



ELSEVIER

Journal of Power Sources 97–98 (2001) 251–253

JOURNAL OF
**POWER
SOURCES**

www.elsevier.com/locate/jpowersour

X-ray absorption study of cobalt vanadates during cycling usable as negative electrode in lithium battery

S. Laruelle^a, P. Poizot^a, E. Baudrin^a, V. Briois^b, M. Touboul^a, J-M. Tarascon^{a,*}^a*LRCS, Universit de Picardie and CNRS, 33 Rue St. Leu, F-80039 Amiens, France*^b*LURE, BP 34, Centre Universitaire Paris Sud, 91898 Orsay Cedex, France*

Received 6 June 2000; accepted 11 December 2000

Abstract

X-ray absorption spectroscopy has been used to characterize the structural and electronic changes induced by cycling in a $\text{CoV}_2\text{O}_6/\text{Li}$ battery. The XANES and EXAFS spectra recorded at both vanadium and cobalt K-edges show that a demixion of the starting compound occurs during cycling leading to a cobalt oxide domains embedded in a lithiated vanadium oxide matrix. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: X-ray absorption spectroscopy; Lithium battery; Vanadium oxide; Cobalt oxide

1. Introduction

Vanadium-based oxides were reported to display attractive electrochemical properties versus Li, such as uptake and removal of a large amount of lithium ions at low potential. Over the last few years, our group has devoted much effort towards the synthesis of a wide variety of either crystalline or amorphous divalent and trivalent element vanadates [1,2] containing occasionally structural water. Their electrochemical performances versus Li were investigated, so as to screen the best material. Amongst them, those having an initial capacity as high as 1000 mAh/g are numerous. However, whatever be their initial capacity, all of them exhibit a large capacity fading upon cycling, whose origin is not yet understood.

A possible clue to account for such a limited cycleability could arise from a better understanding of the relation between structure and electrochemical properties. Searching for such relation is complicated by the fact that these materials are becoming amorphous during the first discharge as shown by a preliminary semi in situ X-ray diffraction study. So we are left with only a few techniques able to probe the structure of amorphous materials. One of them is the X-ray absorption spectroscopy (XAS). We then used this technique to characterize the structural and electronic modifications induced by cycling in a $\text{CoV}_2\text{O}_6/\text{Li}$ battery.

2. Experimental

As numerous vanadates based compounds, CoV_2O_6 has been synthesized by the ‘chimie douce’ process which consists in a coprecipitation reaction. For that, NH_4VO_3 and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ aqueous solutions were mixed in the corresponding stoichiometric condition. The precipitate hydrated compound, $\text{CoV}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$, was annealed at 350°C for 24 h. A well crystallized CoV_2O_6 powder is thus obtained. The electrochemical measurements were carried out using the Swagelok-type cell configuration with cobalt vanadates as the active positive electrode and Li metal as anode. The plastic cathode electrode was made using the Bellcore’s plastic LiION technology. A borosilicate glass fiber sheet saturated with a 1 M LiPF_6 electrolyte solution in 1:1 dimethyl carbonate:ethylene carbonate was used as separator. The cells were cycled over a 0.02–3.5 V voltage range with a rate of 1 Li for 5 h.

X-ray absorption spectra were performed with the EXAFS IV spectrometer (LURE-Université de Paris Sud, France) that uses a double crystal silicon (3 1 1 and 1 1 1) monochromator and were carried out in the transmission mode with ionization chambers in front and behind the absorber. The experiments were performed at both vanadium and cobalt K-edges on the plastic CoV_2O_6 electrodes submitted to different states of charge–discharge: after the first and second plateau during the first discharge, at the end of the first discharge down to 0.02 V and then after the 10th charge and discharge.

* Corresponding author. Tel.: +33-322827571; fax: +33-322827590.
E-mail address: jean-marie.tarascon@sc.u-picardie.fr (J-M. Tarascon).

The EXAFS analysis was performed following a classical procedure based on the Fourier transform of the EXAFS oscillation [3]. This procedure provides pseudo-radial distribution functions (PRDF) with peaks related to the different shells of neighbors of the absorbing atom.

