

## A STUDY OF THE INCORPORATION REACTION OF LITHIUM INTO $V_6O_{13}$ IN A RECHARGEABLE LITHIUM BATTERY

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### Summary

Practical C- and AA-size ambient temperature, rechargeable Li/ $V_6O_{13}$  cells have been constructed using pure  $V_6O_{13}$ , prepared in our laboratory, as cathode active material. X-ray diffraction pattern  $d$  values of  $V_6O_{13}$  prepared by us are the same as those given by JCPDS, and cathodes of this material have performed satisfactorily.

Cathodic discharge products of test cells have been analyzed by XRD and ESR. New expanded diffraction lines have been discovered in XRD patterns. From XRD and ESR results, it is considered that the incorporation of lithium into  $V_6O_{13}$  is the main reduction reaction in the  $V_6O_{13}$  cathodic process.

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### Introduction

Secondary lithium batteries have been actively pursued for more than twenty years. Transition metal oxides and sulfides are potentially attractive for use as positive active materials. Studies on vanadium oxide have been carried out by Murphy [1, 2] and Abraham [3]. We have designed and constructed C- and AA-size hermetically sealed, rechargeable Li/ $V_6O_{13}$  cells [4] following improvements in the cathodic material,  $V_6O_{13}$  (NS), cathode-preparation techniques, electrolyte studies and long-term cycling tests.

In this paper, studies on the cathode reaction of  $V_6O_{13}$  have been made employing X-ray diffraction (XRD) and electron spin resonance (ESR) measurements. The cathodic discharge products in the test cells have been analyzed by XRD and ESR, and new expanded diffraction lines have been discovered in the XRD patterns. From the results obtained by XRD and ESR, it is considered that the incorporation reaction of lithium ions into  $V_6O_{13}$  is the main reaction in the  $V_6O_{13}$  cathodic process.

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## Experimental

$V_6O_{13}$  (NS) was prepared according to the method described by Murphy *et al.* [1]. Ammonium metavanadate was thermally decomposed by heating under flowing argon gas at 500 °C and 550 °C, separately, for several hours. XRD analysis of the final product revealed that only a small amount of  $V_2O_5$  and  $V_2O_4$  (less than 5%) was present in the  $V_6O_{13}$  (NS). The  $V_6O_{13}$  particle size, determined by SEM, was 1 - 10  $\mu\text{m}$ .

Propylene carbonate (PC) was twice distilled over lithium strips at approximately 5 mm Hg pressure and at about 95 °C, 2-Methyltetrahydrofuran (2-MeTHF, Aldrich Chemical Company, U.S.A.) was also twice purified by distillation over  $\text{CaH}_2$ .  $\text{LiAsF}_6$  (USS Agri-Chemical Co., electrochemical grade) was used as received.

The  $V_6O_{13}$  electrodes were made by pressing two sheets of  $V_6O_{13}$  powder, acetylene black, and PTFE paste onto an expanded nickel grid, and then drying under argon atmosphere at 260 °C. For XRD and ESR measurements, the glass test cells were assembled as follows: single layer of Celgard 5511 separator was wrapped around the lithium anode which was "U" shaped around the cathode. The cathode had a total area of 3.6  $\text{cm}^2$ , about 150 mg of active material and 40 mA h capacity. These test cells were discharged galvanostatically at various depths of discharge. To construct practical C- and AA-size cells, Celgard 2400 film was placed between a spirally wound cathode and lithium foil. The hermetically sealed cells were completed by employing vacuum filling and TIG welding techniques.

X-ray diffraction data were obtained using the Chinese- Y-2 system with  $\text{Cu K}\alpha$  radiation, 35 kV/20 mA, and a scanning speed of  $1^\circ \text{min}^{-1}$ .

The ESR measurement was carried out at a frequency of 9300  $\text{Mc s}^{-1}$  and a magnetic field of about 3300 Gauss using a JES-3BX instrument.

The cells were assembled in a glove box, in which dry air was circulating.

