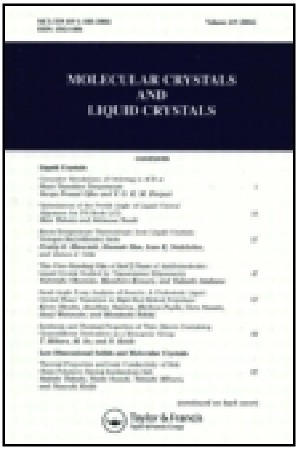

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Electrochemical Insertion of lithium into perovskite structure NbO_2F

Claude Bohnke [a], Odile Bohnke [a] & Jean Louis Fourquet [a]

[a] Laboratoire des Fluorures (UPRES A 6010 CNRS), Université du Maine, Avenue O. Messiaen BP 535, 72085, Le Mans Cedex, France

Version of record first published: 04 Oct 2006

To cite this article: Claude Bohnke, Odile Bohnke & Jean Louis Fourquet (1998): Electrochemical Insertion of lithium into perovskite structure NbO_2F, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 311:1, 23-29

To link to this article: http://dx.doi.org/10.1080/10587259808042361

Mol. Cryst. Liq. Cryst., 1998, Vol. 311, pp. 23–29
Reprints available directly from the publisher
Photocopying permitted by license only

Electrochemical Insertion of lithium into perovskite structure NbO_2F

Claude BOHNKE, Odile BOHNKE, Jean Louis FOURQUET
Laboratoire des Fluorures (UPRES A 6010 CNRS), Université du Maine
Avenue O.Messiaen BP 535, 72085 Le Mans Cedex, France

Electrochemical insertion of lithium into perovskite structure NbO_2F has been investigated. Lithium insertion leads to a structural transformation from the initial cubic unit cell to the $LiNbO_3$-type structure which presents a hexagonal symmetry. The maximum lithium uptake is 1.2 Li/Nb at room temperature. It corresponds to 60% of the expected maximum. Insertion has been followed by discharge experiments associated with impedance spectroscopy. The experimental results show that the electrochemical process can be characterized by an electrode reaction - layer formation - diffusion sequence. An equivalent circuit model which includes charge transfer reaction, layer formation, constant phase elements and diffusion impedance is proposed. The mechanism of insertion is discussed on the basis of the crystallographic structure of the perovskite. The layer may be viewed as a shell of a high inserted compound surrounding a relatively unaffected nucleus which is formed as insertion proceeds.

Keywords :electrochemical insertion ; impedance spectroscopy ; oxide fluoride

INTRODUCTION

Topotactic insertion of lithium into perovskite type compounds, ABX_3, where B is a transition metal presents significant interest because of their potential use as electrode materials in secondary batteries or electrochromic devices. These compounds can present either totally empty A-sites or some vacancies in these A-sites. Therefore they can offer the possibility of inserting lithium ions. Lithium is ionic in this material, and the charge is compensated by a reduction of the host cations B.

Chemical lithium insertion with n-buthyllithium in hexane has been already reported in NbO_2F [1-4]. A maximum lithium uptake of 2Li/Nb, at 50°C, has been reported by Murphy et al. [1]. According to the studies of Permer et al. [2,3] and Renou [4] the chemical lithiation of this oxide fluoride leads to a change in the structure from the NbO_2F to the $LiNbO_3$-type structure, with the existence of a two-phase domain in the composition range $0.2 < x < 1.3$.

The aim of this study is to investigate the electrochemical insertion of lithium into this oxide fluoride. We particularly focused our attention on the change of the electrical properties of the inserted materials as insertion proceeds. Insertion has been followed by discharge experiments associated with impedance spectroscopy. The experimental results are discussed in relation to the structure of both the starting and the inserted materials.

EXPERIMENTAL

NbO_2F was synthetized by dissolving Nb_2O_5 in HF (aq. 48%) followed by evaporation to dryness. The resulting powder is heat-treated in a gold boat at 100°C under vacuum for 5 hr. X-ray powder diffraction measurements were used to verify the purity of the product and were carried out with a PHILIPS 1130 diffractometer using the Cu Kα radiation and a vertical holder.

Insertion of lithium performed by galvanostatic discharge and complex impedance spectroscopy were carried out by using a three-electrode cell with a lithium reference electrode and a lithium counter electrode. The working electrode was a 5 mm diameter pellet (geometric area = 0.2 cm^2) of a mixture of the electroactive material, graphite powder and PTFE in the ratio 50:25:25 (in weight %). The mass of the electroactive material was of the order of 30 to 50 mg. The working electrode and the electrochemical cell were prepared as previously described for intercalation material studies [5]. The electrolyte was a solution of anhydrous $LiClO_4$ (0.1mole.L^{-1}) dissolved in anhydrous propylene carbonate (PC).

