

# $\delta$ -LiV<sub>2</sub>O<sub>5</sub> as a positive electrode material for lithium-ion cells

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## Abstract

The  $\delta$ -phase of LiV<sub>2</sub>O<sub>5</sub> has been identified as an excellent candidate material for the positive electrode in a lithium-ion battery. Transmission electron microscopy (TEM) has shown, on the atomic level, that no major chemical bond breakage or basic structural changes occur during the lithiation of V<sub>2</sub>O<sub>5</sub> through the formation of the  $\delta$ -phase. The stability of the crystal lattice during lithiation is expected to lead to a secondary battery with a long cycle life and the performance characteristics of the lithium vanadium pentoxide in primary cells. These characteristics include its excellent ability to be discharged at relatively high rates and high temperature stability. © 1997 Elsevier Science S.A.

**Keywords.** Lithium-ion cells; Positive electrode material; Vanadium pentoxide

## 1. Introduction

Vanadium pentoxide was identified in the 1960s as a useful positive electrode material for lithium electrochemical cells. Over the last three decades vanadium pentoxide has been studied extensively in the USA, Japan, France, and other countries as a useful positive electrode material for lithium batteries. An Li/V<sub>2</sub>O<sub>5</sub> rechargeable battery was patented (*US Patent No. 3 929 504*) in 1975.

In practice, Li/V<sub>2</sub>O<sub>5</sub> secondary cells never found significant commercial use because of poor cycle life and safety issues, both associated with the poor cycling characteristics of lithium metal.

The advent of lithium-ion technology in the early 1990s resolved the issue of lithium metal cycling at meaningful rates by incorporating lithium into carbons. Our ongoing work in this area indicates that suitable carbons are now available that can be cycled numerous times between appropriate voltage limits with minimal capacity loss and no observable dendritic growth. Once the problems associated with cycling of the negative electrode were resolved, attention was given to the identification of positive electrode materials. In principle, lithium-ion cell positives are made using a lithiated (discharged) form of the active material, in this case Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub>. For best results one needs to determine the optimum  $x$  value and the method for making the lithiated material. Experimental results and a review of the literature indicate that room

temperature synthesis of LiV<sub>2</sub>O<sub>5</sub>, where  $x=1$ , is most desirable.

Experimentally, the behavior of the open-circuit voltage versus depth-of-discharge (Fig. 1) indicates the formation of two new solid phases when up to 1 F of lithium is inserted into the V<sub>2</sub>O<sub>5</sub> positive electrode. An additional plateau at a significantly lower voltage is observed when  $x > 1$ .

The phase diagram [1] explains the observed plateaus in Fig. 1, assuming that room temperature phases are formed during discharge. Such an assumption is supported by the work by Cava et al. [2]. Furthermore, the work by Cava et al. indicates that during discharge, up to  $x=1$ , the basic layered structure of V<sub>2</sub>O<sub>5</sub> is maintained up to and including the  $\delta$ -phase. The retention of the layered structure from  $x=0$  to  $x=1$  over a wide temperature range should allow for complete electrochemical reversibility, that is, regeneration of the original  $\alpha$ -V<sub>2</sub>O<sub>5</sub> structure upon charge within proper voltage limits.

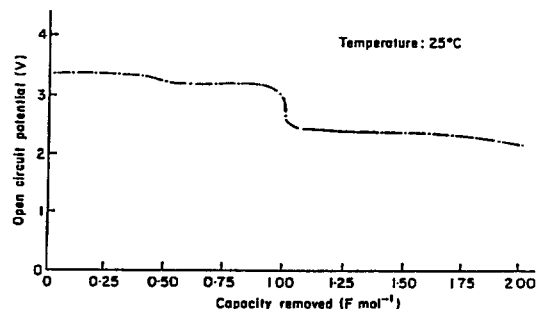


Fig. 1. Open-circuit voltage of a LiV<sub>2</sub>O<sub>5</sub> cell vs. depth-of-discharge.

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Such is not the case when  $x > 1$  and, as experimental work in  $\text{Li}/\text{V}_2\text{O}_5$  secondary cells indicates, the cycling performance of electrodes that have been discharged beyond  $x = 1$  shows significant fading [3]. This degradation is probably associated with Cava's report [2] that when cells are discharged to  $x > 1$  a new potential plateau appears at about 2.4 V, associated with a new phase of a different basic structure, ( $\gamma\text{-LiV}_2\text{O}_5$ ), which is structurally irreversible.

On reviewing this information it appears that  $\delta\text{-LiV}_2\text{O}_5$  would be the most desirable material for a lithium-ion cell and we set out to prepare the material both electrochemically and chemically.