## Results and discussion

### *XRD measurements of the cyclic reaction products of the $V_6O_{13}$ cathode*

The glass test cells were galvanostatically cycled to the desired depths at 1  $\text{mA cm}^{-2}$ . Figure 1 shows a set of X-ray diffraction patterns of the resulting products at various DOD. The XRD patterns of shallow discharge products of the  $V_6O_{13}$  cathode (15%, 30% DOD, formation of  $\text{Li}_{0.9}\text{V}_6\text{O}_{13}$  and  $\text{Li}_{1.8}\text{V}_6\text{O}_{13}$ , respectively) are unchanged. Beyond 40%, new lines were observed, apparently XRD patterns, with the increase in DOD (50%, 75% and 100%, formation of  $\text{Li}_{3.0}\text{V}_6\text{O}_{13}$ ,  $\text{Li}_{4.5}\text{V}_6\text{O}_{13}$  and  $\text{Li}_{6.0}\text{V}_6\text{O}_{13}$ , respectively). The relative intensity of the set of new peaks increased gradually. They are considered to be new lines. The increase in the  $d$  values of the crystal lattice of  $V_6O_{13}$  along (001) occurs, to some extent, with increase in X values. This means that the initial crystal lattice of  $V_6O_{13}$  expands with the incorporation of lithium ions.

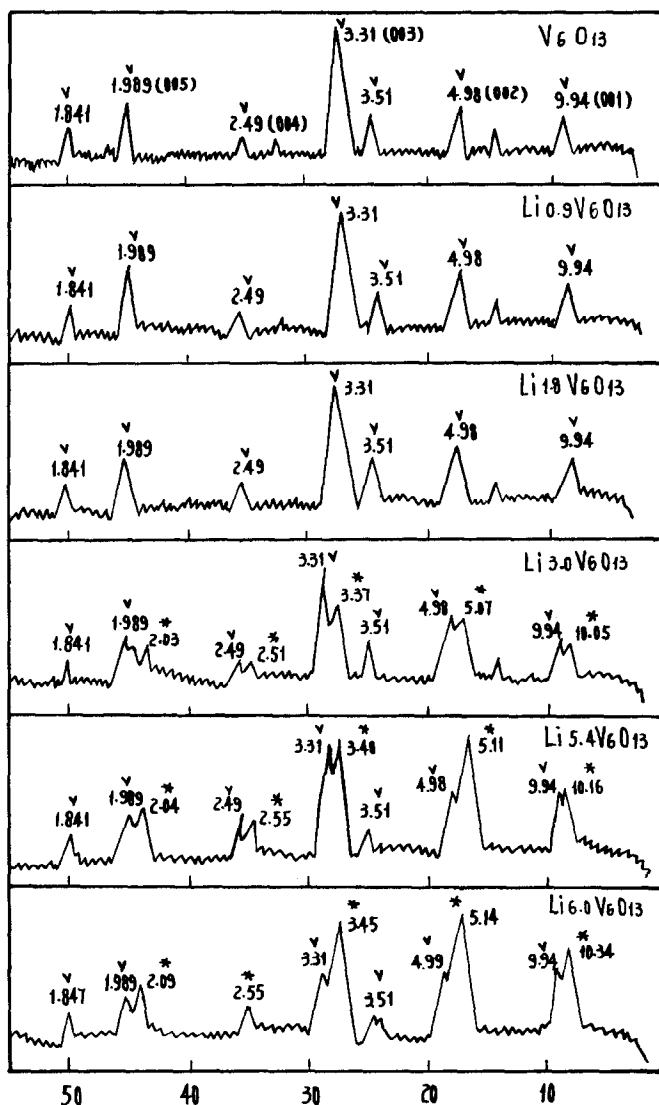


Fig. 1. X-ray diffractogram of  $\text{Li}_x\text{V}_6\text{O}_{13}$  after discharge of the cathode. V,  $\text{V}_6\text{O}_{13}$  spectra; \*, new line of  $\text{Li}_x\text{V}_6\text{O}_{13}$  spectra.

An XRD study at various DOD (15%, 30%, 50%, 75%, and 100%) of the recharge product of the  $\text{V}_6\text{O}_{13}$  shows that the patterns return to those of the original  $\text{V}_6\text{O}_{13}$  cathode. The results are shown in Fig. 2.

An XRD study of the discharge products of the  $\text{V}_6\text{O}_{13}$  cathode after 21 cycles indicates that the new, expanded diffraction lines, which are similar to those of the first cycle, still appear in the XRD pattern as shown in Fig. 3. An XRD study of the recharge products of the  $\text{V}_6\text{O}_{13}$  cathode after 21 discharges at 100% DOD shows that the patterns return to those of the original  $\text{V}_6\text{O}_{13}$  cathode.