The discharge of the electrodes was performed under galvanostatic conditions (20 to 5 μA) by using the galvanostatic intermittent titration technique (GITT) followed by complex impedance spectroscopy at the end of the electrode relaxation, as described previously [5]. The impedance plots in the Nyquist plane were obtained in the 100 kHz - 1 mHz with a 10 mV (r.m.s) applied voltage.

RESULTS

The crystallographic structure of NbO$_2$F is shown in Fig.1. This oxide can be described in a cubic unit cell with a = 3.9048 Å with the Pm3m space group [2]. It is built up of corner sharing octahedra NbX$_6$ (X = O, F) that enclose a twelve-coordinated A-site. These A-sites which are totally empty are located at the body center of a cube formed by the centers of eight octahedra.

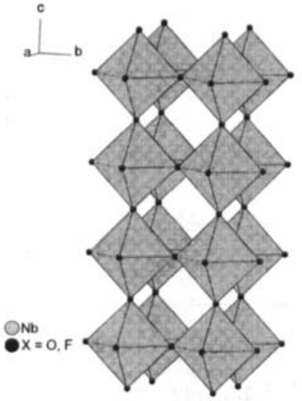

FIGURE 1 Crystal structure of NbO$_2$F
(X=O, F statistically distributed)

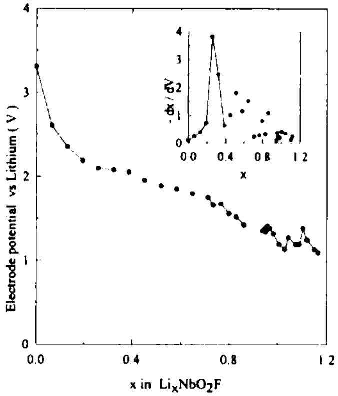

FIGURE 2 GITT curve for NbO$_2$F/C/PTFE electrode in LiClO$_4$ (0.1 mole L^{-1})-PC electrolyte and incremental differential capacitance *vs* insertion ratio x

Fig.2 presents a discharge curve obtained by GITT after insertion (-20 μA for 2 hr) and relaxation of the electrode for 18 hr. It shows three parts : a decrease of the potential for $0 < x < 0.2$, the appearance of a plateau at $x = 0.2$ and a decrease of the potential up to $x = 1.2$. At this stage of the insertion, and even at low reaction rate ($I = -5$ μA), intercalation into the graphite and Li deposition could not be avoided. The variation of the electrode potential and the appearance of the plateau are better seen by plotting the differential capacity (-dx/dV) as a function of x as shown in the inset of Fig.2.

Fig.3 shows a typical impedance diagram in the Nyquist plane recorded under open-circuit conditions after complete relaxation of the electrode. In the high frequency domain the spectra consist of one arc which can be ascribed to the charge transfer reaction at the electrode/electrolyte interface associated to the double layer capacitance of the electrode/electrolyte interface. At higher frequencies we can observe the onset of the arc due to the electrical properties of the $LiClO_4$-PC electrolyte. At low frequency the diagram consists of a second arc. The two arcs are ascribed to reactions at the oxide electrode/electrolyte interface. The electrochemical process involves reactions with different time constants. The reaction which corresponds to the high frequency semi-circle has a time constant of the order of 50 - 800 ms depending on the x value and can be attributed to the charge transfer reaction at the electrode/electrolyte interface. The reaction which corresponds to the intermediate frequency semi-circle has a time constant of the order of 50 - 700 s. This reaction can be ascribed to the formation of a high inserted film on the grain surface of NbO_2F. This assumption is supported by the HREM observations made by Permer [2,3]. Indeed, this author has clearly shown that during insertion the diffusion of Li into the host starts from the surface of thegrains leading to non homogeneous particles. The HREM image of a crystal fragment from the sample $Li_{0.3}NbO_2F$ shows a relatively well-ordered cubic structure surrounded by a layer close to the surface where the atoms are arranged in a hexagonal pattern which corresponds to the $LiNbO_3$-type structure compound or β-phase [2]. In order to take into account these reactions which take place during the electrochemical process we propose the following equivalent electrical model shown in Fig.4.

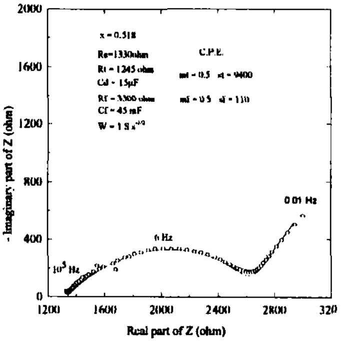

FIGURE 3 Impedance spectrum of Li_xNbO_2F/C/PTFE electrode in $LiClO_4$ (0.1 mole L^{-1}) - PC electrolyte. The circles refer to the experimental data and the full line to the overall calculated fit.

