Electrochemical behaviour of chemically lithiated $Li_xV_2O_5$ phases $(0.9 \leq x \leq 1.6)$

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Abstract

$Li_xV_2O_5$ phase ($x = 0.9$, 1.16 and 1.6) has been prepared by chemical reduction of V_2O_5 using *n*-butyllithium. Electrochemical charge–discharge characteristics of fresh and aged compounds have been investigated. Lithium ions cannot be fully deintercalated during the charge due to a chemical oxidation in air. This effect is more pronounced when x increases and with ageing. New behavior and attractive properties are reported for $Li_{1.16}V_2O_5$ electrodes aged for a few days in air. A specific capacity of 300 Ah/kg is available in the range 1.8–3.8 V after the 20th cycle, which represents an improvement of 15–20% compared to V_2O_5. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Lithium polymer technology is a serious candidate for application such as electric vehicle. Solid polymer electrolyte (SPE) requires a temperature higher than 60°C to obtain sufficient continuous power. At this temperature, the use of a 3 V vs. Li/Li^+ cathodic material is better to avoid electrolyte degradation in SPE in operating conditions. Vanadium oxide is preferred since its specific capacity and cycle life are higher than those of manganese oxides. One way used to reduce the problems caused by lithium anode such as deepening, is to choose a cathode which presents a 'lithium reservoir'. In this paper, we report the preliminary electrochemical results obtained with the lithiated vanadium oxide $Li_xV_2O_5$.

2. Experimental

$Li_xV_2O_5$ compounds are obtained by chemical lithiation. One gram of V_2O_5 powder dispersed in 20 ml of fresh distilled hexane is reduced by a *n*-butyllithium solution (1.6 M in hexane, Aldrich) added in stoichiometric proportions, under argon atmosphere. The reaction is described by Whittingham and Dines [1,2] owing to the following scheme:

$$V_2O_5 + xC_4H_9Li \rightarrow Li_xV_2O_5 + x/2C_8H_{18}$$
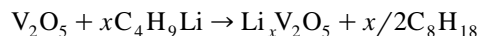
The mixture is stirred and maintained under argon during 48 h for $x < 1$ and during one week for $x > 1$. The powder is washed with hexane and the recovered powder is dried under vacuum at room temperature to eliminate solvent traces.

Lithium and vanadium contents in $Li_xV_2O_5$ samples are determined by ICP-AESC (Inductive Coupling Plasma-Atomic Emission Spectroscopy). Three $Li_xV_2O_5$ compounds are prepared. The analysis yield to the following formulae: $Li_{0.9}V_2O_5$, $Li_{1.16}V_2O_5$ and $Li_{1.6}V_2O_5$.

Simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) are carried out with a heating rate of 10 K/min, in atmosphere of flowing argon using a Netzsch STA 409 instrument equipped with data manipulation software.

X-ray powder diffraction study is performed with a Siemens D 5000 diffractometer with Co-Kα radiation. The powder patterns of vanadium oxide and lithiated vanadium oxide are indexed by means of the computer program U-Fit [3].

The electrochemical characteristics of $Li_xV_2O_5$ compounds are determined with a three-electrode electrochemical cell. The working electrode (10 mg) consists of a

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mixture of active material (80 wt.%), graphite (7.5 wt.%), acetylene black (7.5 wt.%) and Teflon (5%). The mixture is pressed onto a stainless steel grid, with a geometric area of 1 cm^2. The counter and reference electrodes consist of lithium wires in separate compartments. The electrolyte used is 1 M LiClO$_4$ in propylene carbonate. Propylene carbonate, double-distilled, is obtained from Fluka and used as received. Anhydrous lithium perchlorate is dried under vacuum at 170°C for 12 h. Electrochemical measurements are performed under galvanostatic control using a Mac Pile system.