3. Results and discussion

The evolution of the M–O (M = Co and V) and M–M' (M' = Co or V), distances and the electronic change within the CoV_2O_6 vanadate have been investigated by XAS not only during the first discharge but through subsequent cycles. The first discharge voltage composition curve for CoV_2O_6 exhibits a first plateau at 2.4 V and another one at 0.6 V having 1.5 and 2.5 lithiums, respectively, followed by a gradual voltage decrease down to 0.02 V leading total uptake of 10 Li per formula units. X-ray measurements have shown the appearance of a new phase after the second plateau, that could not be identified due to its poor crystallinity, then a progressive amorphization occurs and become complete at the end of the discharge as deduced from the XRD pattern that becomes featureless. This amorphization remains upon subsequent cycles.

The CoV_2O_6 structure consists of a three-dimensional packing of CoO_6 chains and VO_5 bipyramids, the vanadium and cobalt being respectively in the +5 and +2 oxidation state. The intense prepeak observed on the XANES spectrum (Fig. 1a) is indicative of the vanadium five-fold coordination. As soon as the cell is discharged (e.g. upon Li uptake) we note a progressive decrease of the prepeak intensity which is consistent with a change of the vanadium coordination sphere symmetry that evolves from distorted pyramidal to more symmetrical situation, e.g. octahedral. Simultaneously, the V–O distances in the first coordination shell is shifted at larger distances whereas the V–M' (M' = V or Co) distances are shortened compared to the distances which characterize the CoV_2O_6 structure. The Co–O and Co–M' distances exhibit the same behavior than the changes observed at the V K-edge with respect to the CoV_2O_6 structure on the first and second plateau of the first discharge. Drastic differences around cobalt are observed at the end of the discharge: the second nearest neighbor contribution (Co–M') centered around 2.6 Å totally disappears whereas the first nearest neighbor (Co–O) contribution located around 1.6 Å strongly decreases in intensity. Then, the PRDF is dominated by a broad contribution centered around 2.0 Å.

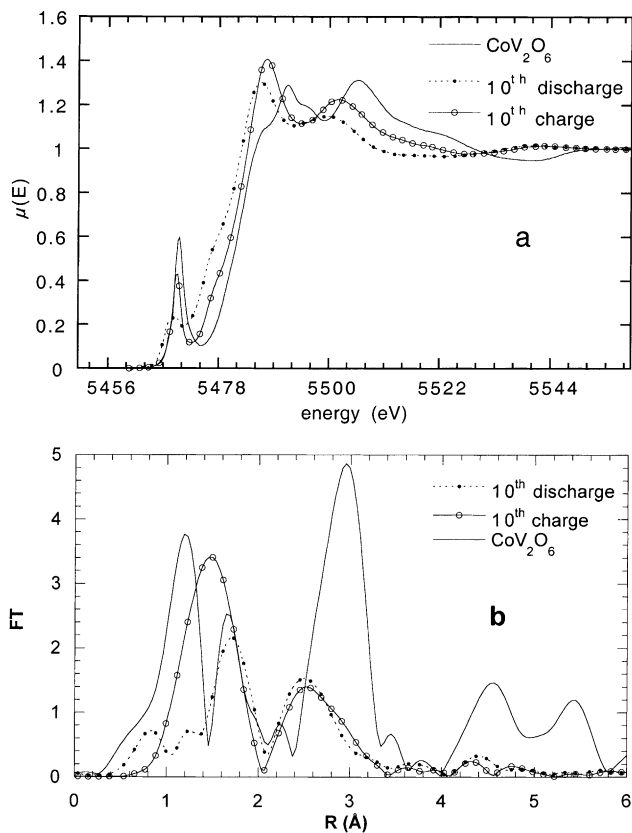


Fig. 1. (a) Vanadium K-edge XANES spectra of CoV_2O_6 , after 10th discharge and charge; (b) moduli of the vanadium K-edge Fourier transform of CoV_2O_6 after 10th discharge and charge. Distances have not been corrected from phase shift.

