePO4/C composites in which the phosphorus, iron and carbon originate from the same precursor. The synthesis and characterization of LiFePO4/C as well as their electrochemical properties in lithium cell are reported.

2. Experimental

Fe(II) methyl phosphonate, $Fe[CH_3PO_3(H_2O)]$ (hereafter FeMP), and Fe(II) phenyl phosphonate, $Fe[C_6H_5PO_3(H_2O)]$ (hereafter FePP), have been synthesized as previously reported [5,6]. The latter compounds can be isolated as
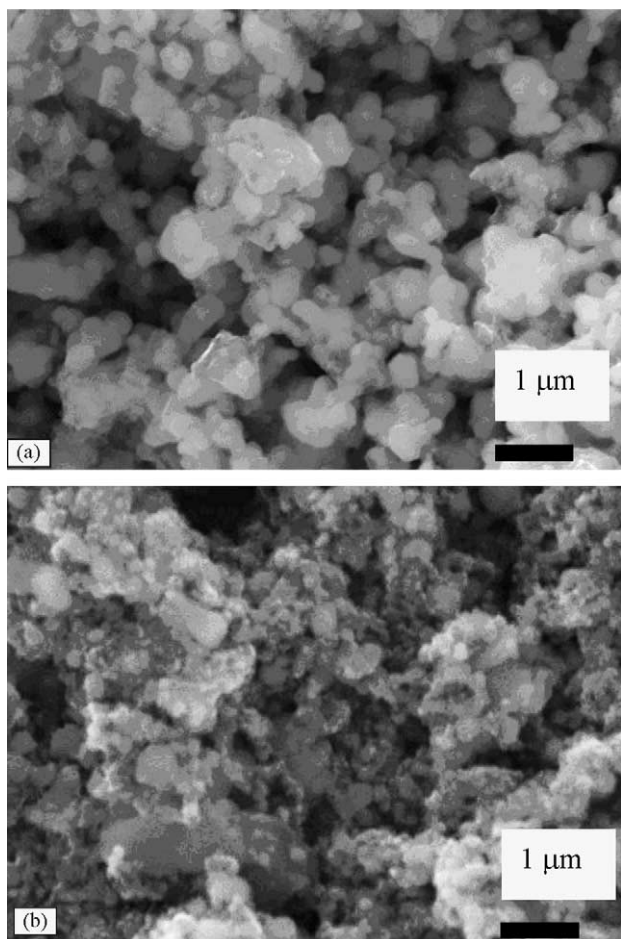

Fig. 1. SEM micrograph of crystalline LiFePO$_4$ prepared starting from methyl (a) and phenyl phosphonate (b).

white microcrystalline powders and are stable to the air and moisture. Li$_2$CO$_3$ and FeMB or FePP were ball-milled in the ratio 1:2 in air to get an intimate mixture. Grey powders of LiFePO$_4$ were obtained by heating the precursor mixtures in