3. Results and discussion

Fig. 1 shows the indexed X-ray diffraction patterns of freshly prepared Li$_{0.9}$V$_2$O$_5$, Li$_{1.16}$V$_2$O$_5$ and Li$_{1.6}$V$_2$O$_5$ samples. For the lithium contents 0.9 and 1.16, the diffraction lines are well defined indicating a good crystallinity. They have been indexed in the orthorhombic system which belongs to the A_{mam} space group and correspond to the δ phase of Li$_x$V$_2$O$_5$ [4]. These results are in agreement with the phase diagram of Li$_x$V$_2$O$_5$ [5–9]. For both compounds

a very small amount of γ phase is detected on the diagrams (significant peak located around 19.3° 2θ, noted '*' on the diagram [10]). This phase should not exist for Li$_{0.9}$V$_2$O$_5$ but could be explained by a lack of homogeneity in the material [11].

A broader XRD pattern is obtained for the material Li$_{1.6}$V$_2$O$_5$. Moreover it can be also indexed in the orthorhombic system indicating that the δ phase is in majority. Other diffraction lines can be detected and reveal the presence of additional phases in this material, likely the γ phase, in agreement with the phase diagram of Li$_x$V$_2$O$_5$.

V$_2$O$_5$ calculated parameters (space group P_{mmn}) are $a = 11.507$ Å, $b = 3.561$ Å and $c = 4.369$ Å. For the lithium content 0.9, 1.16 and 1.6, the unit cell parameters of the δ phase are calculated. Our average values, $a = 11.232 \pm 0.004$ Å, $b = 3.600 \pm 0.001$ Å and $c = 9.898 \pm 0.003$ Å, are in agreement with δ phase parameters found in literature [4].

The DSC and TGA curves of the Li$_{0.9}$V$_2$O$_5$ compound are given in Fig. 2. The first endothermic effect between 40 and 120°C, is constituted by a broader peak associated with a small weight loss (1%) and can be explained by departure of residual water and solvent traces. It is just
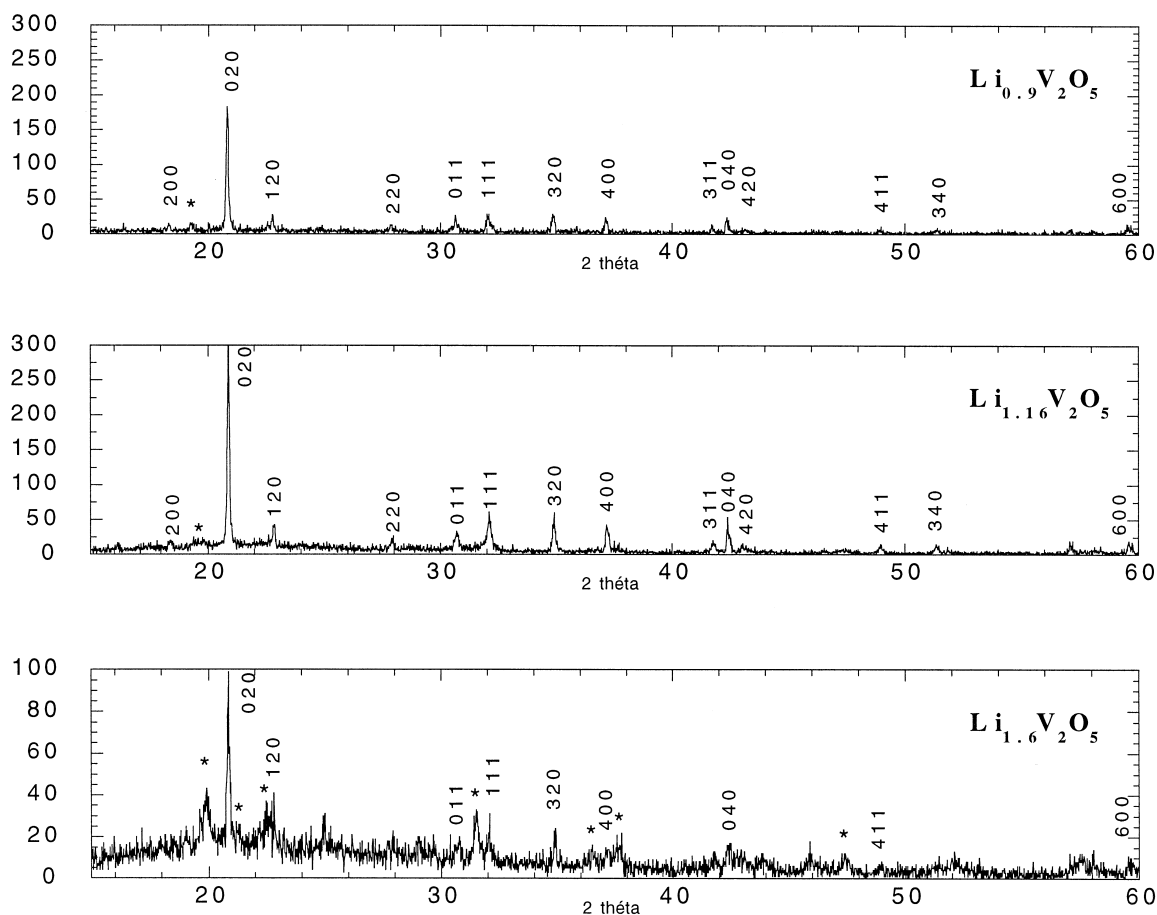

