

ω -Li_xV₂O₅ — a new electrode material for rechargeable lithium batteries*

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Abstract

The electrochemical intercalation of lithium in V₂O₅ down to a voltage smaller than 1.9 V leads irreversibly to the formation of a new material, ω -Li_xV₂O₅ ($x \sim 3$), that exhibits very good electrochemical behavior. The new structural framework characteristic of ω -Li_xV₂O₅ is maintained during the lithium deintercalation, as shown by the occurrence of a solid solution and by the very good reversibility of the intercalation process. This material can also be obtained by reaction with an excess of *n*-butyllithium. Its X-ray diffraction pattern is characteristic of a very disordered structure, nevertheless a few broad diffraction lines remain and are, furthermore, independent of the amount of intercalation. The specific energy related to the electrochemical reaction is very high: 450 W h kg⁻¹ of V₂O₅ after 100 cycles in the 1.9–3.4 V range under 180 μ A cm⁻². Moreover, this value can be considerably increased if the cycling domain is extended (800 W h kg⁻¹ of V₂O₅ between 1.9 and 4 V).

Introduction

The intercalation of lithium in V₂O₅ in the vicinity of room temperature has been studied intensively during the seventies [1–4]. The structures of these materials, which are often metastable, differ from those of the vanadium bronzes mainly studied in our lab. by Galy, Pouchard, Casalot, Darriet, and Hagemuller [5–8].

As oxides presently seem to be the most promising materials from the application point of view in order to obtain electrochemical cells able to compete with Ni–Cd, renewed interest has been devoted to Li_xV₂O₅ systems [9–14]. All these studies show very good reversibility of the lithium intercalation reaction for $0 < x < 1$. For higher amounts of intercalation an important loss of capacity versus the cycle number [14, 15] and, moreover, complete irreversibility after a deep discharge ($x > 2.4$) [9, 12] have been reported.

As the potential (versus Li) remains quite high (2 V), even for large amounts of intercalation ($2 < x < 3$), we have tried to investigate what happens after a strong reduction.

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Experimental

Lithium has been intercalated electrochemically and chemically in commercial V_2O_5 .

In the electrochemical experiment a lithium foil was used as the negative plate and a mixture of V_2O_5 with ketjen black (80–20%) as the positive electrode.

A (1 M) solution of $LiClO_4$ in propylene carbonate was used as electrolyte in most of the experiments. Nevertheless, in some cases, when a charge voltage close to 4 V was required, a 1 M solution of $LiClO_4$ in a propylene carbonate–dimethoxyethane (PC–DME) (50%–50%) mixture was used. All the electrochemical studies were monitored by an HP 1000 A 600 computer with home-made software described previously [16]. The OCV curves were obtained according to the following scheme. The cell was discharged (or charged) for 4 h under a constant current of $180 \mu A cm^{-2}$, the circuit was then opened until the cell voltage variation was reduced to less than $0.1 mV h^{-1}$. When this condition was reached a new discharge (or charge) occurred.

The chemical intercalation was carried out with an excess of *n*-butyllithium with regard to the $Li_3V_2O_5$ composition. The material was maintained in suspension in the hexane solution of *n*-butyllithium by stirring for 3 days in the glove box. It was then filtered, washed with hexane, and dried under vacuum.

Results and discussion

Figure 1 shows the electrochemical cycling curve obtained from V_2O_5 if the first discharge of the cell is extended down to 1.9 V. The first plateaux (I and II), which exhibit a potential greater than 3 V and an $Li_xV_2O_5$ ($0 < x < 1$)

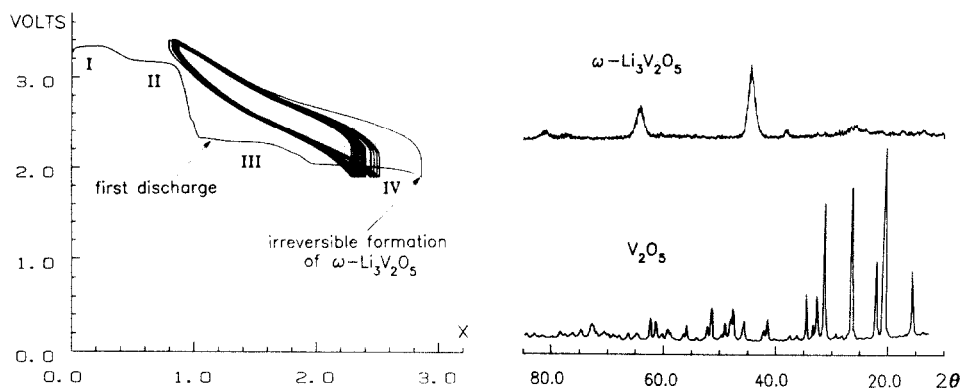


Fig. 1. Cycling of an $Li/LiClO_4$ -PC/ V_2O_5 +ketjen black cell at $180 \mu A cm^{-2}$.

