

Crystal chemistry of electrochemically inserted $\text{Li}_x\text{V}_2\text{O}_5$ *

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Abstract

The capacity of $\text{Li}/\text{V}_2\text{O}_5$ batteries is improved by the extension of the usual cycling domain from $0 \leq x \leq 1$ to $0 \leq x \leq 1.8$. Such behavior is attributed to the formation of a γ - LiV_2O_5 bronze for $x \geq 1$. Reversible deintercalation of lithium from the γ -phase leads to a new form of V_2O_5 that explains the enhancement of cell potential.

Introduction

Room temperature, secondary lithium batteries have attracted attention over the last few years, particularly due to their high energy density. Of them, $\text{Li}/\text{V}_2\text{O}_5$ is one of the most promising systems. An extension of the usual cycling domain from $0 \leq x \leq 1$ to $0 \leq x \leq 2.35$ was suggested by Wiesener *et al.* [1] on the basis of a cyclic voltammetry study, but satisfactory results were not obtained on a secondary battery [2].

Despite a large number of investigations devoted to the structural evolution of the $\text{Li}_x\text{V}_2\text{O}_5$ compounds prepared at room temperature, only recently have Okada *et al.* provided X-ray diffraction data beyond $x = 1$ [3]. Their results appear different from those obtained at 150 °C by Hub *et al.* [4]. Recently, we have found that cycling in the 3.8–2 V range (which corresponds roughly to $0 \leq x \leq 1.8$) can increase the battery capacity along with an increase in the electrode potential while the system remains reversible over a large number of cycles. Such behavior was attributed to the appearance of a new γ -phase for $x \geq 1$ [5]. On the other hand, few studies have been devoted to electrochemical and structural evolutions during charge and further discharges of an $\text{Li}/\text{V}_2\text{O}_5$ battery. In the present paper, we show that complete deintercalation of lithium from a cathode discharged down to 2 V is possible, leading to the formation of a new form of V_2O_5 derived from the γ -phase.

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Experimental

This study was carried out using coin cells. The cathode consisted of a mixture of commercial V_2O_5 powder (ground to an average grain size of $2 \mu\text{m}$), graphite, carbon black, and PTFE. The anode was a lithium foil and the electrolyte a solution of LiAsF_6 in PC/EC/DME. Discharge was carried out at a constant current density of 0.3 mA cm^{-2} . Measurement of the discharge time was used to control the overall lithium content of the cathodic material. Cells were cycled between 3.8 and 2 V. Electrode characterization was performed at various insertion rates in this potential range, corresponding roughly to $0 \leq x \leq 1.8$ except for the first discharge materials which were investigated to $x=2$. After reaching potential equilibrium, cathodic materials were recovered in a glove box under argon atmosphere. They were characterized by X-ray diffraction using $\text{Cu K}\alpha_1$ radiation. Graphite played the role of an internal standard for the determination of lattice parameters.

Cyclic voltammetry experiments were undertaken using a three electrode cell. The electrolyte was the same as that for the discharge studies. The working electrode was a mixture of V_2O_5 (10%) and graphite attached to an aluminium holder with a CMC glue. Counter and reference electrodes were made from lithium foil.

Results

Figure 1 gives the potential versus x plots for an $\text{Li}_x\text{V}_2\text{O}_5$ cathode. A comparison with the OCV versus x plot previously reported by Dickens *et al.* [6] shows that the first discharge curve, D_0 , is not far from equilibrium. This curve exhibits plateaux at 3.4 V and 3.2 V. Actually, the electrode potential only remains x -independent between $x=0$ and $x=0.35$.

As $x \rightarrow 1$ the potential drops steeply to ≈ 2.3 V then further lithium insertion proceeds with a smooth evolution down to 2 V.

The recharge from $x \approx 1.8$ and the second and third discharges are characterized by a shortening of the plateaux at 3.4 V and 3.2 V and the

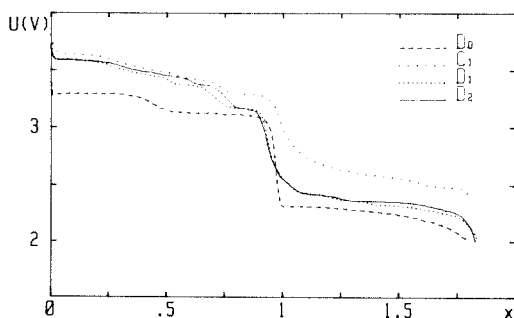


Fig. 1. First discharge (D_0); charge (C_1); second (D_1) and third (D_2) discharge of an $\text{Li}/\text{V}_2\text{O}_5$ battery.