Fig. 1. X-ray diffraction patterns (λCo-Kα) of the lithiated compound Li$_x$V$_2$O$_5$ ($x = 0.9$, 1.16 and 1.6). Indexed peaks correspond to the δ phase, (*) indicates the γ phase.

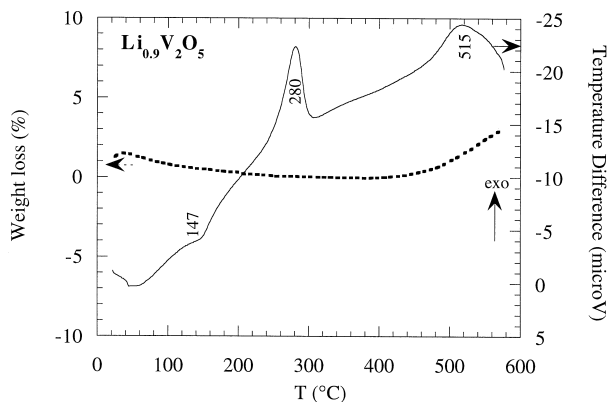Fig. 2. TGA/DSC curves of the compound $Li_{0.9}V_2O_5$. Heating rate: 10°C/min.

followed by a weak peak around 150°C corresponding to the reversible phase transition $\delta \to \varepsilon$. An exothermic effect appears around 280°C, associated with no weight variation. It corresponds to the irreversible phase transition $\varepsilon \to \gamma$. For temperatures higher than 400°C, exothermic transformations with a gain in weight occurred. It is due to the formation of $LiVO_3$ or/and $Li_{1.1}V_3O_8$. These results are in good agreement with the thermal phase diagram presented by Murphy et al. [5] and Pecquenard [9].

The charge–discharge curves, obtained with $Li_{0.9}V_2O_5$, $Li_{1.16}V_2O_5$ and $Li_{1.6}V_2O_5$ between 2.1 and 3.8 V at a $C/10$ rate, are shown in Fig. 3. They are compared with the signal of initial compound V_2O_5. Their initial potentials are respectively, 3.200, 2.991 and 2.568 V. The last two starting potentials, much higher than that usually reported for $Li_xV_2O_5$ for $x > 1$ (2.2–2.4 V), could indicate a possible chemical oxidation by oxygen or a contamination by ambient moisture.