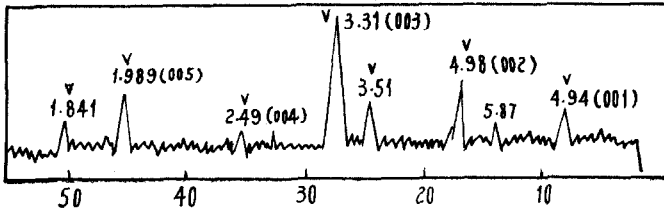


Fig. 2. X-ray diffractogram of the cathode after recharge and various DOD (15%, 30%, 50%, 75% and 100%). V,  $V_6O_{13}$  spectra.

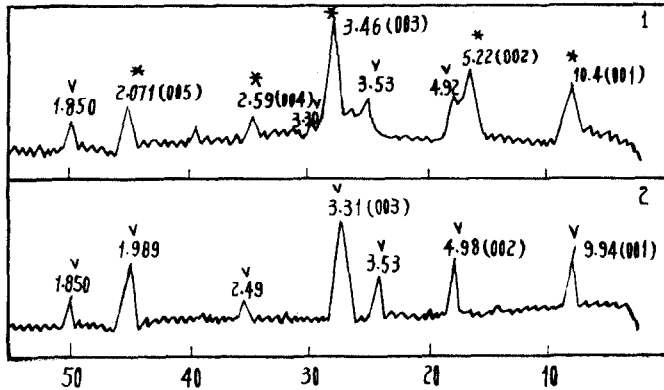
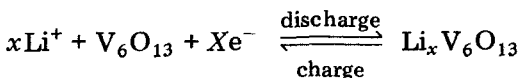


Fig. 3. X-ray diffractogram of  $Li_x V_6 O_{13}$  after 21 cycles of the cathode. V,  $V_6 O_{13}$  spectra; \*, spectra for new lines of  $Li_x V_6 O_{13}$ ; 1, 21st discharge; 2, 21st recharge.

To sum up, it is considered that during the cathode discharge process, the initial crystal lattice of  $V_6 O_{13}$  expands with the incorporation into it of lithium ions; during the reverse process (recharge process), the de-incorporation of lithium ions from the crystal lattice of  $V_6 O_{13}$  occurs as suggested by Murphy *et al.* [1].



#### *ESR studies on the cyclic reaction products of the $V_6 O_{13}$ cathode*

ESR measurement was carried out at a frequency of  $9300 \text{ Mc s}^{-1}$  and a magnetic field of about 3300 Gauss. An MnO sample was applied as a standard. The cathode consisted of  $V_6 O_{13}$ , acetylene black, and PTFE. The ESR spectrum of the cathode before reaction is shown in Fig. 4. The PTFE shows no absorbed peaks; a large peak (between No. 3 and No. 4 lines) results from the acetylene black, no additional peaks occurred before discharge. The ESR spectrum of the discharged  $V_6 O_{13}$  cathode is shown in Fig. 5. It shows the formation of  $Li_{5.4} V_6 O_{13}$  after discharge of the cathode. An obvious peak (sometimes exhibiting hyperfine structure) featuring scattering  $V^{4+}$  ions is observed (according to the spectrum of the standard  $V^{4+}$  ions in the  $VOSO_4$  sample). Its intensity increases with the increase in DOD of the cathode. The

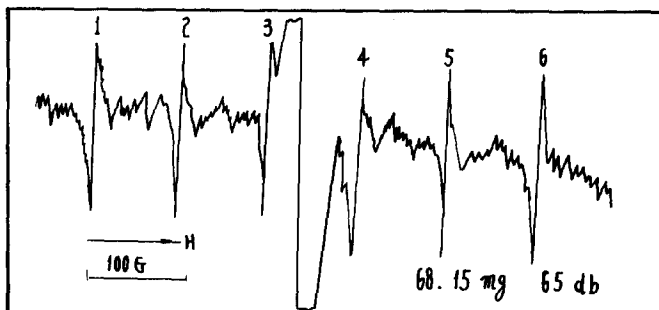


Fig. 4. ESR combined spectra of components of the cathode mixture.

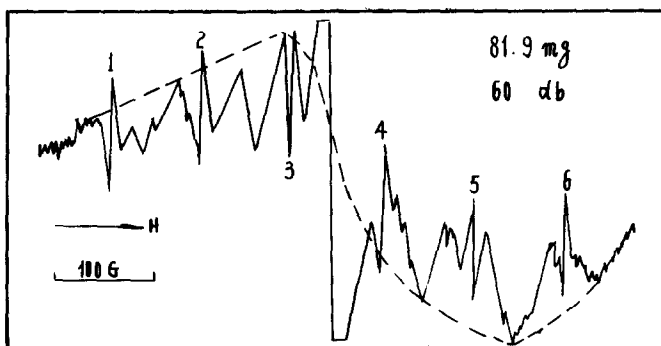


Fig. 5. ESR spectrum of  $V^{4+}$  ions in cathode discharged to  $Li_{5.4}V_6O_{13}$  product.