formation of an additional plateau at 3.6 V for $0.2 \leq x \leq 0$ (Fig. 1). In addition to the potential enhancement of ≈ 200 mV for 100 A h kg^{-1} , the second and subsequent discharges exhibit a less rapid drop at $x \approx 1$, with the formation of a smooth shoulder at ≈ 2.7 V and, for $x \geq 1$, instead of a continuous variation, two quasi plateaux appear separated by a small potential decrease at $x \approx 1.25$. These results provide evidence of an irreversible evolution of the system when the first discharge is carried beyond $x = 1$. Study of further cycling shows that the behavior of the system becomes reversible again for $0 \leq x \leq 1.8$, provided the electrode potential is held above 2 V.

The complex reduction mechanism of V_2O_5 is also reflected by cyclic voltammetric experiments. Voltammograms, Fig. 2, exhibit the same main characteristics as reported previously for different electrochemical conditions [7] and temperature [8]. All the features of the discharge curve are seen even more clearly. The two peaks at 3.35 V and 3.15 V correspond to two-phase regions. Discharge to 2 V exhibits an important reduction peak at ≈ 2.25 V. This reaction is reversible, as shown by the corresponding oxidation peak at 2.5 V. The shoulder appearing at 3.55 V, and another new oxidation peak at 3.65 V, can be related to the plateau at 3.6 V and a region of weak slope at 3.5 V, which both involve oxidation of the γ -phase, as discussed below. The corresponding reduction peaks are situated at 3.55 V and 3.45 V. Voltammograms for subsequent cycles are the same, confirming the reversibility of the system.

Figure 3 shows the lattice constant variation of the various phases as x increases from 0 to 1. The structural evolution is similar to that previously

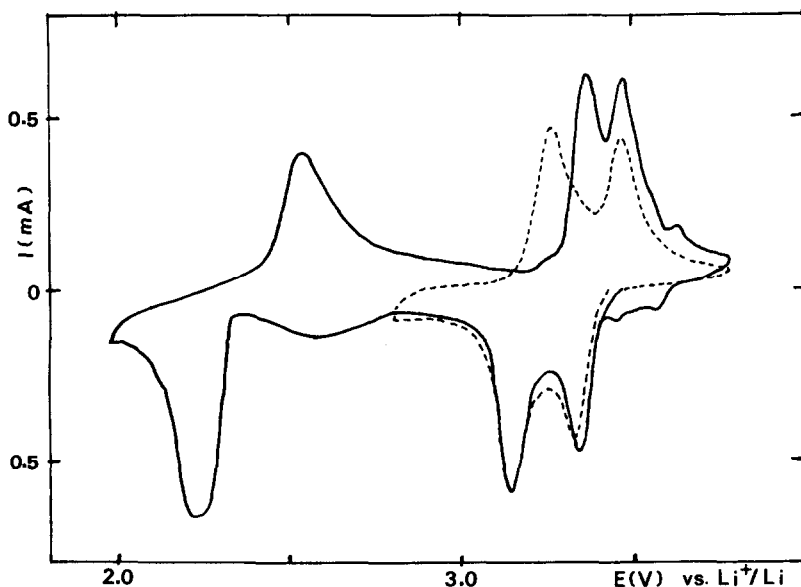


Fig. 2. Cyclic voltammograms of V_2O_5 in PC/EC/DME 1 M LiAsF_6 between 3.8 and 2.8 V (---) and between 3.8 and 2 V (—); sweep rate: 20 mV min^{-1} .

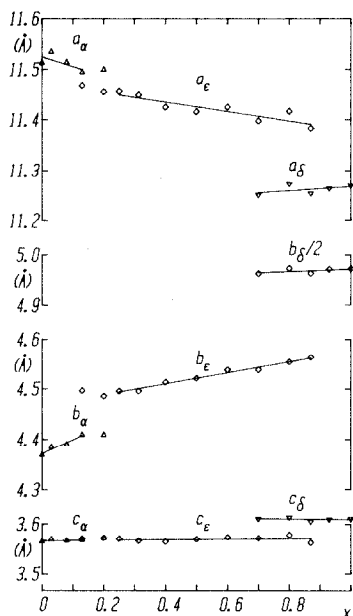


Fig. 3. Variation of the lattice constants of $\text{Li}_x\text{V}_2\text{O}_5$ as x increases.

reported by Murphy *et al.* for $\text{Li}_x\text{V}_2\text{O}_5$ compounds prepared by the reduction of V_2O_5 using a solution of LiI in acetonitrile [9]. For $0 < x \leq 0.05$ an orthorhombic phase is observed. Previous authors have suggested [10] that it is isostructural with the $\alpha\text{-Li}_x\text{V}_2\text{O}_5$ bronze obtained at high temperature and studied by Hagemmuller *et al.* [11].