a tubular furnace under inert atmosphere (N$_2$ gas) at temperatures above 600 °C for at least 16 h [7]. Thermogravimetric (TGA) data of the precursor mixtures were obtained in flowing dry nitrogen at a heating rate of 10° min^{-1} on a Stanton-Redcroft STA-781 thermoanalyzer. Experimental X-ray powder diffraction data were collected on a Seifert XRD-3000 diffractometer, Bragg-Brentano geometry, equipped with a curved graphite monochromator [λ(Cu Kα) = 1.54056 Å] and a scintillation detector. The data was collected with a step size of 0.02°, 2θ and at count time of 8 s per step over the range $4° < 2\theta < 80°$. The diffractometer zero point was determined from an external Si standard. X-ray Powder Diffraction patterns were fitted by using a Rietveld profile analysis [8]. Morphology of the powders was studied by scanning electron microscopy (SEM, Jeol JSM-5510LV). Composite cathode tapes were made by roll milling a mixture of 75 wt.% active material and 10 wt.% binder (Teflon, DuPont). Carbon (KJB Carbon) was added to have a 15 wt.% final carbon content. Electrodes were punched in form of discs typically with a diameter of 10 mm. The electrode weight ranged from 7.4 to 10.7 mg. Electrochemical characterization of LiFePO$_4$ was performed in T-shaped battery cells with lithium metal as counter and reference electrode. The cells were filled with a 1 M solution of LiPF$_6$ in ethylene carbonate/diethyl carbonate (1:1). Potential Step Voltammetry (PSV) was carried out in a three electrodes cell configuration with a Mac Pile II Potentiostat/Galvanostat system under a constant scan rate of 10 mV h^{-1} in the range 2.0–4.0 V versus Lithium. To test the effect of different discharge rates, a cell was subjected to various discharge rates, i.e. C/10, 1C, 3C, 10C, 20C and 30C. The cell was always charged using the same procedure to ensure identical initial conditions: a constant current step at 1C rate until the voltage reached 4.0 V, followed by a constant voltage step until the current fell below C/10 rate. The cycling tests were carried out automatically by means of a battery cycler (Maccor 4000).
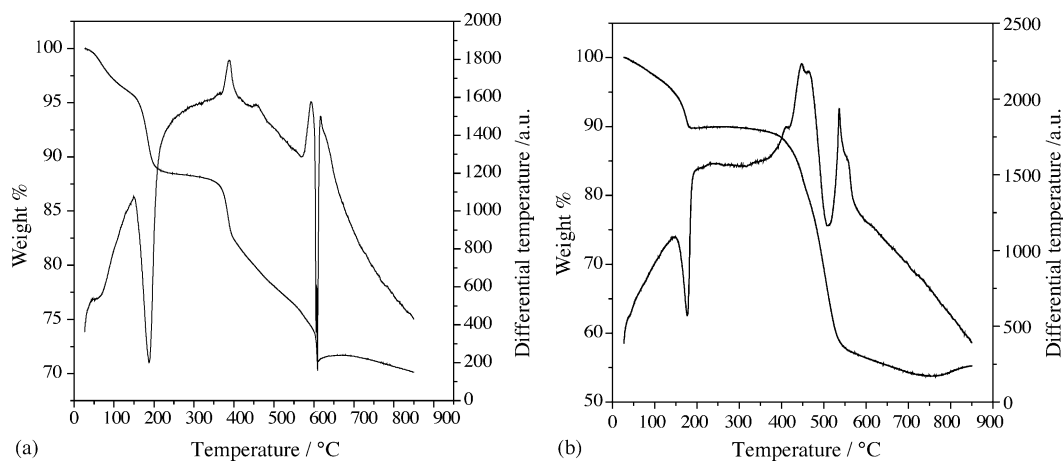

Fig. 2. TGA (—) and DTA (—) curves for mixtures of lithium carbonate with methyl (a) and phenyl phosphonate (b) recorded over the temperature range from ambient to 800 °C at a heating rate of 10 °C min^{-1}.

3. Results

3.1. Chemical analysis

The molar ratio for Li:Fe:P, as obtained from the chemical analysis, was almost 1:1:1 for both the compounds. 2.5 and 12.0 wt.% carbon, formed during the decomposition of FeMP and FePP, were found in the samples, respectively. Considering that the theoretical carbon contents in the final materials correspond to 8.8 and 33 wt.% it follows that part of carbon is lost during the firing process.

3.2. SEM characterization

Fig. 1a is a SEM micrograph of the sample prepared starting from FeMP. The LiFePO$_4$ phase forms spherical aggregates of about 1 μm in diameter. Fig. 1b shows the material obtained using FePP. The grain structure of the material is very similar to the previous one but it results less homogeneous.