Fig. 2. X-ray diffraction patterns of chemically formed $\omega-Li_3V_2O_5$ and V_2O_5 .

composition range, correspond to the classical cycling of $\text{Li}/\text{V}_2\text{O}_5$ cells. In the corresponding 3.6–3 V range very good reversibility of the $\text{Li}_x\text{V}_2\text{O}_5$ electrode is obtained and almost 100% of the theoretical capacity is recovered at each discharge.

During the third plateau some structural reorganizations, leading to the reversibility loss previously mentioned, are observed. In fact, it seems that in this voltage domain, an irreversible transition occurs from the $\text{Li}_x\text{V}_2\text{O}_5$ system, characterized by the potential plateaux I and II, to a new one. This reaction is not, however, complete, and even after a large number of cycles, a mixture of the various materials is recovered. This behavior shows that all the phases involved in these reactions are metastable.

At the end of the fourth plateau a new material, $\omega\text{-Li}_x\text{V}_2\text{O}_5$ ($x \sim 3$), is irreversibly formed. This irreversibility is emphasized by the shape of the following charge, that does not show any of the characteristic plateaux obtained with V_2O_5 . Nevertheless, the lithium deintercalation from this material is completely reversible, as shown by the following cycles reported in Fig. 1. In this case about 20 cycles have been drawn, but in some long-range experiments over one hundred cycles have been obtained.

$\omega\text{-Li}_x\text{V}_2\text{O}_5$ with x close to 3 has also been obtained by reaction with an excess of *n*-butyllithium on V_2O_5 . Its X-ray diffraction pattern is reported in Fig. 2 in comparison with that of the starting V_2O_5 phase. It characterizes a very disordered structure as only a few broad diffraction lines are present. The interplanar distances obtained from the main lines ($d_1 = 2.04 \text{ \AA}$ and $d_2 = 1.45 \text{ \AA}$) differ from those reported for all other $\text{Li}_x\text{V}_2\text{O}_5$ phases. The X-ray diffraction pattern of the electrochemically obtained $\omega\text{-Li}_x\text{V}_2\text{O}_5$ is identical with this one. Moreover, no significant change is observed after electrochemical deintercalation or even after a large number of cycles. This result shows, unambiguously, that the new structure that characterizes $\omega\text{-Li}_x\text{V}_2\text{O}_5$ ($\text{Li}_3\text{V}_2\text{O}_5$) is very stable as it is maintained even after removal of almost all of the intercalated lithium ($\text{Li}_{0.20}\text{V}_2\text{O}_5$).

Cells have been constructed using this material; their cycling curves are similar to that found for the electrochemically-formed material during deep discharge. Nevertheless, it should be noted that during the first charge of the chemically formed $\omega\text{-Li}_x\text{V}_2\text{O}_5$ a particular shape of curve is obtained. At the beginning of the charge, the polarization seems to be rather large, suddenly decreasing during the process. From this point onwards the cycling curve is identical with that reported in Fig. 1.

In order to illustrate the occurrence of the irreversible structural transition from V_2O_5 to $\omega\text{-Li}_x\text{V}_2\text{O}_5$, an open circuit voltage study has been carried out, the results of which are reported in Fig. 3. In this experiment, an $\text{Li}/\text{V}_2\text{O}_5$ cell has been discharged under constant current to the LiV_2O_5 composition. From this point the cell has been discharged for 4 h, then allowed to relax until a constant potential was reached. This process was repeated continuously until the $\text{Li}_3\text{V}_2\text{O}_5$ composition was reached; the cell was then recharged using the same process. In the vicinity of the end of charge the current was lowered to reduce the cell polarization.

Another OCV curve (Fig. 4) was derived from a cell which had previously been cycled for 20 times, as the example shown in Fig. 1, under a constant current of $180 \mu\text{A cm}^{-2}$. The continuous cycling was interrupted after a charge when the composition of the electrode was $\text{Li}_{0.50}\text{V}_2\text{O}_5$, and from this composition an overall cycle with relaxation was carried out.

