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# Electrochemical performance of different Li-VOPO<sub>4</sub> systems

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## Abstract

An electrochemical study of Li insertion in the  $\alpha_{II}$ ,  $\gamma$  and  $\delta$  forms of VOPO<sub>4</sub> and the optimization of their cycling performance are presented. The potentials of the intercalation–deintercalation processes and the specific capacities upon discharge have been correlated to the crystal structures of these phases. It is evidenced that the obtained capacities can be improved up to eight times by optimizing the synthesis route or the carbon/active material contact. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Li-VOPO<sub>4</sub> systems; Intercalation–deintercalation process; Synthesis route

## 1. Introduction

Owing to the low density and the high reductive properties of lithium, a great amount of attention has been focused on the development of lithium batteries as power sources for use in portable devices or electric vehicles. So far, investigations have been mainly devoted to oxides as intercalation compounds for reversible electrodes.

VOXO<sub>4</sub> compounds (X = S, P, As) present well-open two-dimensional (2D) or 3D frameworks which facilitate lithium intercalation process. In addition, these compounds present fairly good theoretical specific capacities (from 135 to 166 mAh/g depending on the nature of the X element). The present study deals with electrochemical performance and lithium intercalation mechanisms involving different lamellar crystalline forms of VOPO<sub>4</sub>. Although already known, these phases had never been considered yet as host materials for lithium batteries. Some of us however, have showed that the 3D  $\beta$ -VOXO<sub>4</sub> family, especially  $\beta$ -VOPO<sub>4</sub> [1], presents fairly good electrochemical properties.

The structural skeletons of the  $\alpha_{II}$ ,  $\gamma$  and  $\delta$  forms of VOPO<sub>4</sub> are built up from planes of distorted VO<sub>5</sub> square pyramids connected by PO<sub>4</sub> tetrahedra. From one phase to the other, the V=O vanadyl bonds are oriented along *c* but shows various orientations [2] (Fig. 1). For  $\alpha_{II}$ -VOPO<sub>4</sub>, all the vanadyl bonds point towards the interplanar spaces. For  $\gamma$ -VOPO<sub>4</sub>, the V=O bonds are all parallel, half within the

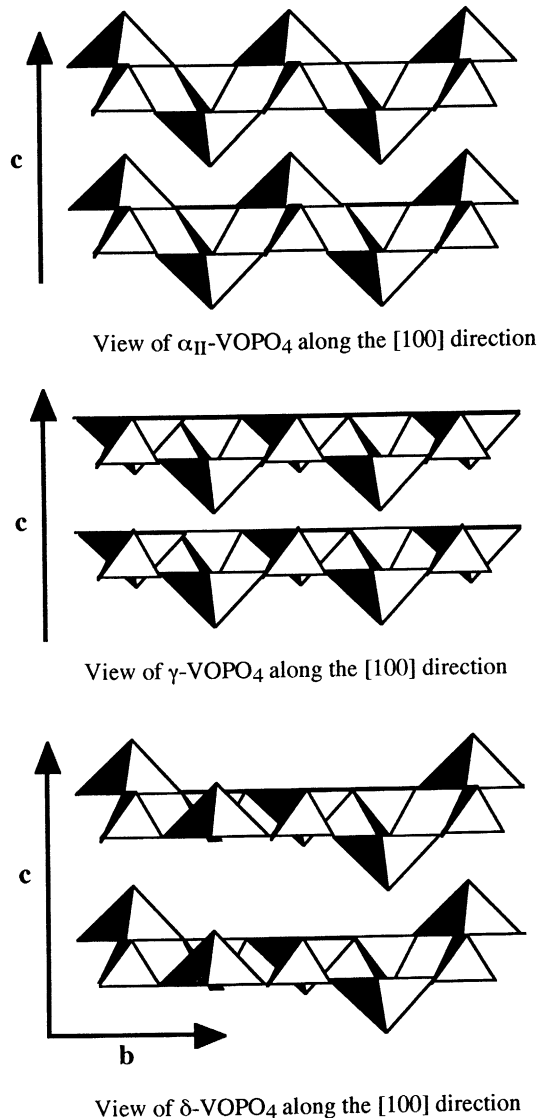
planes and half towards the interplanar spaces. For  $\delta$ -VOPO<sub>4</sub>, the VO<sub>5</sub> units, linked by PO<sub>4</sub> tetrahedra, form *b*-directed chains the V=O bonds of which point alternatively “up” and “down”, within the interplanar spaces and the planes.