For $0.05 \leq x \leq 0.35$ the α -phase coexists with another orthorhombic ϵ -phase, which explains the potential plateau observed in this composition range (Fig. 1, curve D_0). The upper limit of the existence domain of the ϵ -phase, as well as the lower limit of that of the next δ -phase [12], is difficult to determine since, as shown in Fig. 3, the lattice constants of the ϵ -phase still vary slightly in the two-phase domain. Such behavior may explain why no true plateau is observed in the corresponding composition range. As discharge proceeds, a layer of δ -phase forms at the grain surface. Then, the chemical potential of Li equilibrates between the two out-of-equilibrium phases, but the back transformation of δ into ϵ , which is required to reach (metastable) equilibrium, seems to be sluggish.

The structure of the ϵ -phase is generally considered as being very close to that of V_2O_5 . This assumption has been confirmed by a structural refinement using X-ray powder diffraction data and the Rietveld method. The results given in Table 1 show that the structure of the ϵ -phase is characterized, with regard to that of V_2O_5 , by an increase of the interplanar distance and a weak puckering of the layers.

A preliminary neutron diffraction study suggests that the site occupied by lithium is different from that in the α -phase [13]. This can be correlated

TABLE 1

Positional and thermal parameters of ϵ -Li_{0.46}V₂O₅

$a = 11.417 \text{ \AA}$		$b = 3.565 \text{ \AA}$	$c = 4.508 \text{ \AA}$	Space group $Pm\bar{m}n$	
Atom	Position	x	y	z	$B (\text{\AA}^2)^a$
V	4f	0.1006	0.2500	0.8947	-0.076
O1	4f	0.1132	0.2500	0.5401	1.408
O2	4f	0.9284	0.2500	-0.0091	-0.511
O3	2a	0.2500	0.2500	0.0211	1.627

$R_i = 8.03\%$, $R_p = 10.14\%$, $R_{wp} = 13.48\%$

^aNegative values of B parameters could be due to the layered-like structure that should give rise to asymmetric line shapes not taken into account in the calculation using Cagliotti's law.

with the difference in oxygen polyhedra surrounding vanadium atoms: whereas in the ϵ -phase vanadium atoms are located in a square pyramid, in the α -phase they occupy a triangular bipyramid resulting from the shift of one of the oxygen atoms due to electrostatic interactions with intercalated lithium atoms [11].

The existence domain of the δ -phase seems relatively narrow, as suggested by the V versus x curve. Beyond $x \approx 1$, in addition to the δ -phase, another phase isostructural with the so-called γ -phase, obtained by solid-state reaction of LiVO₃ with VO₂ at 650 °C [14] appears; this result is in agreement with that of Okada *et al.* [3].

For $x \approx 1.6$ and $x \approx 2$, X-ray diffractograms show a mixture of the δ -phase with a new ζ -phase, also observed by electrochemical insertion ($x \geq 1.4$) of lithium into a γ -LiV₂O₅ bronze [15]. This ζ -phase transforms reversibly into the γ -phase during the subsequent charge process.

At the present stage of the investigation, no additional phases could be detected, either by X-ray diffraction or electron microscopy. For $x \geq 1.8$, X-ray diffraction lines become less sharp and intense suggesting that some disorder occurs.

As seen in Fig. 4, the structure of the electrode material during subsequent cycles differs strongly from that of the first discharge, in agreement with the electrochemical behavior. As the first re-charge proceeds, both δ - and γ -phases persist down to $x \approx 0.9$. For $x \approx 0.7$ the δ -phase has disappeared and the γ -phase coexists with ϵ . For $x \approx 0.5$, α is substituted for ϵ and then a mixture of V₂O₅ and γ is observed. As x tends to zero, the lattice parameters of γ undergo an important change, leading ultimately to a new form of V₂O₅ that we call γ' -V₂O₅. An X-ray diffractogram of the recharged material is compared with that of normal n -V₂O₅ in Fig. 5, and shows that the cathode is a mixture of both forms of V₂O₅.