For $Li_{0.9}V_2O_5$ and $Li_{1.16}V_2O_5$, the charge and the discharge curves exhibit the electrochemical features usually reported for the oxide V_2O_5 [12,13]. Indeed, during the
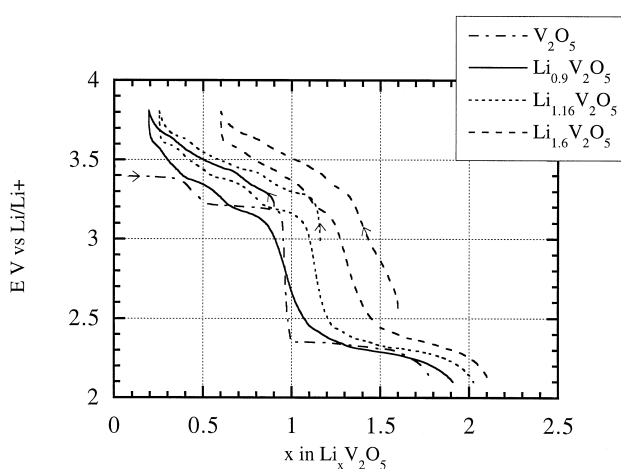
charge process the two well-known steps located at 3.3 V and 3.4 V appear for both materials. Moreover, a last step observed at 3.6 V reveals the presence of the γ phase according to the results of Cocciantelli et al. [11,14]. The oxidation reaction does not involve the total deinsertion of lithium ions: only 0.7 and 0.9 lithium ions are respectively removed against 0.9 and 1.16, as expected. Two possibilities can be then considered to explain this result. First, 0.2 and 0.26 lithium ions can be respectively 'trapped' in the host lattice. Second, as suggested by the starting potential values, a chemical oxidation by oxygen could explain the lower faradaic yield found during the charge process. This chemical oxidation could result in the formation of species like Li_2CO_3 or LiOH at the surface of the compound.

During the subsequent discharge of $Li_{0.9}V_2O_5$ and $Li_{1.16}V_2O_5$, the three reversible steps located at 3.6, 3.4 and 3.2 V are followed by a sharp potential drop to 2.2–2.3 V. 1.7 and 1.75 lithium ions are respectively inserted. In the case of V_2O_5, about 1.8 lithium ions are inserted during the first discharge at the same rate. The fact that the amount of lithium inserted in the lithiated material is almost the same as that expected for the parent oxide, seems rather to confirm the occurrence of a chemical oxidation before the electrochemical evaluation.

The same phenomenon is observed with the rich lithiated compound. For $Li_{1.6}V_2O_5$, the charge signal corresponds to 1 F/mol of oxide, showing that 0.6 lithium ion is not removed. The presence of the irreversible γ phase in large amount in this material is responsible for the well defined step located at 3.6 V. During the following discharge, 1.5 lithium ions are intercalated in the material. This faradaic yield, much lower than that expected for V_2O_5, shows that in the case of the lithium rich compound $Li_{1.6}V_2O_5$ the chemical oxidation is not alone responsible of the affected yield. In particular, it is believed that the damaging presence of the puckered γ phase in larger amount in this material plays an important role.
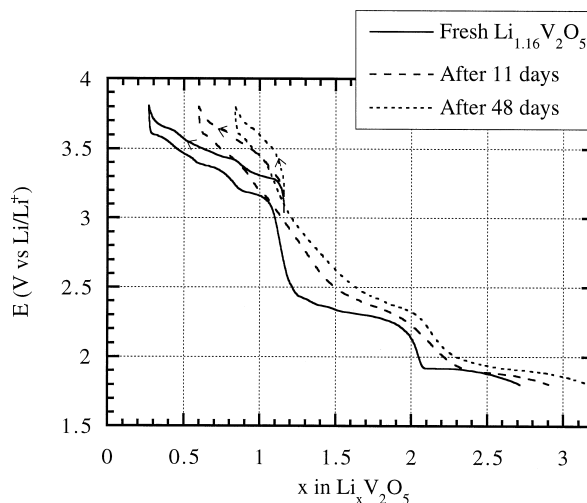

Fig. 3. Charge–discharge curves of the lithiated compound $Li_xV_2O_5$ ($x = 0.9$, 1.16 and 1.6) obtained at $C/10$ rate. V_2O_5 discharge curve obtained at the same rate is given for comparison.

