

## Sonochemically Synthesized Vanadyl Phosphate Dihydrate Cathodes

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### Introduction

Recently, chemical bonding nature-potential level correlation has been investigated for Nasicon-type electrode materials  $\text{Li}_x\text{M}_2(\text{XO}_4)_3$  ( $\text{M}$  = transition metal;  $\text{X}$  = S, P, As) [1,2], where the higher ionicity of the M-O bond was found to give rise to the higher potential of the  $\text{M}^{n+}/\text{M}^{(n+1)+}$  redox couple. Electrochemical lithium insertion in the rhombohedral  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  [3] and the  $\beta$ -form of  $\text{VOPO}_4$  [4] was investigated. The potentials in batteries based on these materials showed 3.77 and 3.98 V vs.  $\text{Li}^+/\text{Li}$ , respectively. However, less attention has been paid to vanadyl phosphate dihydrate  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$  because of being more interested in its catalytic property.  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$  has been usually prepared by long-term boiling of a  $\text{V}_2\text{O}_5$  suspension in aqueous phosphoric acid according to Ladwig's method [5]. We have developed a method for rapid synthesis of  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ .

In this paper, we report on sonochemical synthesis of  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$  and its electrochemical lithium insertion characteristics.

### Experimental

$\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$  was sonochemically prepared as follows. The aqueous phosphoric solution contained  $\text{V}_2\text{O}_5$  powder was exposed to high-intensity ultrasound radiation for 15 min by employing a direct immersion titanium alloy horn operating at 20 kHz, with intensity of  $\sim 70 \text{ W}/\text{cm}^2$ . The temperature of the reaction solution rose to  $70^\circ\text{C}$  during sonication. The resulting yellow solid was filtered, washed several times with acetone and dried at ambient atmosphere.

The synthesized material was characterized using X-ray diffraction (XRD), Fourier transformed infrared (FTIR), transmission electron microscopy (TEM) and thermogravimetric analysis (TGA).

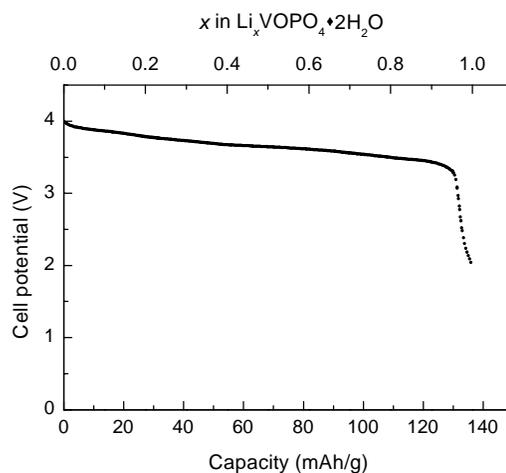
Electrochemical studies were carried out using a Macfile-II galvanostat system. A Swagelok-type cell consisted of the mixture of the synthesized  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ , the Super P black (MMM Carbon Co.) and the polytetrafluoroethylene (70:20:10 wt%) as a cathode, Li foil as an anode and 0.95 M solution of  $\text{LiPF}_6$  in ethylene carbonate/ dimethyl carbonate (50:50 vol%) as an electrolyte, which was discharged and charged under the constant current ranging from 4.16 to 39.4 mA/g.

### Results and Discussion

XRD confirms the phase purity of tetragonal  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$  with  $a = 6.2 \text{ \AA}$  and  $c = 7.4 \text{ \AA}$ . The particle size of the sonochemically synthesized material is determined to be  $1 - 3 \mu\text{m}$  by TEM, which is smaller than the size (about  $10 \mu\text{m}$ ) of the sample prepared by the long-term refluxing method.

Electrochemical reduction of  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$  under a constant current of 4.16 mA/g (corresponding to 0.03 C) shows that almost 1 Li can be inserted, which results in the capacity of 135 mAh/g (Fig. 1). The cell potential shows a plateau at 3.6 V. Little

change in capacity under high discharge rate of 0.3 C is observed. Sonochemically prepared sample exhibits also good reversibility for the electrochemical lithium insertion/extraction. Preliminary results on the electrochemical performance indicate that sonochemically synthesized  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$  can be a promising cathode material for rechargeable lithium battery.



**Figure 1.** First discharge curve for the sonochemically synthesized  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$

### References

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