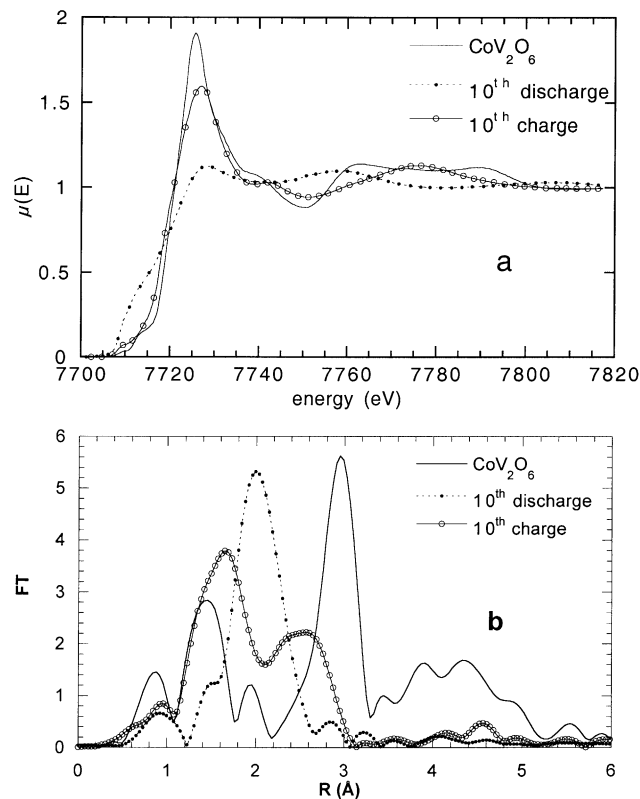


Fig. 2. (a) Cobalt K-edge XANES spectra of CoV_2O_6 after 10th discharge and charge; (b) moduli of the cobalt K-edge Fourier transform of CoV_2O_6 after 10th discharge and charge. Distances have not been corrected from phase shift.

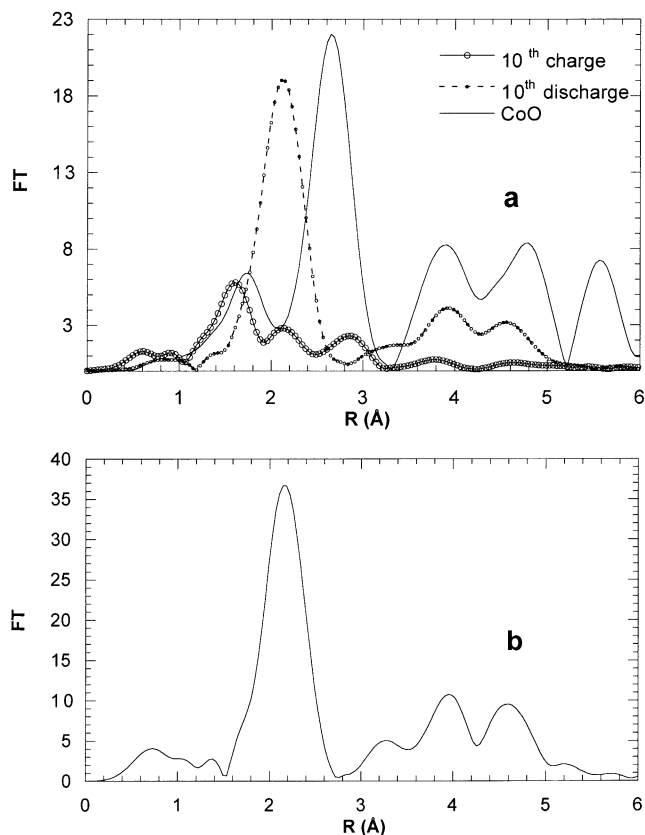


Fig. 3. (a) Moduli of the cobalt K-edge Fourier transform of CoO after 10th discharge and charge. Distances have not been corrected from phase shift; (b) moduli of the cobalt K-edge Fourier transform of Co metal foil. Distances have not been corrected from phase shift.