3.3. Thermoanalytical data

The TG/DTA curves of mixtures of lithium carbonate with FeMP and FePP are reported in Fig. 2a and b, respectively. Weight losses of 30 and 45% were seen in the TG curves over the temperature region 50–800 °C. Endothermic effects are evident in the DTA curves at 180 °C. It has been reported

that the dehydration of some hydrate metal phosphites proceeds by both anion disproportion and condensation. The mass loss of 10–11% corresponds to the presence of about 1.2–1.4 molecules of water per mole of compounds. Part of the water, probably physically adsorbed on the sample is lost at temperatures lower than 100 °C. The remaining part is lost at about 200 °C and corresponds to crystallization water. At higher temperatures two exothermic effects are displayed in the DTA curves, namely at 400 (Fig. 2a) and 450 °C (Fig. 2b) which are accompanied by a weight loss in the TG curves of about 20 and 34%. These effects are related to the decomposition of carbonate and organo-phosphonates and the formation of LiFePO$_4$.

3.4. X-Ray characterization

The X-ray powder diffraction patterns of LiFePO$_4$ prepared from FeMP and FePP precursors are identical. They were indexed in the orthorhombic space group *Pnma* (olivine-like structure) [9] and the unit-cell parameters of LiFePO$_4$ samples obtained from the two precursors are reported in Table 1. The similarity between the unit-cell parameters found in our material and those reported in the literature indicates the presence of LiFePO$_4$ as olivine form. The Rietveld refinement was performed on a model based on the single-crystal structure of LiFePO$_4$ [9]. Fig. 3 shows the result of fitting the experimental X-ray diffraction pattern for LiFePO$_4$ prepared from FeMP. Analogous results have been observed
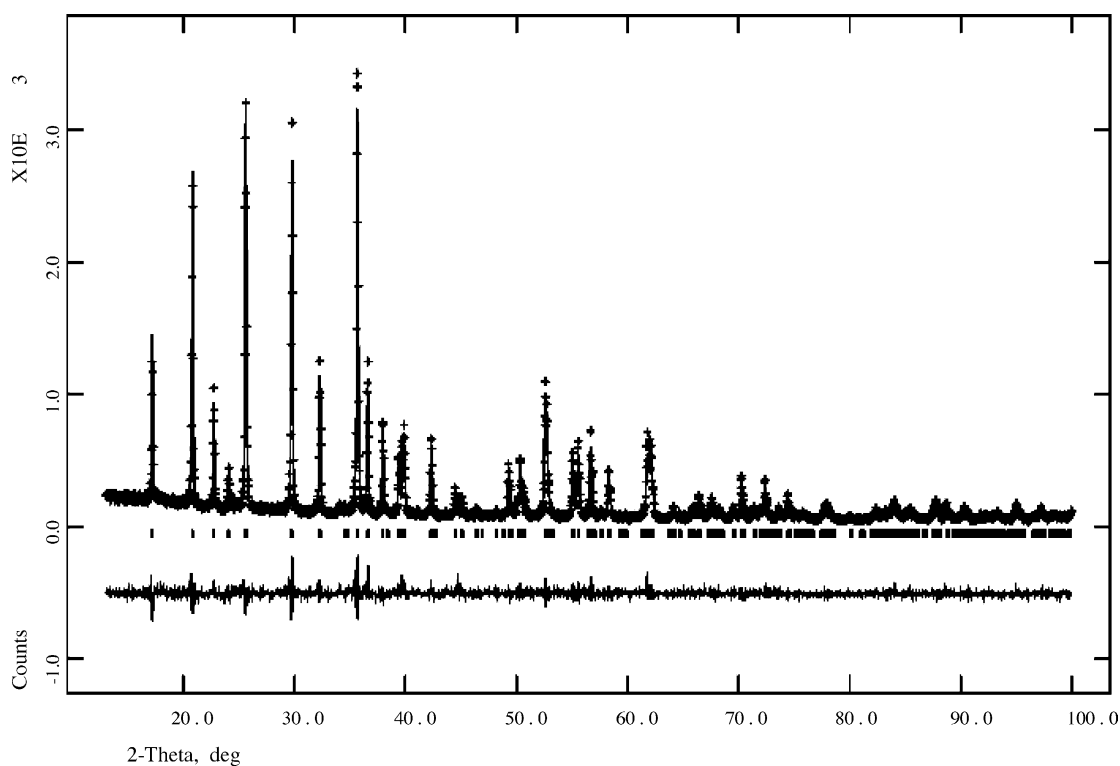

