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**Report:**

In an effort to develop new positive electrode materials for lithium ion batteries, we are studying layered materials  $\text{VOPO}_4 \cdot x\text{H}_2\text{O}$ , with  $0 \leq x \leq 2$ . Recently, we demonstrated that the electrochemical behavior of the  $\alpha_{\text{II}}\text{-VOPO}_4$  system [1] is more complex than for other anhydrous  $\text{VOPO}_4$  phases [1, 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 redox process occurs in two main steps at 3.7 and 3.5 V for the first reduction and at 3.9 and 3.7 V for the following cycles. The 3.5 V process fades on cycling and has completely disappeared upon the second reduction. In order to probe the origin of this evolution, we undertook an *ex-situ* XRD study in

transmission mode on the starting material and on samples stabilized at the following potential: 3.55 and 3.00 V on the first reduction, 3.67, 3.85 and 4.00 V on the first oxidation, 3.75 and 3.00 V on the second reduction and 4.30 V on the second oxidation, using the synchrotron radiation source at ESRF. The results demonstrate a strong correlation between the electrochemical and structural behavior: first of all *ex-situ* studies on the high resolution BM16 line with time resolution on the order of minutes, show that all the electrochemical steps observed during the cycling are first order transitions related to the transformation from  $\alpha_{II}$ -VOPO<sub>4</sub> to  $\alpha_{II}$ -LiVOPO<sub>4</sub>.

It has been found that the initial sample used for the X-ray experiments is not pure as the refinement results give 80 % of  $\alpha_{II}$ -VOPO<sub>4</sub> and 20 % of  $\beta$ -VOPO<sub>4</sub>. The major part of the first reduction **3.55 V** sample is  $\alpha_{II}$ -VOPO<sub>4</sub>; peaks of the corresponding lithiated phase are however, clearly seen, showing that the 3.7 V process is not related to an impurity or another VOPO<sub>4</sub> phase. The reflections corresponding to the  $\beta$  phase are not seen anymore as it is completely reduced (the V<sup>5+</sup>/V<sup>4+</sup> redox couple is at 4.00 V in the  $\beta$ -VOPO<sub>4</sub> host matrix). The reflections corresponding to  $\alpha_{II}$ -LiVOPO<sub>4</sub> are more intense, as can be seen on the X-ray powder diffraction pattern of the sample equilibrated at **3.00 V**. In contrast, the peaks assigned to the  $\beta$ -phase do not evolve as the same peak width and intensity are observed for the **3.55** and the **3.00 V** samples. The following phases are observed on the **3.67 V** sample (i.e. after the first step of the first oxidation):  $\alpha_{II}$ -LiVOPO<sub>4</sub>,  $\beta$ -LiVOPO<sub>4</sub> and  $\alpha_{II}$ -VOPO<sub>4</sub>. The  $\alpha_{II}$  phase reappears as the lithium is partially removed from the host matrix but with a higher peak-width value, sign of a loss of crystallinity. This loss of crystallinity caused by small distortions and rearrangements during the formation process might be responsible for the change of potential of one of the electrochemical step. The composition refinements show that only 14 % of  $\alpha_{II}$ -VOPO<sub>4</sub> are present in the sample whereas a large majority of  $\alpha_{II}$ -LiVOPO<sub>4</sub> and  $\beta$ -LiVOPO<sub>4</sub> is observed. The amount of  $\beta$ -LiVOPO<sub>4</sub> stays unchanged and no reflections corresponding to  $\beta$ -VOPO<sub>4</sub> is observed on the X-ray diffraction pattern of the sample reoxidized to **3.85 V**. The Bragg reflections for the  $\alpha_{II}$  phase show a loss of intensity and an increase in the peak-width supporting further loss of crystallinity upon cycling. Two intense peaks appear, for  $d = 3.10$  and  $3.08 \text{ \AA}$  that will be discussed later. These peaks disappear from the **3.75 V** sample pattern on the second reduction. Then, these reflections are ascribed to a phase reducible by lithium intercalation. The ratio of  $\alpha_{II}$ -LiVOPO<sub>4</sub> is higher than for the first reduction at the same potential, consistent with the shift of the main intercalation process up to 3.90 V upon the second electrochemical cycle.

At the end of the second discharge (**3.00 V**), the reductions of  $\beta$ -VOPO<sub>4</sub> and  $\alpha_{II}$ -VOPO<sub>4</sub> are found to be complete as well as at the end of the first reduction. The reflections corresponding to  $\alpha_{II}$ -LiVOPO<sub>4</sub> show an increase in the peak-width and a decrease in the reflected intensity whereas the 3D structure of  $\beta$ -

VOPO<sub>4</sub> shows a good crystallinity retention upon cycling, consistent with a more resistant structure [3]. Then, the electrochemical cyclings of Li/ $\alpha_{II}$ -VOPO<sub>4</sub> and Li/ $\beta$ -VOPO<sub>4</sub> systems seem to occur in an independent way as the ratio of these phases and their lithiated equivalents undergo no important variation at the end of reduction or oxidation. The unassigned peak on the 4 V sample at the end of the second oxidation, at  $2\theta = 12.8^\circ$  (3.08 Å) is both less intense and sharper than at the end of the previous oxidation although the other peak at  $2\theta = 12.7^\circ$  (3.10 Å) is considerably more intense. These two peaks could be related to the same phase, which might undergo a formation process on cycling too. In addition, on all the reduced samples some unassigned peaks have been found. These peaks could not be observed by the use of laboratory X-ray diffractometer due to the lack of resolution of the equipment and the background caused by the amorphous carbon of the electrode. Moreover, at the end of each cycle, the integrated intensity corresponding to the  $\alpha_{II}$  phase has decreased, confirming the presence of other phases in the sample. A large part of the peaks (but not all) can be indexed in the tetragonal system with the following lattice parameters  $a = 8.7231(5)$  and  $c = 7.5227(5)$  Å. Refinements give respectively 37 % and 64 % for this unknown phases at the end of the first and second cycle that we called  $\alpha_{III}$ -VOPO<sub>4</sub>.

Previous X-ray experiments on pure  $\alpha_{II}$ -VOPO<sub>4</sub> sample after oxidation to 4.3 V did not show any additional peaks as seen on the pattern acquired on the synchrotron for the same potential. Then the phase(s) associated to these peaks should be seen as "independent" impurities and not as a product of the formation process. As a matter of fact, these impurities could be caused by the high potential i.e. high instability of the samples equilibrated at 4.3 V.

The second possible explanation concerning the loss of crystallinity is related to a completely different type of disorder: the formation of the material at low potential is realized by the lithium insertion that has to invert the direction of the V=O vanadyl bonds from outside to inside of the structural planes for steric and electrical reasons. During the intercalation/deintercalation process, the formation of new layered VOPO<sub>4</sub>-like phases is possible. These phases would present V=O orientations different from the  $\alpha_I$ ,  $\alpha_{II}$ ,  $\gamma$  and  $\delta$  phases. In the two latter phases, one V=O bond over two is directed outside of the structural layers; then it is possible to imagine new phases with, for example, 1/3 or 1/4 V=O bond pointing towards the interlayer space (Fig. 10). The presence of microdomains of these new phases would be equivalent to a disorder in the orientation of the vanadyl bonds in the material and would lead to a loss of crystallinity, as observed by XRD, upon the electrochemical cycling. Moreover, during the intercalation process, all these phases yield  $\alpha_{II}$ -LiVOPO<sub>4</sub>. That is consistent with the important presence of poorly crystallized phases, observed by XRD in the oxidized samples.

References:

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