

	Experiment title: In situ XRD characterization of structural changes in the Li/V ₂ (SO ₄) system upon Li-intercalation-deintercalation using synchrotron radiation	Experiment number: CH-427
Beamline: BM16	Date of experiment: from: 25/01/98 to:30/01/98	Date of report: 26/02/99
Shifts: 9	Local contact(s): Gavin Vaughan	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

J. Gaubicher*, T. Le Mercier*, J. Angenault and M. Quarton

Laboratoire de Cristallochimie du Solide, Université Pierre et Marie Curie-Paris VI, 4 place Jussieu, 75252 Paris Cédex 05, France

Y. Chabre*

Laboratoire de Spectrométrie Physique, Université Joseph Fourier- Grenoble I and CNRS, BP 87, 38402 Saint Martin d'Hères, France

C. Masquelier*

Laboratoire de Chimie des Solides, Bat. 414, Université Paris-XI Orsay, 91405 Orsay, FRANCE

Report:

In an effort to develop new positive electrode materials for lithium ion batteries, we are studying Nasicon-type materials $A_xM_2(XO_4)_3$, with $A = Li$, $M =$ transition metal, and $X = P, S$. Recently, we demonstrated that the electrochemical behavior of the $Li/V_2(SO_4)_3$ system [1] is more complex than inferred from previous reports [2]. Through the use of very slow stepwise potentiodynamic cycling with corresponding XRD studies, we were able to identify the particular behavior of this system that resulted during cycling: the first reduction involves two electrons per formula unit and occurs as a two steps process at 2.63 and 2.59V, whereas only a single process, that begins at 2.75V, is observed throughout the first oxidation. Upon further cycling, the reduction process remains unchanged, whereas two new oxidation de-intercalation peaks emerge close to 2.60V at the expense of the 2.75V peak that progressively disappears. In order to probe the origin of this evolution, we undertook an *in-situ* XRD study in transmission mode on thin plastic electrochemical cells, using the synchrotron radiation source at ESRF.

The results demonstrate a strong correlation between the electrochemical and structural behavior: *In-situ* studies on the high resolution BM16 line with time resolution on the order of minutes, show that the first step of **the first reduction process** (above 2.60V) is a first order transition. The new phase could not be observed by the use of laboratory X-ray diffractometer due to its close structural similarity with that of the parent $V_2(SO_4)_3$. The completion of **the first reduction process** below 2.60V corresponds to the formation of a new $Li_2V_2(SO_4)_3$ monoclinic phase. The phase transition occurs through a reorganization of the polyhedra connectivity such as pairs of edge-sharing VO_6 , absent in the initial $V_2(SO_4)_3$ appears [3]. Interestingly, lithium de-intercalation during the first oxidation from 2.75V causes the initial $V_2(SO_4)_3$ to reform. The refinement of the corresponding XRD data indicates that some structural defects have been generated by the reconstructive phase transformations.

The main feature of **the second reduction process** is that below 2.60V its completion leads to a mixture of two phases, the monoclinic $Li_2V_2(SO_4)_3$ and a new phase that is isostructural with $V_2(SO_4)_3$. We believe that the defects associated with the reconstructive processes which occur upon the first reduction, could aggregate and form two types of microdomains: defected and original grains. The defects would prevent the reconstructive mechanism and drive to the phase isostructural with the initial $V_2(SO_4)_3$. The nondefected microdomain should behave the same as during the first cycle and lead to the appearance-disappearance of the monoclinic $Li_2V_2(SO_4)_3$ along with creation of defects. Thus at the end of the following discharges one can expect the proportion of the monoclinic $Li_2V_2(SO_4)_3$ phase to decrease. Since *in-situ* XRD shows that the oxidative deintercalation from the phase isostructural with $V_2(SO_4)_3$ begins close to 2.60V, this structural evolution results in the disappearance of the 2.75V oxidation process to the benefit of the one close to 2.60V [4].

References:

- [1] J. Gaubicher, J. Angenault, Y. Chabre, T. Le Mercier and M. Quarton, *Mol. Crystals and Liquid Crystals*, **311**, 45 (1998).
- [2] K.S. Nanjundaswamy, S. Okada, A. Manthiram, J.B. Goodenough, H. Ohtsuka, H. Arai et J. Yamaki, *Solid State Ionics*, **92**, 1 (1996).
- [3] G. Vaughan, J. Gaubicher, T. Le Mercier, J. Angenault, M. Quarton and Y. Chabre, *Chem. Mat.*, *submitted*.
- [4] J. Gaubicher, G. Vaughan, T. Le Mercier, C. Masquelier, J. Angenault, Y. Chabre and M. Quarton, *manuscript in preparation*.