At the beginning of the second discharge, intercalation of lithium seems to occur first into the γ' -V₂O₅, and therefore the formation of α , ϵ and

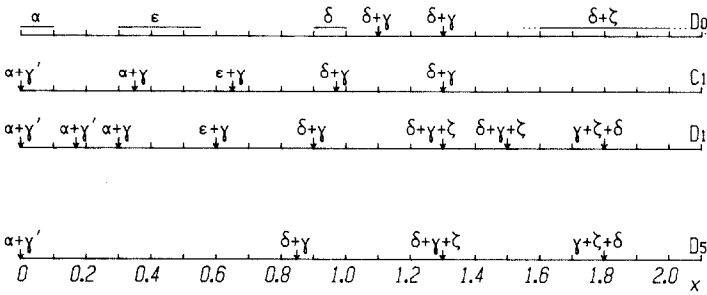


Fig. 4. Results of X-ray diffraction analysis of electrochemical cycling between 3.8 and 2 V for first discharge (D_0); charge (C_1); second (D_1) and fourth (D_5) discharges.

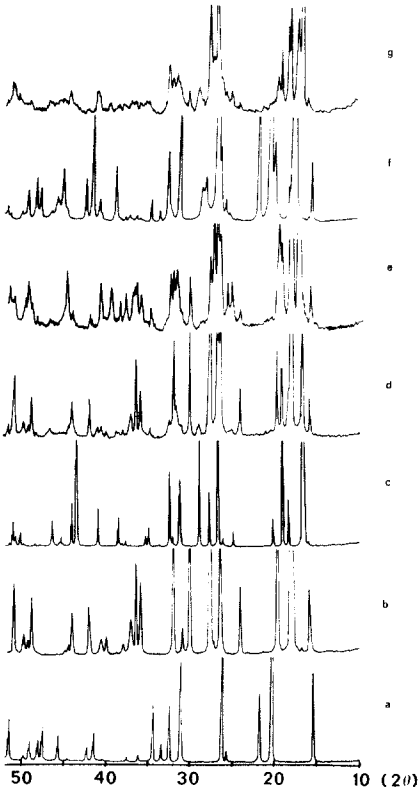


Fig. 5. X-ray diffractograms of $n\text{-V}_2\text{O}_5$ (a); $\delta\text{-LiV}_2\text{O}_5$ (b); $\gamma\text{-LiV}_2\text{O}_5$ (c); $\text{Li}_x\text{V}_2\text{O}_5$ products of first discharge with $x=1.3$ (d); $x=1.7$ (e); $\text{Li}_0\text{V}_2\text{O}_5$ after first charge (f); and $\text{Li}_{1.8}\text{V}_2\text{O}_5$ after second discharge (g).

δ -phases is observed for overall x values higher than in the first discharge. Unlike in the first discharge, the γ -phase coexists with δ and ζ at $x=1.8$ (Fig. 5(g)).

Discussion

It is well known that lithium insertion into V_2O_5 ($0 < x < 1$) is topotactic [16]. Thus as x increases from 0 to 1, α , ϵ and δ phases are formed, keeping the V_2O_5 skeleton unchanged but with a puckering of layers and an increase in the interlayer spacing (Fig. 6).