$V^{4+}$  ion content in the  $Li_{5.4}V_6O_{13}$  compound can be calculated to be 12%. The results show that some of the  $V^{5+}$  ions can be reduced to  $V^{4+}$  ions ( $3d^1$ ) and  $V^{3+}$  ions ( $3d^2$ ) at different potentials because of the relatively small energy difference states of the  $V^{3+}$ ,  $V^{4+}$  and  $V^{5+}$  ions [5]. Corresponding with above results, there are two plateaux on the discharge curves (see Fig. 6). Oxidation and reduction are responsible for the appearance of voltage plateaux but these are shallow. No new phases are observed in the ESR spectrum, so the predominant reaction in the cathode process is the incorporation of the lithium ions into  $V_6O_{13}$ .

#### Storage behavior of C- and AA-size cells

Practical C- and AA-size ambient temperature, rechargeable  $Li/V_6O_{13}$  cells have been made using  $V_6O_{13}$  prepared in our laboratory. The capacity of the C-size cell is 1.8 A h and its weight is 44 g; the capacity and weight of the AA-size cell are 0.6 A h and 18 g, respectively. The cells have a spirally wound structure and organic solvent-based electrolytes (e.g., 1.2 M  $LiAsF_6/2-MeTHF:THF$ ).

A comparison of the capacities of fresh and stored AA-size cells was carried out under the same discharge conditions (30 mA constant current). It was found that the capacity loss after two years storage was very small; the discharge voltage is only about 20 - 30 mV less than that of a fresh cell.

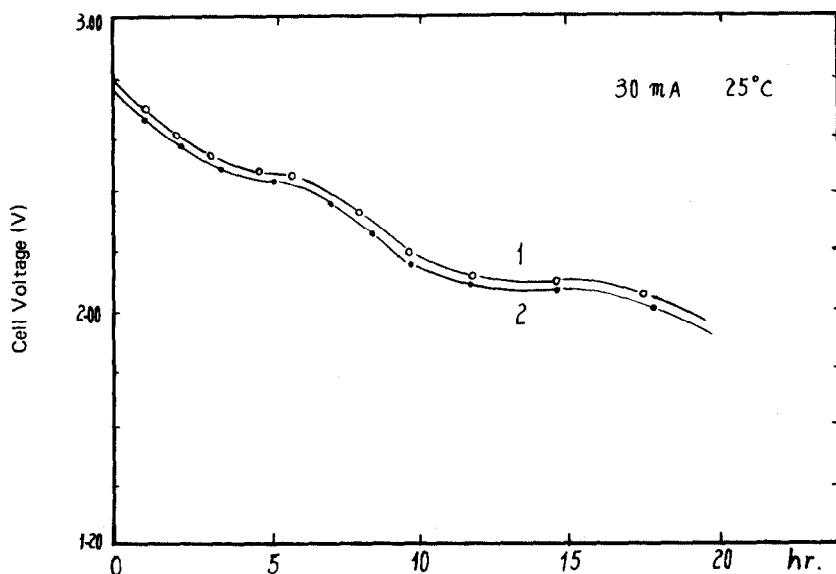


Fig. 6. Discharge curve of AA-size  $\text{Li}/\text{V}_6\text{O}_{13}$  cell. 1, Fresh cell; 2, cell stored for two years.

The results are given in Fig. 6. The discharge capacity for a C-size cell after two years storage is about 97% of the fresh cell.

### Conclusions

Practical C- and AA-size ambient temperature, rechargeable  $\text{Li}/\text{V}_6\text{O}_{13}$  cells have been constructed using pure  $\text{V}_6\text{O}_{13}$ , prepared in our laboratory, as cathode active material. It was found that only a small capacity loss was sustained after two years storage at room temperature.

The cathodic discharge products in the test cells have been analyzed by XRD and ESR. New, expanded diffraction lines have been found in the XRD patterns. From the XRD and ESR results, it is considered that the incorporation of lithium into  $\text{V}_6\text{O}_{13}$  is the main reduction reaction in the  $\text{V}_6\text{O}_{13}$  cathodic process.

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