Fig. 3. Observed (++++) and calculated (—) powder X-ray diffraction profiles of the Rietveld refinement for LiFePO$_4$ obtained from Fe(II) methyl phosphonate. The bottom curve is the difference plot on the same scale intensity. The tic marks are the calculated 2θ angles for Bragg peaks.
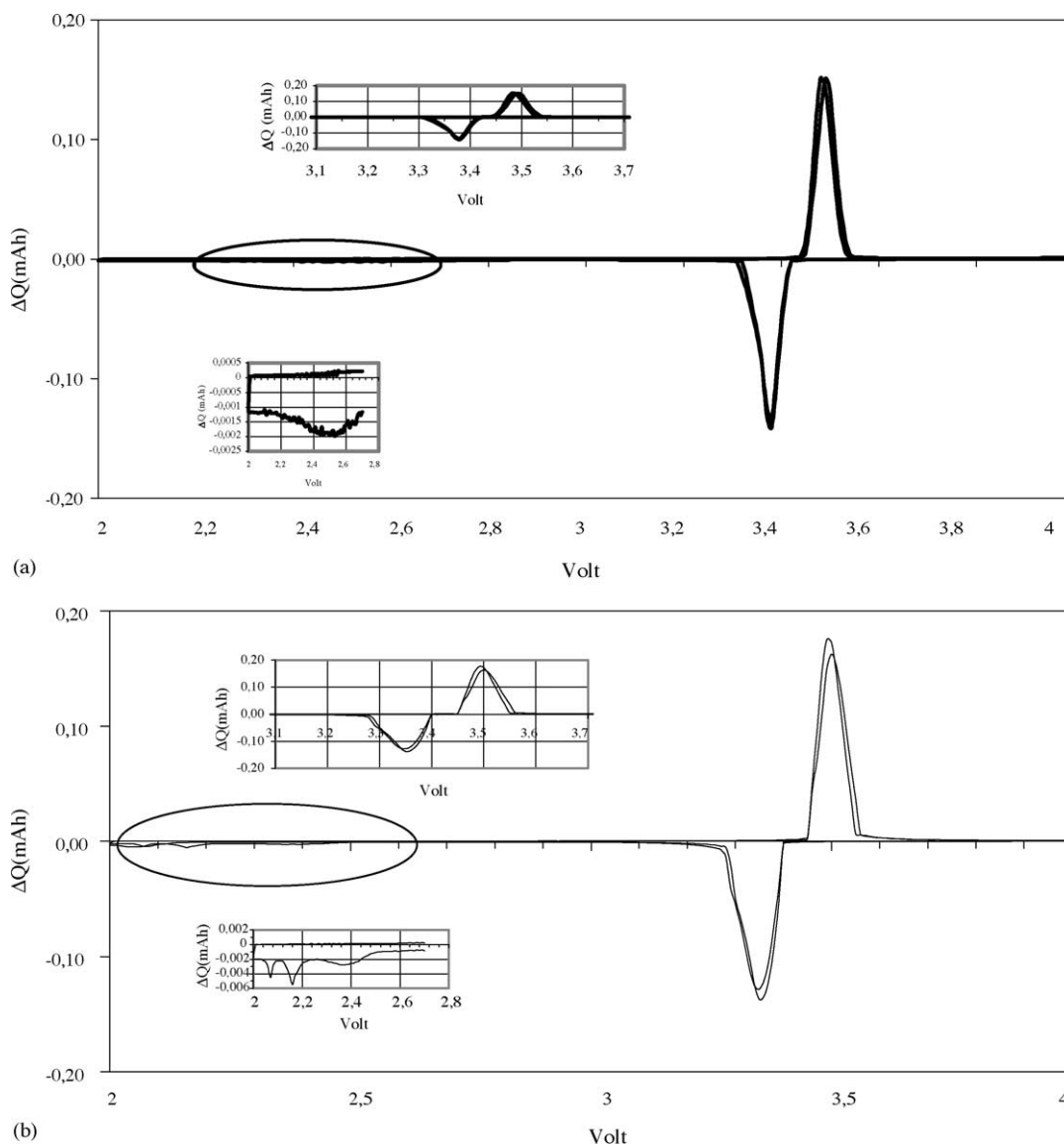
Fig. 4. Potential step voltammetry curves for the materials prepared starting from methyl (a) and phenyl phosphonate (b). Scan rate: $10 \, mV \, h^{-1}$. Voltage range: 2.0–4.0 V vs. lithium.

