



ELSEVIER

Journal of Power Sources 97–98 (2001) 491–493

JOURNAL OF
**POWER
SOURCES**

www.elsevier.com/locate/jpowersour

General behavior upon cycling of LiNiVO_4 as battery electrode

Cécile Rossignol, Guy Ouvrard*

Institut des Matériaux Jean Rouxel, UMR 6502 CNRS, Université de Nantes, 2 Rue de la Houssinière, BP 32229, 44322 Nantes Cedex 03, France

Received 22 June 2000; received in revised form 1 December 2000; accepted 4 December 2000

Abstract

X-ray absorption spectroscopy (XAS) study on the nickel and vanadium oxide LiNiVO_4 gives a lot of information on the local structural changes and the redox processes involved upon lithium uptake. This paper is mainly devoted to the comparison between the behaviors of two pristine materials which differ only by the annealing temperature. The general behavior at the atomic level is identical: in a first step, a reduction and a coordination change of vanadium from tetrahedral to octahedral, then a reduction and pairing of nickel, and few changes for the main part of the lithium uptake. The reversibility is insured by vanadium which move from octahedra to tetrahedra and is reoxidized to its pristine oxidation state. From the XAS results, we may conclude that the differences in the electrochemical curves is due to side reaction with the electrolyte. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Anode; Lithium battery; XAS; Transition metal oxides

1. Introduction

LiNiVO_4 is among the transition metal oxides which present such good electrochemical performances as they are considered as possible negative electrodes in lithium ion batteries [1]. All these oxides have a very similar behavior. The first step of the discharge corresponds to an amorphization of the material and is irreversible. In the second part, a large amount of lithium can be reversibly inserted. Among these oxides, the tin derivatives have been largely studied. In this case, stoichiometries and some experimental results are in agreement with the correlative formation of Li_2O and elemental metal which may react reversibly with lithium [2]. These conclusions are poorly supported by X-ray diffraction because the compounds are amorphous. EXAFS proves that the mechanism is more complicated than expected and indicates the formation of lithium–metal–oxygen complexes acting as an oxygen reservoir on charge and a lithium reservoir on discharge [3]. X-ray absorption spectroscopy (XAS) is known to be a very efficient tool in the structural determination of the local atomic arrangement. Moreover, modifications of the metal absorption edge (XANES) may give valuable information on the redox process. We have used this technique to define the local structural changes and the redox process in LiNiVO_4 upon cycling, by experiments on both nickel and vanadium edges. In a previous paper, the general behavior of this compound has already been

described [4]. We focus here on the influence of the crystallization state on the electrochemical performances.

2. Experimental

Lithium reaction was performed in Swagelock batteries whose the negative is made of metallic lithium and, in our experiments, LiNiVO_4 has been considered as a positive electrode. The starting phase has been prepared in following a ‘chimie douce’ method [5]. The obtained amorphous powder was annealed at two different temperatures: 500 and 600°C leading to slightly different crystalline states, especially in the grain sizes and their distribution. XAS data have been collected at the vanadium and nickel K edges, in the transmission mode, in using the synchrotron beam provided by the DCI storage ring at LURE (Orsay, France). The samples have been extracted from the electrochemical cells and properly conditioned in a glove box to avoid air and moisture contamination.

3. Results

The voltage–composition curves, close to equilibrium, are shown in Fig. 1 for the materials annealed at 500 and 600°C. The general shape is the same with a large voltage drop at the very beginning ($x = 0.6$ and 0.2, points **A** and **1**, respectively, in Fig. 1), which is more intense for the second compound. A first plateau follows, ending at **B** ($x = 1.5$)

* Corresponding author. Tel.: +33-240-37-39-17; fax: +33-240-37-39-95.
E-mail address: ouvrard@cnsr-imn.fr (G. Ouvrard).