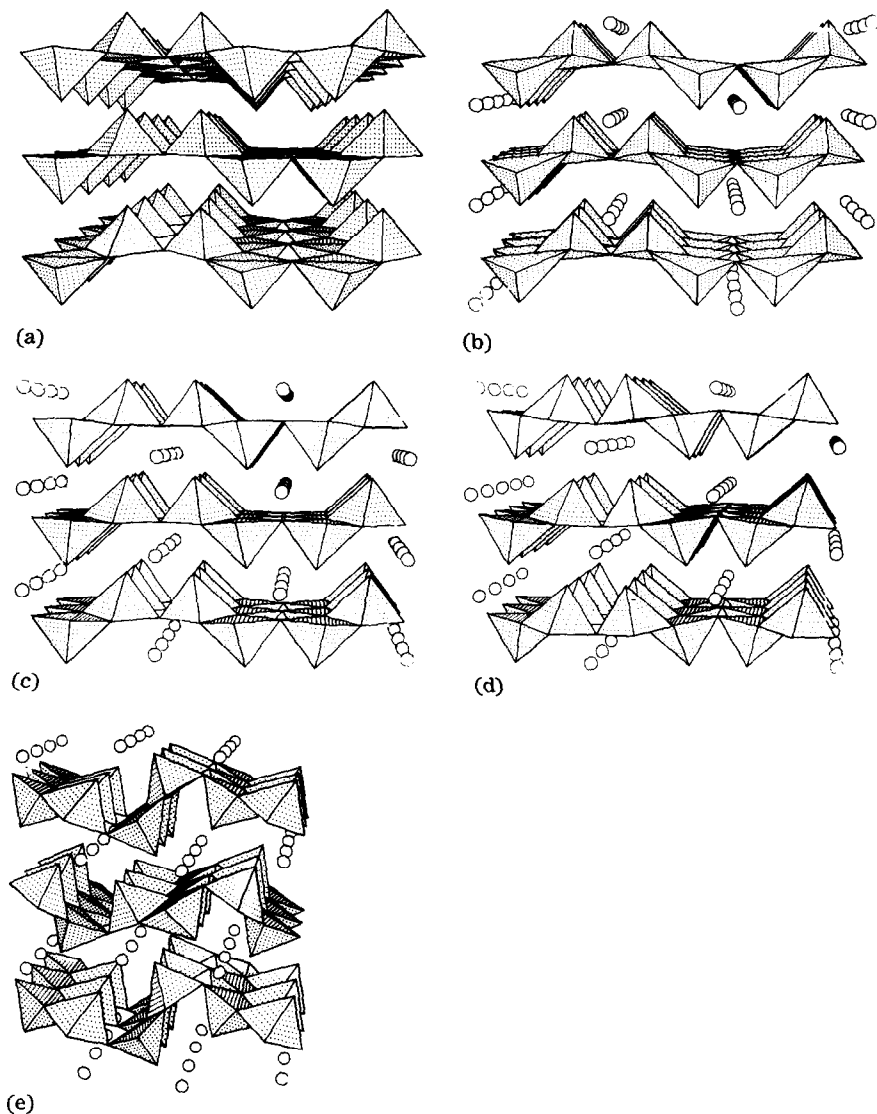


Fig. 6. Comparison of the arrangement of VO_n polyhedra in V_2O_5 (a); α - $Li_xV_2O_5$ (b); ϵ - $Li_xV_2O_5$ (c); δ - $Li_xV_2O_5$ (d); γ - $Li_xV_2O_5$ (e).

Although a two-phase domain ($\epsilon + \delta$) is observed by X-ray diffraction for $0.55 < x < 0.9$ the potential is not strictly independent of x . This result can be correlated with the slight variation of the lattice constants of the ϵ -phase with x , and shows that stable or metastable equilibrium can hardly be reached: as x increases beyond a given value, δ -phase forms at the grain surfaces before the upper limit of the existence domain of the ϵ -phase is reached.

Further reduction beyond $x=1$ leads to an irreversible transformation of the δ -phase into the γ -phase, which is the thermodynamic stable form [9]. Obviously, the rate of transformation increases with the x value as shown by comparison with data for electrodes cycled in a narrower potential range, but it is difficult to answer the question whether or not more than one lithium per V_2O_5 can be intercalated into the δ -phase. The important change in the structure of cathodic materials at $x=1.8$ (Fig. 4) with the number of cycles may be understood in the following way: during the first discharge, the quantity of the δ -phase transformed into γ is such that, in order to reach the overall composition, all of the γ -phase must be transformed into ζ , which is able to insert a larger amount of lithium. From the second discharge it seems that the amount of γ -phase, produced by the irreversible $\delta \rightarrow \gamma$ transformation, is large enough to accommodate lithium with only a partial transformation of γ into ζ over the considered composition range. This phenomenon can be correlated with the decrease of polarisation from the first discharge (D_0) to the subsequent ones (Fig. 1).

The most striking features of the evolution of the system with cycling is the increase of electrode potential by about 200 mV and the tendency for a reversible behavior to appear after a few cycles; this has led to interesting applications [5]. Such behavior can be explained by the structural evolution determined by X-ray diffraction. The γ -phase formed for $x \geq 1$ can be deintercalated and leads, for $x=0$ to a new form of V_2O_5 . This result has been confirmed by study of the chemical deintercalation of lithium from a γ - LiV_2O_5 bronze prepared by solid state reaction at 650 °C, as well as from a sample obtained by annealing the δ -phase at 350 °C [15].