for LiFePO$_4$/C composites obtained from the FePP precursor. This method does not give information on the possible presence of amorphous phases, but it has been found a useful tool to identify small fractions of crystalline impurities such as Fe$_2$P or Li$_3$PO$_4$.

3.5. Potential step voltammetry

In Fig. 4 are reported the PSV curves for both the materials. ΔQ is the capacity (expressed in mAh) recorded during each potential step, corresponding to the change of Li$^+$ concentration during the voltage step (10 mV).

In the curve related to FeMP (Fig. 4a) two distinct effects can be observed. The most relevant is located at 3.48 V in charge and 3.38 V in discharge and can be related respectively, to the oxidation and reduction of Fe^{2+}. A second small

event is located around 2.5 V (see the insert in Fig. 4a). In the case of FePP (Fig. 4b), three very small signals appear in the low voltage region (2.37, 2.16, and 2.07 V) being the principal one located at the same voltage as for FeMP. During the first charge 87% of iron is oxidized in the sample synthesized from FeMP. Upon discharge two different processes can be evidenced. The predominant one is related to the reduction of Fe^{3+} to Fe^{2+} and corresponds to the insertion of 0.86 equivalent of Li$^+$ per mol. This amount roughly corresponds to the amount of iron as evaluated during the oxidation process. The second one is very small and it contributes to the total discharged capacity making the discharged capacity larger than the capacity accumulated during the first charge. This capacity was related to impurities able to intercalate 0.121 Li$^+$ per mol. The purity of the sample synthesized from FePP was 96% as determined during the first oxidation process. The

Table 1
Rietveld refinement, atomic coordinates and equivalent isotropic displacement parameters for $LiFePO_4$ obtained from Fe(II) methyl phosphonate

Element	Wyckoff Pos.	x	y	z	Occupancy	U_{iso} (A^2)
Li	4a	0.0	0.0	0.0	1.0	0.0053
Fe	4c	0.2826(1)	0.25	0.9740(4)	1.0	0.0159
P	4c	0.0957(8)	0.25	0.4215(6)	1.0	0.0065
O1	4c	0.0927(7)	0.25	0.7434(2)	1.0	0.0050
O2	4c	0.4579(8)	0.25	0.2878(12)	1.0	0.0050
O3	8d	0.1612(5)	0.0518(2)	0.2827(8)	1.0	0.0050

Cell parameters	
a (Å)	10.325(2)
b (Å)	6.005(1)
c (Å)	4.691(1)
α (°)	90.0
β (°)	90.0
γ (°)	90.0
Cell volume ($Å^3$)	290.87(1)
Symmetry space group	*Pnma*
Chemical formula weight	157.68
Cell formula units Z	4
R_p (%)	7.71
R_{wp} (%)	10.15
$R_{(F^2)}$ (%)	7.25

capacity recorded during the discharge and related to iron reduction was as high as the theoretical value. This could be explained considering the material formed by a mixture of 95% $LiFePO_4$ and 5% $FePO_4$ both with an olivine type structure.