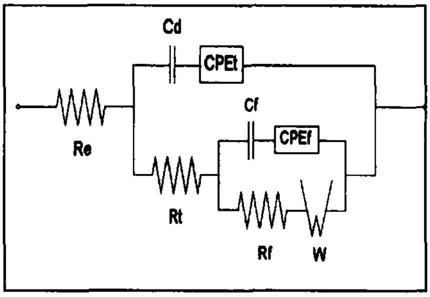

FIGURE 4 Equivalent circuit for an electrochemical process characterized by a charge transfer reaction-high inserted film formation-diffusion sequence.

This model involves the ohmic resistance Re made of the electroyte and the electrode resistances, the charge transfer reaction characterized by its resistance Rt in parallel with the double layer capacitance Cd, the formation of the surrounding layer characterized by its resistance and capacitance Rf and Cf and the diffusion process into the bulk of the material by a Warburg element. To take into account the electrical inhomogeneities of the electrode we added two CPE elements for charge transfer and film formation. The electrochemical process occuring during discharge is then characterized by an electrode reaction - high inserted film formation - diffusion sequence. The faradaic process is represented by a charge tranfer resistance Rt for the ion insertion reaction, an impedance W for mass transport in the bulk of the oxide fluoride and a resistance Rf due to the formation of a high inserted layer during insertion. The non faradaic process is represented by the double layer capacitance Cd and the capacitance Cf of the film surrounding the particles. Finally, the ohmic resistance made of the electrical contacts, the electrolyte and the electrode resistances is represented by the resistance Re. A good fitting is obtained between the experimental data and this electrical model as shown in Fig.3 where the line displays the fitted impedance diagram. We have to note that for $0.2 < x < 0.7$ the low frequency of the impedance diagram can be fitted without any diffusion contribution. On the other hand, for $x > 0.7$ diffusion has to be introduced in the fitting procedure. This fitting procedure leads to the determination of the kinetics parameters of the insertion reaction into NbO_2F. Fig.5 and 6 show the variation of Rt, Cd and Rf, Cf respectively

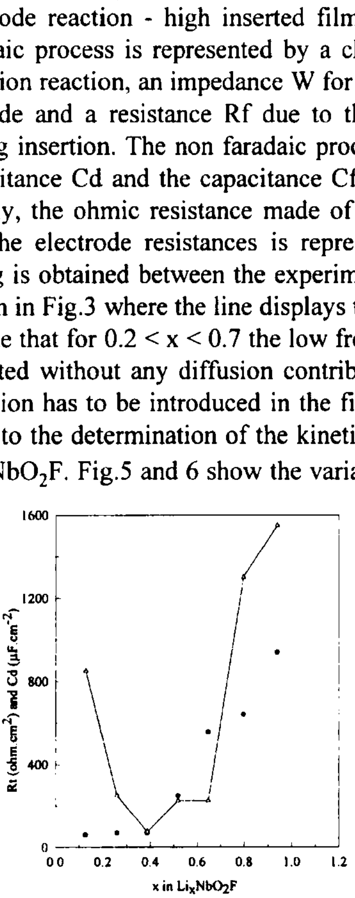

FIGURE 5 Variation of the charge transfer resistance Rt (●) and the double layer capacitance Cd (Δ) as a function of x.

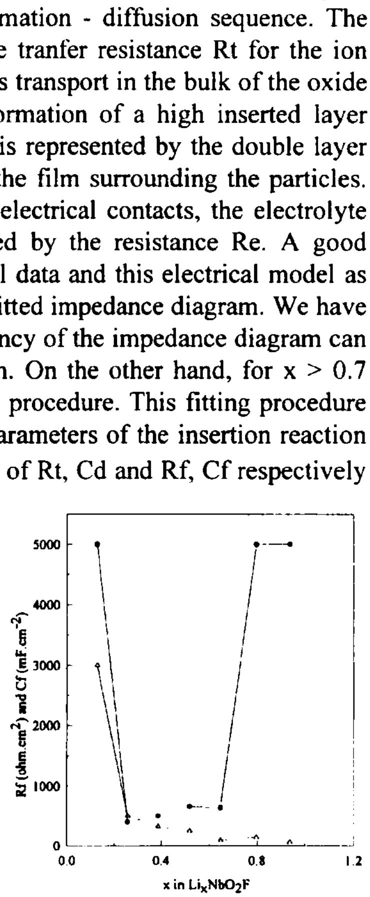

FIGURE 6 Variation of Rf (●)and Cf (Δ) of the high inserted film as a function of x.