In such experiments plotted versus the degree of intercalation (Figs. 3 and 4), the relaxation process is represented by the vertical line which follows the discharge or the charge step. The OCV value is therefore given by the top of this vertical line during the intercalation process or by its bottom during the deintercalation step.

The difference between the OCV values and between the shapes of the charge and discharge OCV curves (Fig. 3) shows that an irreversible structural modification has occurred in the vicinity of the $\text{Li}_3\text{V}_2\text{O}_5$ composition. Moreover, the OCV curve obtained by deintercalation of $\omega\text{-Li}_3\text{V}_2\text{O}_5$ characterizes the existence of a solid solution throughout the intercalation domain. The results reported in Fig. 4 emphasize the occurrence of a single-phase system, they also show an increase in polarization with degree of intercalation.

The shape of the curve exhibits only a slight difference from that reported in Fig. 3. We must point out that in this case, since 20 cycles had previously taken place, the cell capacity had decreased before the OCV experiment. This suggests that part of the material has become electrochemically inactive, therefore the x values reported in Fig. 4 do not correspond exactly to the true amount of intercalation within the electrode material.

In order to show the practical possibilities of this material as a positive electrode, long-range electrochemical tests have been undertaken. Figure 5 shows the variation in experimental specific energy per kilogramme of V_2O_5

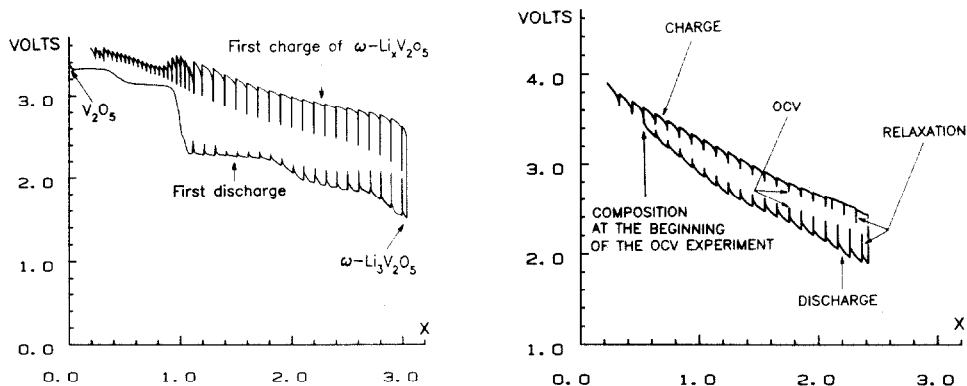


Fig. 3. Intermittent discharge (with formation of $\omega\text{-Li}_x\text{V}_2\text{O}_5$) and charge of an $\text{Li/LiClO}_4\text{-PC/V}_2\text{O}_5 + \text{ketjen black}$ cell at $180 \mu\text{A cm}^{-2}$. From $x = 1$ onwards, the current has been interrupted every 4 h and the cell allowed to relax until the voltage stabilized at 0.1 mV h^{-1} .

Fig. 4. One intermittent discharge-charge cycle (with relaxation up to 0.1 mV h^{-1} every 4 h) following 20 continuous cycles of an $\text{Li/LiClO}_4\text{-PC}/\omega\text{-Li}_x\text{V}_2\text{O}_5 + \text{ketjen black}$ cell at $180 \mu\text{A cm}^{-2}$.

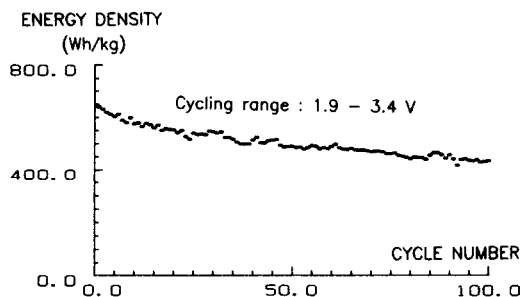


Fig. 5. Evolution of the experimental specific energy per kg of V_2O_5 vs. the cycle number for an $Li/LiClO_4\text{-PC}/\omega\text{-Li}_xV_2O_5 + \text{ketjen black}$ cell cycled at $180 \mu A cm^{-2}$ between 1.9 and 3.4 V.

versus the cycle number, obtained in the 3.4–1.9 V potential range under $180 \mu A cm^{-2}$. In these conditions the specific energy is rather high, as $650 W h kg^{-1}$ are recovered at the first discharge of the $\omega\text{-Li}_xV_2O_5$ phase. Moreover, after 100 cycles the specific energy is still greater than $450 W h kg^{-1}$. This result must be compared, for example, with that found for TiS_2 in which $475 W h kg^{-1}$ would be recovered at the first cycle if one lithium per TiS_2 was actually exchanged, whereas experimentally only 0.8–0.9 lithium is electrochemically involved.