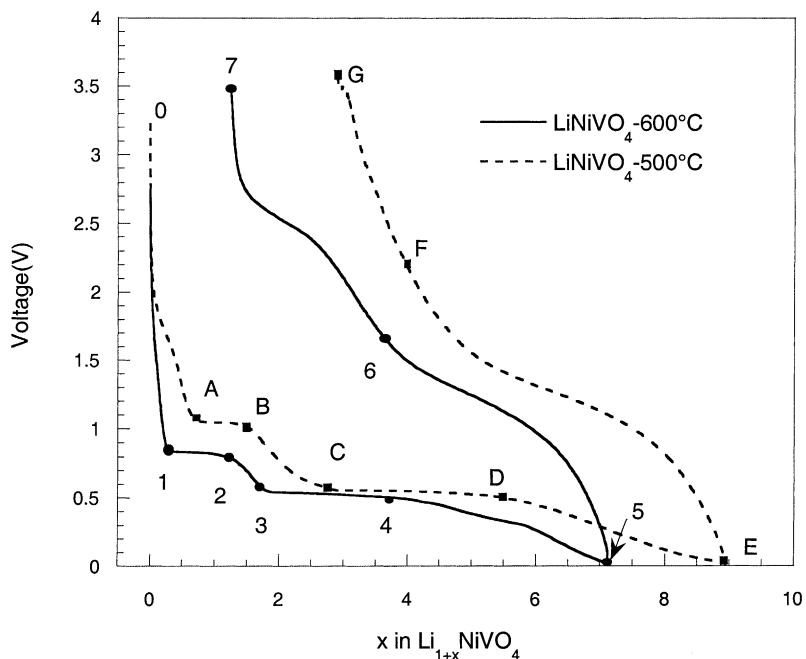


Fig. 1. First cycle of LiNiVO_4 -600°C and LiNiVO_4 -500°C/Li batteries.

and 2 ($x = 1.1$), respectively, and then voltage drops down to 0.5 V. The end of this process, in C ($\text{Li}_{3.6}\text{NiVO}_4$) and 3 ($\text{Li}_{2.6}\text{NiVO}_4$), respectively, corresponds to the beginning of the reversible part of the battery. The discharge can be extended with a slow voltage decrease to the final compositions $\text{Li}_{10}\text{NiVO}_4$ (point E) and Li_8NiVO_4 (point 5), respectively. Upon charging from these points, about six lithium per formula unit can be removed from the material. It is evident that the general shape of the voltage–composition curve is maintained with a shift towards higher lithium content for the less annealed compound. It corresponds to more than a doubling of the irreversible capacity of the material.

Previous XAS studies on the 600°C annealed material have shown that the first step of the discharge is a structural modification of the pristine inverse spinel structure [6], in which vanadium atoms move from tetrahedra into octahedra. Vanadium is reduced from the oxidation state V to IV. The second short voltage drop does not involve vanadium atoms. Surprisingly, the nickel environment is largely modified during this step. It corresponds to a Ni–Ni pair formation. Correlatively, nickel is reduced from II to the unusual oxidation state I. Despite the large uptake of lithium (more than five Li per formula unit), subsequent discharge will not modify markedly the vanadium and nickel environments. Moreover, the metal oxidation states are only slightly

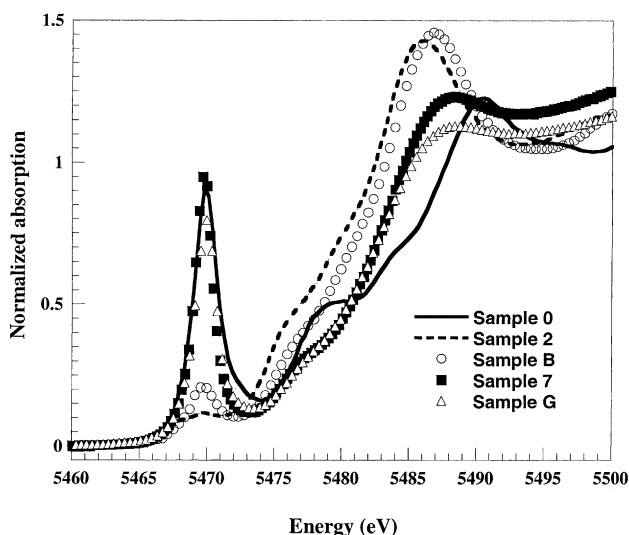


Fig. 2. Vanadium K edge for various lithium content in LiNiVO_4 .

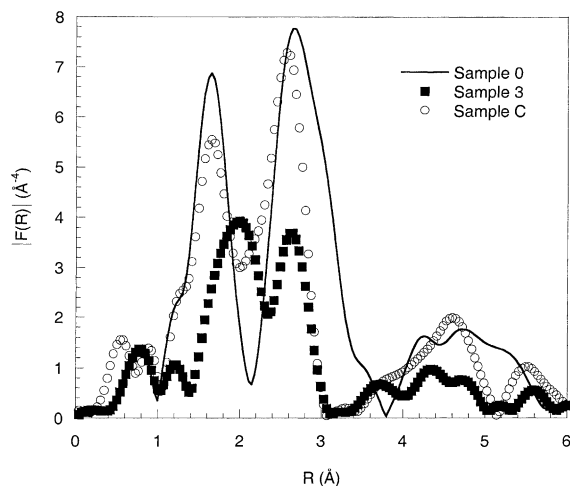


Fig. 3. Moduli of the nickel K edge EXAFS Fourier transforms for various lithium content in LiNiVO_4 .