as a function of x. Rt increases almost linearly with x for $x > 0.4$. On the other hand Cd, Rf and Cf show sudden breaks at $x = 0.2$ and $x = 0.7$. At $x = 0.2$, the break may be ascribed to the formation of the $LiNbO_3$-type structure phase in the cubic phase which leads to the decrease of Rf, Cf and Cd. At $x = 0.7$ Rf and Cd increase abruptly. At the same time the two CPE prefactors increase suggesting that the electrical inhomogeneity of the material increases. It can be noted that the electrode tends to become more and more amorphous as insertion proceeds, this is seen in the discharge curve of Fig.2.

DISCUSSION

The electrochemical insertion of lithium in this materials leads to the progressive amorphisation of the material as insertion proceeds. This is also observed during chemical insertion with n-BuLi [2]. Both the discharge and the incremental capacitance curves can be well understood only by refeering to the structural variation of the compounds. Plateaus in the discharge curve and then peaks in the incremental capacitance curve can be the signature of a structural changes or the existence of a two-phase domain. These explanations can be obtained only by considering the structure of both the starting and the inserted materials since both of these phenomena give rise to the same curve shape. The shape of the impedance spectroscopy diagrams may be explained by the formation of a high inserted film at the surface of the grain during insertion characterized by a resistance and a capacitance. This explanation is supported by the HREM observations made by Permer [2] during chemical insertion with n-BuLi. This result suggests that the particles are not homogeneous. From a general point of view, the lithium insertion is assumed to involve both a fast electron diffusion into the grain and a slower diffusion of Li^+ ions inwards from the surface of the particles.

The initial insertion causes a continuous decrease of the cubic unit cell volume with increasing Li content because the perovskite holes are too large to host the small Li^+ ions. The shrinkage of the holes is accomplished by a tilt of the NbX_6 octahedra. As soon as $x > 0.2$, the distorted cubic cell transforms into the β-phase ($LiNbO_3$-type structure which presents a hexagonal symmetry), and then a two-phase domain appears. Since the diffusion of Li^+ ions starts from the surface of the grain, a layer of high inserted compound may form at outermost parts of the grain. This process leads to the formation of a nonhomogeneous particles made of a layer of high inserted material surrounding a less inserted grain. This will cause strains to build up within the particles. When x increases the thickness of the layer increases and consequently the strains increase. At high Li content this layer probably falls off as small fragments of β-phase. The sudden change in the parameters Rt, Cd, Rf and Cf observed at $x = 0.2$ (Figs 5 and 6) is linked to the formation of the layer of the new β-phase surrounding the distorted cubic particles. The second break observed at $x = 0.7$ in Cd and Rf may be linked to the breakdown of the shell and to the formation of very small particles of β-phase. We can also observe that this process is accompanied with a sudden increase of the prefactor of the two CPE impedances. This result is consistent with the increase of the roughness of the electrode due to the formation of small particles of β-phase and/or with the increase of non conductive paths between the two phases. We can also show that the transfer resistance Rt is only sensitive to the existence of a two-phase domain.

CONCLUSION

The interpretation of both the discharge curves and the impedance spectroscopy diagrams is greatly facilitated by the contribution of HREM microscopy [2] and powder X-ray diffraction analysis performed on this chemically inserted material. The kinetics parameters obtained from impedance spectroscopy are sensitive to the variation of the microscopic structure of the composite electrode as insertion proceeds. The appearance of a two-phase domain is clearly shown. The low frequency part of the impedance diagrams can be ascribed to the formation of a layer of high inserted compound surrounding a distorted cubic grain. It may be represented by a parallel resistance-capacitance circuit associated with a constant phase element. For high lithium content ($x > 0.7$) the formation of very small particles made of the β-phase and consequently the amorphisation of the material are observed. The formation of small particles of a new phase in the electrode may limit considerably the reversibility of the material. Charge-discharge experiments associated with impedance spectroscopy will then be performed to study the evolution of the kinetics parameters as a function of the number of cycles performed on the electrode.

References

[1.] D.W.Murphy, M.Greenblatt, R.J.Cava and S.M.Zahurak, Solid State Ionics 5, 327 (1981).

[2.] L.Permer, Chem. Communications 8, 1 (1991).

[3.] L.Permer and M.Lundberg, J.Solid State Chem. 81, 21 (1989).

[4.] M.F.Renou, Doctoral Dissertation, U. du Maine, Le Mans (1984).

[5] C.Bohnké, O.Bohnké, J.L.Fourquet, J.Electrochem.Soc. 144, 1151 (1997)