## 2. Experimental

The different forms of VOPO<sub>4</sub> were prepared by simple and cheap methods [3].  $\alpha_{II}$ -VOPO<sub>4</sub> was obtained by dehydration of  $\alpha$ -VOPO<sub>4</sub>·2H<sub>2</sub>O at 685°C overnight under air flow; we also obtained  $\alpha_{II}$ -VOPO<sub>4</sub> (labelled p) from a new route involving the oxidation under oxygen flow and subsequent dehydration of VOHPO<sub>4</sub>·0.5H<sub>2</sub>O [4] at 680°C overnight.  $\gamma$ -VOPO<sub>4</sub> was obtained by dehydration of VOPO<sub>4</sub>·2H<sub>2</sub>O at 700°C during 48 h under air flow.  $\delta$ -VOPO<sub>4</sub> was obtained by oxidation under oxygen flow and dehydration of VOHPO<sub>4</sub>·0.5H<sub>2</sub>O at 450°C during 170 h. Chemical lithiations have been performed at room temperature, during 350 h, using 0.1 M lithium iodide.

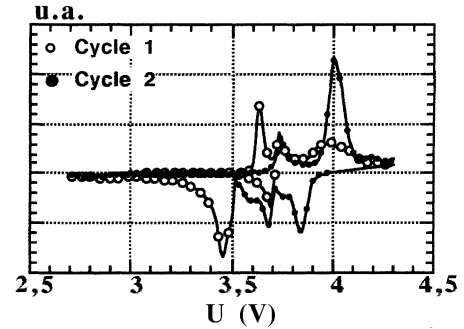
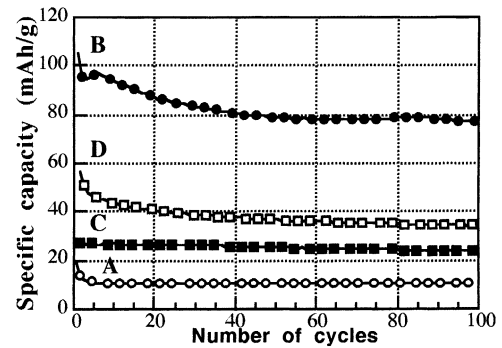
X-ray powder diffraction patterns were obtained from pure phases or positive electrode mixtures (phase-75% + carbon black-20% + PVDF-5% in weight) using a Philips PW1050 goniometer with Cu K $\alpha$  radiation. The X-ray diffraction patterns of  $\alpha_{II}$ ,  $\gamma$  and  $\delta$ -VOPO<sub>4</sub> match those published by Bordes [5] and Calvo et al. [6]. Electrochemical measurements were performed both in galvanostatic and potentiodynamic modes using Swagelok<sup>TM</sup> type cells [7] with Li metal as negative and reference electrode.

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Fig. 1. Structures of the different VOPO<sub>4</sub> forms.