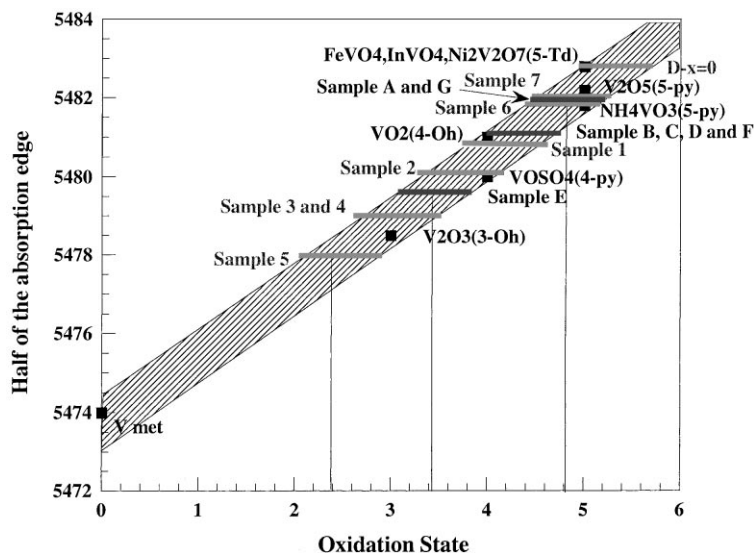


Fig. 4. Position of the absorption edge of vanadium vs. its oxidation state.

reduced, to a degree which does not correspond to a simple charge transfer from fully ionized lithium atoms.

In order to compare the behavior, at the atomic scale, of the material annealed at the two different temperatures, XAS data have been collected at both Ni and V edges for the compositions marked on Fig. 1. The vanadium edge is a clear signature of the reduction and the coordination change of vanadium, from vanadium V into tetrahedra, to vanadium IV into octahedra. In this matter, the spectra of samples 2 and B (Fig. 2), corresponding to the end of the first voltage plateaus in the 600 and 500°C compounds, respectively, are very similar. These two evidence a large decrease of the pre-edge peak, signature of the coordination change, and a shift of the main edge towards lower energy, which proves the reduction of vanadium. The changes in the nickel environment are well seen in the radial distribution function (RDF) extracted from EXAFS signal. The RDFs of samples 3 and C are similar (Fig. 3). These two show a contribution at a much longer distance than the one observed in the pristine phase, which corresponds to the octahedral oxygen coordination of nickel ($d_{\text{Ni-O}} = 2.05 \text{ \AA}$). The new peak has been analyzed as a nickel–nickel distance of 2.43 Å, very close to the one encountered in the elemental nickel.

As far as charge is considered, the nickel environment is not significantly modified. It is important to notice that the nickel pairs are kept all along the cycling. They correspond to the formation of a new structural arrangement which is very stable and favorable to the electrochemical behavior. The charge involves mainly vanadium atoms, which are found back into tetrahedra at the end of the charge. This coordination is especially evident if we consider the intensity of the pre-edge peak as compared to the one of the pristine phase (Fig. 2). The variation of the edge position shown in Fig. 4 indicates that vanadium recovers its pristine oxidation state V. This figure also shows that the lower oxidation state of vanadium is close to II.

4. Discussion

The main question we tried to answer in this study is about the origin of the irreversibility of the extra lithium which reacts with the 500°C annealed phase as compared to the 600°C one. It can be either a bulk reaction, different from the one previously described, or a decomposition of the electrolyte. Such a decomposition is expected to be catalyzed by the surface of the grain and would be very sensitive to the grain size. From the results, it is clear that the vanadium and nickel environments along with their oxidation state do not depend on the amount of reacting lithium but on the position in the cycling curve. Therefore, the extra inserted lithium does not react with the material itself and has to be attributed to electrolyte decomposition. This study points out the importance of the grain size and the size distribution in the performances of the materials and especially the large effect they may have on the irreversible capacity of the metal oxides used as negative electrodes.

Acknowledgements

The authors thank V. Briois and F. Villain for their help in XAS data collections.

References

- [1] F. Orsini, E. Baudrin, S. Denis, L. Dupont, M. Touboul, D. Guyomard, Y. Piffard, J.-M. Tarascon, *Solid State Ionics* 107 (1998) 123–133.
- [2] I.A. Courtney, J.R. Dahn, *J. Electrochem. Soc.* 144 (6) (1997) 2045–2052.
- [3] G.R. Goward, F. Leroux, W.P. Power, G. Ouvrard, W. Dmowski, T. Egami, L.F. Nazar, *Electrochem. Solid State Lett.* 2 (1999) 367–370.
- [4] C. Rossignol, G. Ouvrard, E. Baudrin, *J. Electrochem. Soc.*, in press.
- [5] S. Denis, E. Baudrin, F. Orsini, G. Ouvrard, M. Touboul, J.-M. Tarascon, *J. Power Sources* 81/82 (1999) 79–84.
- [6] G. Ting-Kuo Fey, Wu. Li, J.R. Dahn, *J. Electrochem. Soc.* 141 (9) (1994) 2279–2282.