In the above mentioned experiment, the cycling voltage range has been arbitrarily restricted to 3.4–1.9 V. In order to study the stability of the $\omega\text{-Li}_xV_2O_5$ phase at higher and lower voltages, it has been extended to 4.0–1.1 V. Under these conditions it is possible to deintercalate lithium down to the $Li_{0.20}V_2O_5$ composition. At the end of intercalation, the voltage drops rapidly; nevertheless, there is no electrode material modification as the shape of the electrochemical curve is not altered at the following cycle.

If the cut-off voltage is lowered to 1.1 V, an electrolyte breakdown reaction occurs, and a potential plateau is therefore obtained at 1.0 V. If, after a few hours at 1.0 V, the cell is recharged, then discharged again, the number of lithium atoms exchanged per V_2O_5 remains the same. This result emphasizes the very high stability of this material at low voltage, as already suggested by its stability in presence of an excess of *n*-butyllithium. In the useful domain 4.0–1.9 V, a specific energy of $800 W h kg^{-1}$ has been obtained (Fig. 6); since, at such a high voltage an oxidation of the electrolyte can occur, experiments have also been carried out in an intermediate voltage range: $700 W h kg^{-1}$ have thus been recovered between 3.6 and 1.9 V.

The influence of current density on electrochemical cycling has also been investigated. The cycling curves obtained for the two current densities are reported in Fig. 7. While over $600 W h kg^{-1}$ are obtained under $180 \mu A cm^{-2}$, as previously reported, $540 W h kg^{-1}$ are still recovered under $450 \mu A cm^{-2}$.

Conclusions

A new material, $\omega\text{-Li}_xV_2O_5$, can be easily obtained either by overdischarge of an Li/V_2O_5 cell or by chemical intercalation with an excess of *n*-butyllithium.

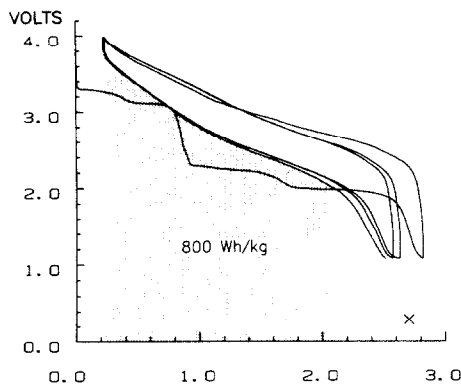


Fig. 6. Cycling of an $\text{Li/LiClO}_4\text{-PC/Li}_x\text{V}_2\text{O}_5 + \text{ketjen black}$ cell between 1.9 and 4.0 V, at $180 \mu\text{A cm}^{-2}$.

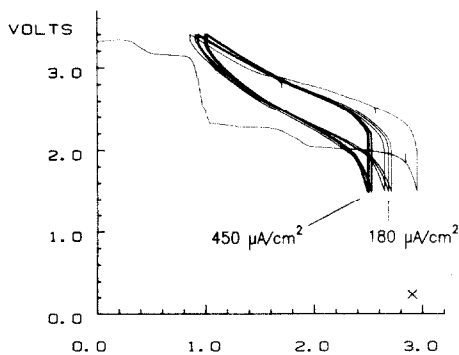


Fig. 7. Cycling of an $\text{Li/LiClO}_4\text{-PC/Li}_x\text{V}_2\text{O}_5 + \text{ketjen black}$ cell between 1.5 and 3.4 V at $180 \mu\text{A cm}^{-2}$ for the first 4 cycles and at $450 \mu\text{A cm}^{-2}$ for the rest.

This material is a very competitive positive electrode for lithium batteries. It exhibits a very high energy density (800 W h kg^{-1} in the 4.0–1.9 V range) and is, moreover, particularly stable, not being modified by over oxidation or reduction [17].

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