To understand the behavior of the vanadate upon cycling, measurements have been done after 10 cycles. Fig. 1a shows the vanadium K-edge XANES spectra of the starting material, after the 10th charge and 10th discharge. At 3.5 V (in the charge state), the vanadium symmetry environment is pyramidal with an oxidation state close to 5 whereas at 0.02 V, the observed energy vanadium shifts of the rising edge and of the prepeak towards lower energies indicate a progressive reduction of the vanadium to an oxidation state close to 2, similar results were found on a previous study on FeVO_4 [4]. The EXAFS spectra (Fig. 1b) show that, in both cases, the V–V or/and V–Co distances (distinction between atoms of close atomic number is difficult by EXAFS) located in the 2–3 Å region is not affected by cycling. Only the V–O first neighbors contribution shifts towards shorter distance with increase in the amount of reacted lithium ions.

The XANES spectra of the Co K-edge (Fig. 2a) clearly indicate that the oxidation state goes reversibly from 2 to 0. Fig. 2b represents the PRDFs around Co atoms. In the charge state, the first peak located around 1.6 Å corresponds undoubtedly to Co–O distances. The second one centered around 2.6 Å can be attributed to Co–Co second nearest

neighbors and, eventually to Co–V distances. At 0.02 V the spectrum is constituted of a single peak centered around 2.0 Å as previously observed after the first discharge. This distance can match with Co–Co first nearest neighbor distances in cobalt metal cluster in agreement with the XANES spectrum which indicates an oxidation state of 0 to cobalt. Interestingly the peak centered around 2.6 Å in Fig. 1b, that we assigned either to V–V distances or V–V and V–Co distances, is not any longer present in Fig. 2b, which implies that the peak is related to only V–V distances. Thus, we can conclude that the local vanadium environment is constituted of oxygen and vanadium atoms independently of the charge state of the $\text{CoV}_2\text{O}_6/\text{Li}$ cell.

All these results suggest a demixion of the cobalt vanadate compound upon discharge into a lithiated vanadium oxide and a cobalt compound that can only be cobalt oxide.

To verify this assumption, CoO was electrochemically tested in the same condition of CoV_2O_6 . The PRDFs are reported in Fig. 3a. After the 10th charge, three contributions are visible. One in the 1–2 Å region corresponding to Co–O distances and two in the 2–3 Å region corresponding to Co–Co distances. As expected, at the discharge state, one single distribution is present and can be ascribed to metal Co–Co distances in comparison to the cobalt fcc (Fig. 3b). These results clearly show that a reversible Li-driven redox reaction $\text{CoO} \leftrightarrow \text{Co}$ occurs upon cycling a $\text{CoV}_2\text{O}_6/\text{Li}$ cell and, of course, a CoO/Li cell. The implication of such findings with respect to the field of energy storage will be detailed in a forthcoming paper.

4. Conclusion

On the light of the different absorption experiments, we conclude that during the first discharge of a $\text{CoV}_2\text{O}_6/\text{Li}$ cell a demixion of CoV_2O_6 led to the formation different oxides: CoO and a lithiated vanadium oxide. Upon cycling these two types of oxides act separately with an oxidation state going from 2 to 0 for cobalt and from $5 - \delta$ to 2 for vanadium. To our knowledge this is the first direct evidence of the feasibility of Li-driven reversible Co^{2+} –Co redox reaction in non-aqueous systems.

References

- [1] S. Denis, E. Baudrin, M. Touboul, J.-M. Tarascon, *J. Electrochem. Soc.* 144 (1997) 4099.
- [2] E. Baudrin, S. Laruelle, S. Denis, M. Touboul, J.-M. Tarascon, *Solid State Ionics* 123 (1999) 139.
- [3] B.K. Teo, *EXAFS: Basic Principles and Analysis*, Springer, Berlin, 1986.
- [4] S. Denis, E. Baudrin, F. Orsini, G. Ouvrard, M. Touboul, J.-M. Tarascon, *J. Power Sources* 81–82 (1999) 79–84.