## 2. Experimental

$\delta\text{-LiV}_2\text{O}_5$  was prepared electrochemically by passing current through a vanadium pentoxide electrode in a reactor cell. The negative electrode of the reactor cell was lithium metal and the solution was a stable, lithium-ion conducting, non-aqueous, electrolytic solution compatible with lithium metal and  $\text{V}_2\text{O}_5$ . The voltage of the reaction was not allowed to fall below 2.8 V, to avoid the formation of lithiated vanadium pentoxide phases that are thought to be less reversible than those formed above 2.8 V. After reaching 2.8 V the  $\text{LiV}_2\text{O}_5$  formed in this manner was removed from its current collector, washed, and dried.

$\delta\text{-LiV}_2\text{O}_5$  was also prepared chemically using  $\text{LiI}$  according to the method described by Murphy et al. [4].

## 3. Results and discussion

Both materials were analyzed by X-ray powder diffraction and found to be identical with the  $\delta$ -form of  $\text{LiV}_2\text{O}_5$  previously reported.

The  $\delta$ -materials, prepared electrochemically as well as chemically, and the  $\text{V}_2\text{O}_5$  from which they were made were submitted to Michigan Technological University for analysis by transmission electron microscopy (TEM). Figs. 2 and 3 show the TEM pictures for  $\text{V}_2\text{O}_5$  and chemically prepared  $\text{LiV}_2\text{O}_5$ , respectively, magnified  $\times 6.5 \times 10^6$ . The TEM study of the Tracor samples reveals [6] planar facets on the  $\alpha$ -phase powders that are parallel to the  $\alpha(001)$ -planes and remain planar during lithiation; thus, it is possible to use this feature to observe the relevant changes in the planes with specific orientation relationships with respect to the planar facets.

The lithiation-induced expansion of the lattice spacing for the planes parallel to the planar facets can be directly related to the crystal structures proposed for the  $\text{V}_2\text{O}_5$   $\alpha$ - and  $\delta$ -phases. The symmetry and interplanar spacings indicated by the high resolution images and the corresponding convergent beam electron-diffraction patterns are consistent with the planar facets of the  $\text{V}_2\text{O}_5$  being parallel to the (001) crystallographic planes. This indexing is based on the results of



Fig. 2. Transmission electron microscopy picture of  $\text{V}_2\text{O}_5$  ( $\times 6.5 \times 10^6$ ).

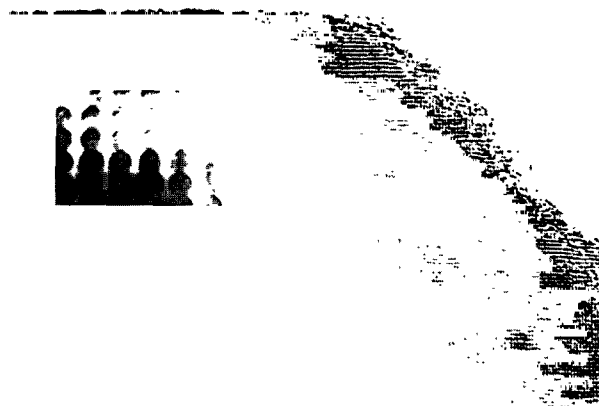


Fig. 3. Transmission electron microscopy picture of  $\text{LiV}_2\text{O}_5$  ( $\times 6.5 \times 10^6$ ).

Enjalbert and Galy [5]. Upon chemical lithiation, X-ray diffraction shows that the  $\delta$ -phase has been produced. TEM analysis of the  $\delta$ -phase reveals that the lattice spacing of the planes parallel to the facets, observed by direct lattice imaging and convergent beam electron diffraction, expands from  $\sim 4.4$  to  $\sim 4.9$  Å. This lattice spacing corresponds to the spacing of the (010) planes based on the crystallographic indexing proposed by Murphy et al. [4].

Based on the observed lithiation behavior of the lattice planes parallel to the crystallite facets, it is proposed that the (010)  $\delta$ -phase planes are topotactic with the (001) planes of the  $\text{V}_2\text{O}_5$ . The lattice images show that the transition from the  $\alpha$ -phase to the  $\delta$ -phase during chemical lithiation occurs without large changes in crystallite size and morphology. The TEM results clearly reveal directly that, for this orientation, there is only a small expansion along the  $c$ -axis when the  $\delta$ -phase is formed and that there is no disruption to the lattice structure. This is believed to be the first direct demonstration of this aspect of atomic level structural behavior of vanadium pentoxide (or any other oxide) during lithiation, according to Hackney [7]. Convergent beam electron diffraction