The evolution of features of the potential versus x curves also results from the irreversible formation of the γ -phase and γ' - V_2O_5 . For instance, during the second discharge, the plateau at 3.6 V is characteristic of a mixture of γ' - $Li_xV_2O_5$ and γ - $Li_xV_2O_5$; insertion into γ then proceeds as the potential drops from 3.6 to 3.4 V and finally the plateaux at 3.4 V ($\alpha + \epsilon$) and at 3.2 V ($\epsilon + \delta$) are reached. For $1 \leq x \leq 1.8$, the second discharge and, more clearly, the third one, are close to that of the pure γ -phase and may be interpreted by the insertion of lithium into γ ($x \leq 1.25$) and the successive formation of ζ -phase ($x \geq 1.25$) [15].

The shrinking of the plateaux corresponding to the mixtures $\alpha + \epsilon$ and $\epsilon + \delta$, as well as that of single phase domains, allows a rough estimate of the quantity of γ -phase formed. For instance, the first discharge up to $x=1.3$ yields a quantity of γ -phase between 30 and 40%, which remains approximately constant when cycling is performed for $0 \leq x \leq 1.3$ and just δ and γ are

present. Discharge to $x = 1.8$ yields between 75 and 85% of the γ -phase and only a small increase with cycling. This clearly shows that the γ -phase mainly forms during the first discharge from $x = 1$ to $x = 1.8$.

Conclusions

Electrochemical intercalation of lithium at room temperature for $0 \leq x \leq 1$ leads to a structural evolution which is similar to that observed using chemical intercalation with a solution of LiI. At this level of discharge the system is reversible. For $x \geq 1$, lithium insertion leads to the irreversible formation of a phase isostructural with the γ - LiV_2O_5 bronze. Then, the formation of a new orthorhombic ζ -phase is observed. Deintercalation of lithium from the γ -phase gives rise to a new form of V_2O_5 and this *in situ* irreversible transformation of the cathodic material leads to an increase in the electrode potential. After a few cycles the system rapidly returns to a reversible behavior provided that x remains smaller than 1.8.

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References

- 1 K. Wiesener, W. Schneider, D. Ilic, E. Steger, K. H. Hallmeier and E. Brackmann, *J. Power Sources*, **20** (1987) 157.
- 2 C. R. Walk, in J. P. Gabano (ed.), *Lithium Batteries*, Academic Press, New York, 1983.
- 3 S. Okada and J. Yamaki, *Ext. Abstr., 176th Meet. Electrochem. Soc., Hollywood, Oct. 15-20, 1989*, p. 62.
- 4 S. Hub, A. Tranchant and R. Messina, *Electrochim. Acta*, **33** (1988) 997.
- 5 J. Labat and J. M. Cocciantelli, *Fr. Patent*, **8 916 337** (1989).
- 6 P. G. Dickens, S. J. French, A. T. Hight and M. F. Pye, *Mater. Res. Bull.*, **14** (1979) 1295.
- 7 N. Machida, R. Fuchida and T. Minami, *J. Electrochem. Soc.*, **136** (8) (1989) 2133.
- 8 J. P. Pereira-Ramos, R. Messina and J. Perrichon, *J. Appl. Electrochem.*, **16** (1986) 379.
- 9 D. W. Murphy, P. A. Christian, F. J. DiSalvo and J. V. Waszczak, *Inorg. Chem.*, **18** (1979) 2800.
- 10 M. S. Whittingham, *J. Electrochem. Soc.*, **123** (3) (1976) 315.
- 11 P. Hagenmuller, J. Galy, M. Pouchard and A. Casalot, *Mater. Res. Bull.*, **1** (1966) 45.
- 12 R. J. Cava and A. Santoro, *J. Solid State Chem.*, **65** (1986) 63.
- 13 J. L. Soubeyroux, personal communication.
- 14 J. Galy, J. Darriet and P. Hagenmuller, *Rev. Chim. Miner.*, **8** (1971) 529.
- 15 J. M. Cocciantelli, M. Menetrier, C. Delmas, J. P. Doumerc, M. Pouchard and P. Hagenmuller, *Solid State Ionics*, submitted for publication.
- 16 S. Crouch-Baker, C-K. Huang and R. A. Huggins, *Proc. Electrochem. Soc.*, **88-6** (1988) 44.