3.6. Electrochemical testing

To test the effect of different discharge rates, a cell was subjected to various discharge rates. Fig. 5 shows the Ragone plot for the cell. The specific energy and specific power are
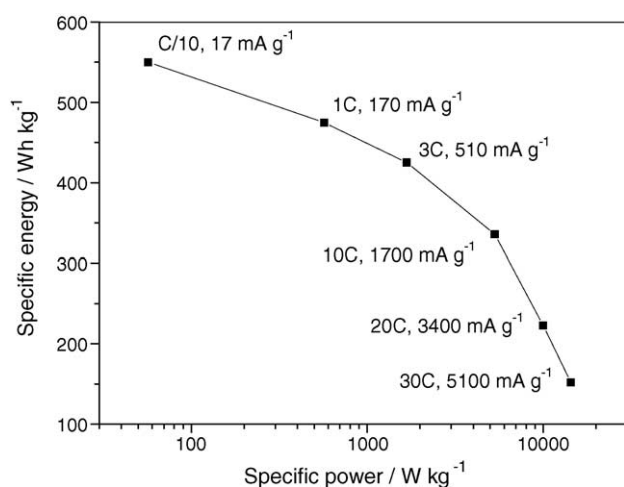

Fig. 5. Ragone plot for the cell based on $LiFePO4$ from phenyl phosphonate. Charge current density was $1.2\,mA\,cm^2$. A constant voltage of 4.0 V was applied at the end of the galvanostatic step until the current density was lower than 1/10th of the charge current. Discharge currents are reported in the figure. The cathode loading of $LiFePO_4$ was $10.2\,mg\,cm^{-2}$. Electrode area was $0.78\,cm^2$.

based on the weight of the active material. The specific energy calculated at C/10 rate was about $520\,Wh\,kg^{-1}$. The specific power calculated at 3C rate was in excess at $1400\,W\,kg^{-1}$ while the specific energy was about 63% of the energy delivered at C/10.

The performance of $LiFePO_4$ prepared with methyl phosphonate as precursor was found to be slightly lower than the previously discussed material and this result can be directly related to the lower carbon content.

4. Conclusions

A new synthetic route leading to a $LiFePO_4$/C composite with very attractive electrochemical properties is proposed. The synthetic way suggested is very simple and the organophosphonate used as precursors are very easy to prepare and stable to the air. Electrodes prepared with the $LiFePO_4$/C synthesized from Fe(II) phenyl phosphonate showed very good electrochemical performance making the synthetic route very promising to prepare a safer and cheaper cathode material for fabrication of large scale lithium-ion batteries.

Acknowledgment

References

[1] N. Ravet, J.B. Goodenough, S. Besner, M. Simoneau, P. Hovington, M. Armand, Proceedings of the 196th ECS Meeting, Hawaii, October 17–22, 1999.

[2] B.A. Johnson, R.W. White, J. Power Sources 70 (1998) 48.

[3] H. Huang, S.-C. Yin, L.F. Nazar, Electrochem. Solid-State Lett. 4 (2001) 170.

[4] P.P. Prosini, D. Zane, M. Pasquali, Electrochim. Acta 46 (2001) 3517.

[5] C. Bellitto, F. Federici, M. Colapietro, G. Portalone, D. Caschera, Inorg. Chem. 41 (2002) 709.

[6] A. Altomare, C. Bellitto, S.A. Ibrahim, M.R. Mahmoud, Inorg. Chem. 39 (2000) 1803.

[7] Italian Patent no. 2003A000048 (2003).

[8] H.M. Rietveld, J. Appl. Crystallogr. 2 (1969) 65.

[9] V.A. Streltsov, E.L. Belokoneva, V.G. Tsirelson, N.K. Hansen, Acta Cryst. B 49 (1993) 147.