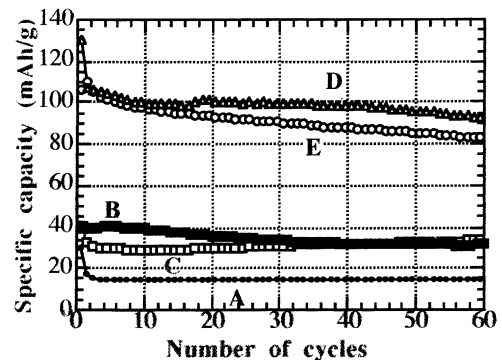
### 3. Results and discussion

For all the  $\alpha_{II}$ ,  $\gamma$  and  $\delta$  phases, the reduction–oxidation process occurs near 4 V, along with a structural transformation. This result is supported by XRD patterns that show apparition of several new lines upon reduction.  $\alpha_{II}$ -VOPO<sub>4</sub> presents a specific behavior on first reduction: the redox process occurs in two main steps at 3.7 and 3.5 V on reduction and three steps at 3.5, 3.7 and 3.85 V on oxidation upon the first cycle and 3.9 and 3.7 V upon the following cycles (Fig. 2). Interestingly, on the second cycle, a well defined redox process appears at 3.9 V at the expense of that at 3.5 V. This strongly suggests that the first cycle leads to a structural modification of the material (further studies are in progress). Galvanostatic tests were performed at nominal regimes of  $C/5$ ,  $C/10$  and  $C/50$ . It appears that the kinetics of the redox process is very low. The specific capacity in discharge depends strongly on the intercalation-deintercalation

Fig. 2. Cyclic voltamogram for the two first cycles of  $\alpha_{II}$ -VOPO<sub>4</sub>.Fig. 3. Capacity vs. cycle number ( $C/5$ ) for  $\alpha_{II}$ -VOPO<sub>4</sub> (A),  $\alpha_{II}$ -VOPO<sub>4</sub>-p (B),  $\gamma$ -VOPO<sub>4</sub> (C) and  $\delta$ -VOPO<sub>4</sub> (D).

regime: 10 mAh/g at  $C/5$  (Fig. 3) and 15 mAh/g at  $C/10$  (Fig. 4) and initially, 140 mAh/g at  $C/50$  (Fig. 5). Furthermore, the capacity fading is significant and reaches 47% of the initial performance (80 mAh/g after 50 cycles) at  $C/50$ .

In order to improve the carbon/active material contact, the electrode mixture have been homogenized in a planetary grinder: the specific capacity reaches 30 mAh/g at  $C/10$  for more than 100 cycles. As observed for  $\beta$ -VOPO<sub>4</sub> [1] and for  $\varepsilon$ -VOPO<sub>4</sub> [8], chemical lithiation has shown to facilitate the redox process. Owing to this method, the specific capacity in discharge has been improved (initial specific capacity:

Fig. 4. Capacity vs. cycle number ( $C/10$ ) for  $\alpha_{II}$ -VOPO<sub>4</sub> (A),  $\alpha_{II}$ -VOPO<sub>4</sub>-ground mixture (B),  $\gamma$ -VOPO<sub>4</sub> (C),  $\gamma$ -VOPO<sub>4</sub>-ground mixture (D) and  $\delta$ -VOPO<sub>4</sub> (E).

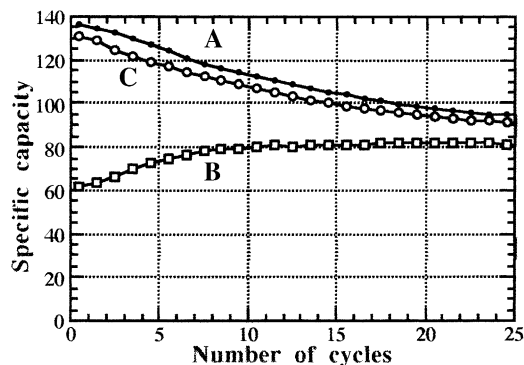


Fig. 5. Capacity vs. cycle number ( $C/50$ ) for  $\alpha_{II}$ -VOPO<sub>4</sub> (A),  $\gamma$ -VOPO<sub>4</sub> (B),  $\delta$ -VOPO<sub>4</sub> (C).

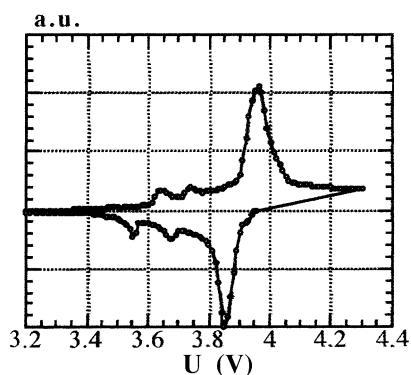


Fig. 6. Cyclic voltamogram for the first cycle of  $\alpha_{II}$ -LiVOPO<sub>4</sub>.