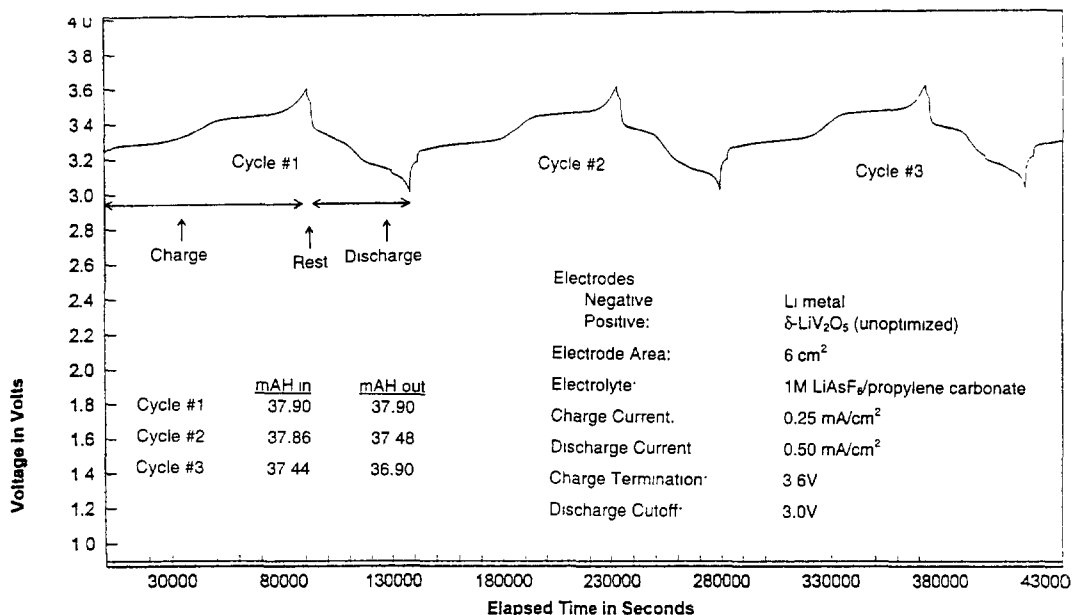


Fig. 4 Initial charge/discharge cycles for a cell having a  $\delta$ -LiV<sub>2</sub>O<sub>5</sub> positive electrode

(CBED) photographs of the material are shown on the TEM photographs to provide additional information on the lattice structure.

Testing has been initiated in laboratory cells containing both chemically prepared and electrochemically prepared  $\delta$ -LiV<sub>2</sub>O<sub>5</sub>. The initial cycles have provided identical performance data for the  $\delta$ -LiV<sub>2</sub>O<sub>5</sub> made by either the chemical or electrochemical method. The first three cycles from such tests are shown in Fig. 4.

#### 4. Conclusions

It has been reported in the literature that cell reversibility is optimized when no chemical bonds are broken during discharge, that is, where ternary phases are formed by an intercalation reaction [8]. The cycling behavior of V<sub>2</sub>O<sub>5</sub> up to LiV<sub>2</sub>O<sub>5</sub> meets this criterion. Consequently,  $\delta$ -LiV<sub>2</sub>O<sub>5</sub> should be an ideal material to provide long cell cycle life in lithium-ion batteries. Furthermore, the excellent high temperature thermodynamic stability (up to 75 °C) and high rate capa-

bility of this material have been well documented in the literature [3].

It has been demonstrated that other battery systems can give higher single cell voltages and higher energy densities for a significant number of cycles, but when long cycle life, power density, or high temperature stability are important, a cell using  $\delta$ -LiV<sub>2</sub>O<sub>5</sub> may be the best choice.

#### References

- [1] C. Delmas, H. Cognac-Auradou, J.M. Cocciantelli, M. Menetrier and J.P. Doumerc, *Solid State Ionics*, 69 (1994) 257
- [2] R.J. Cava, A. Santoro, D.W. Murphy, S.M. Zahurak, R.M. Fleming, P. Marsch and R.S. Roth, *Solid State Chemistry*, 65 (1986) 63
- [3] C.R. Walk, in J.P. Gabano (ed.), *Lithium Batteries*, Academic Press, New York, 1983, Ch. 11, p. 265
- [4] D.W. Murphy, P.A. Christman, F.J. DiSalvo and J.V. Waszczak, *Inorg. Chem.*, 18 (1979) 2800
- [5] R. Enjalbert and J. Galy, *Acta Crystallogr. Sect. C*, 42 (1986) 1467
- [6] S.A. Hackney, B. Cornilsen, C.R. Walk and N. Margalit, *Progress in Batteries and Battery Materials*, Vol. 16, Part I, ITE-JEC, Japan, 1997, p. 59.
- [7] S.A. Hackney, *Personal communication*, Michigan Technological University, June 1996
- [8] M.S. Whittingham, *Electrochem. Soc.*, 123 (1976) 315