75 mAh/g at  $C/5$ ) (Fig. 7). Interestingly, the 3.5 V process has almost completely disappeared on the first oxidation (Fig. 6) and the main process is that at 3.9 V. This strongly suggests the completion of the intercalation–deintercalation mechanism change phenomenon. Interestingly,  $\alpha_{II}$ -VOPO<sub>4</sub>-p obtained from a different precursor presents a much better specific capacity without any optimization attempt (80 mAh/g at  $C/5$  and 115 mAh/g at  $C/10$ ). Granulometric studies, electronic microscopy and XRD experiments have been performed in order to explain the difference between  $\alpha_{II}$ -VOPO<sub>4</sub> and  $\alpha_{II}$ -VOPO<sub>4</sub>-p performance. Both have a comparable grain size (about 2.3  $\mu\text{m}$ ) but the  $\alpha_{II}$ -VOPO<sub>4</sub> powder aggregates much easier than the  $\alpha_{II}$ -VOPO<sub>4</sub>-p. Moreover, the powder X-ray diffraction patterns show that  $\alpha_{II}$ -VOPO<sub>4</sub>-p contains a little bit of  $\gamma$ -VOPO<sub>4</sub> and the TEM photographs of  $\alpha_{II}$ -VOPO<sub>4</sub>-p show some impurity zones at the grain surface. Our hypothesis is that the  $\gamma$  phase has grown on the surface of  $\alpha_{II}$ -VOPO<sub>4</sub> grains and prevents aggregation, acting like a surfactant, and thus, enhances the lithium intercalation.

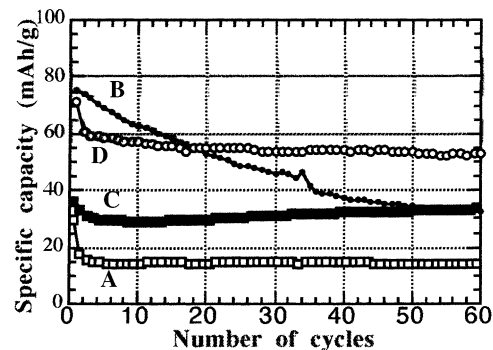


Fig. 7. Capacity vs. cycle number for  $\alpha_{II}$ -VOPO<sub>4</sub> (A,  $C/5$ ),  $\alpha_{II}$ -LiVOPO<sub>4</sub> (B,  $C/5$ ),  $\gamma$ -VOPO<sub>4</sub> (C,  $C/10$ ),  $\gamma$ -LiVOPO<sub>4</sub> (D,  $C/10$ ).

The different intercalation–deintercalation potentials in the  $\gamma$  and  $\delta$  forms of VOPO<sub>4</sub> (respectively, 3.7 V and 3.8 V) show the influence of the structure on its redox potential.  $\gamma$  and  $\delta$ -VOPO<sub>4</sub> show specific capacities that depend on the cycling regime: respectively 25, 40 mAh/g at  $C/5$  (Fig. 3), 30, 105 mAh/g at  $C/10$  (Fig. 4) and a lifetime going up to 400 cycles. These results might be correlated to the interplanar distance: the less open the structure, the lower is the specific capacity and the lower is the intercalation potential (energy required to spread apart the planes). Chemical lithiation has been performed and the results obtained show an improved specific capacity of 55 mAh/g at  $C/10$  (Fig. 7). In order to improve the performance, the electrode mixtures have been homogenized in a planetary grinder:  $\gamma$ -VOPO<sub>4</sub> has shown promising results with capacity values of 80 mAh/g at  $C/5$  and 100 mAh/g at  $C/10$ . Moreover, owing to a formation process of  $\gamma$ -VOPO<sub>4</sub>, the capacity recovered on reduction increases on cycling (Fig. 5).

From these results, it appears that the different forms of VOPO<sub>4</sub> are interesting as intercalation compounds. Further improvements concerning both the cyclability and the specific capacity are expected in order to lead to applications.

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