Fig. 4. Charge–discharge curves of the compound $Li_{1.16}V_2O_5$: Freshly synthesized, 11 days and 48 days after its synthesis. Rate: $C/10$.
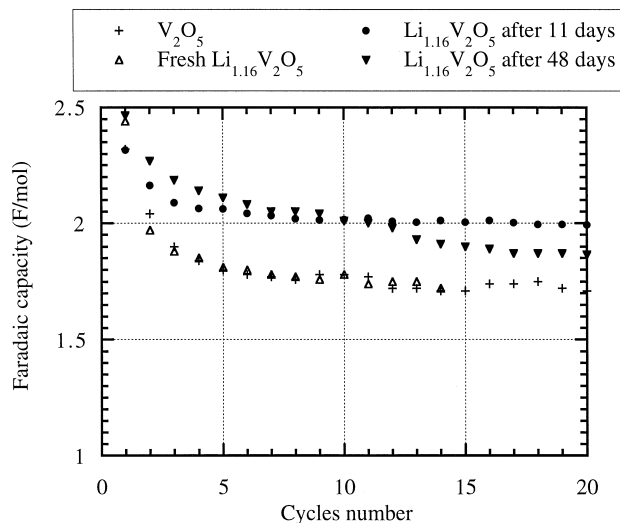
Fig. 5. Cycling behaviour of the compound $Li_{1.16}V_2O_5$ as a function of its age, performed between 1.8 and 3.8 V at $C/10$ rate. Comparison with V_2O_5.

In order to prove that lithium deinsertion is not limited by a kinetic effect, different current density have been applied for the charge and the discharge of $Li_{1.16}V_2O_5$. 0.7 lithium ion is always deintercalated whatever the current density in the range 200–50 μA.

As mentioned above, $Li_xV_2O_5$ is sensitive to chemical oxidation. Then, we have investigated the behaviour of the compound $Li_{1.16}V_2O_5$ after ageing in air atmosphere: 1 day, 11 days and 48 days after its synthesis.

As expected, the initial potential increases to 2.991 V, 3.157 V and 3.230 V, respectively. The XRD pattern performed after 11 days shows that the diffraction lines disappear, the background increases, indicating a diagram typical of an amorphous material. The thermal analysis of ageing compounds present a higher weight loss (5% between 20 and 350°C) than that found with the fresh compound. This result indicates a possible departure of water around 100°C but also a degradation of other species at higher temperature 200–300°C such as carbonate or hydroxide.

The corresponding charge–discharge curves are reported in Fig. 4. The longer the time storage, the 'smoother' the electrochemical response. The different steps of the redox process are ill-defined as reported for amorphous V_2O_5 oxide.

During the first charge, the faradaic yield decreases with ageing: about 0.9 lithium ion is removed from the freshly lithiated compound, 0.55 after 11 days and only 0.3 after 48 days. During the discharge, 2.4, 2.3 and 2.4 lithium ions are respectively intercalated between 3.8 V and 1.8 V against 2.35 for the oxide V_2O_5. The discharge faradaic yield seems to be independent on the time ageing. These results confirm the chemical oxidation of the lithiated compounds. The magnitude of the chemical oxidation can be attributed to the fact that these compounds are stored as thin electrodes in air atmosphere. The surface exposed to the oxygen and moisture is then very developed. Of interest to note is that the chemical oxidation is reversible and does not impede achievement of attractive electrochemical properties.

In Fig. 5 the cycling behaviours of V_2O_5 and $Li_{1.16}V_2O_5$ are compared at different ages. After 20 cycles, the specific capacity available between 1.8–3.8 V is about 280–300 Ah/kg for the 11 and 48 days aged samples against 250 Ah/kg for the freshly lithiated $Li_{1.16}V_2O_5$ and the V_2O_5 oxide, which represents an improvement of 15–20% of the capacity. This improvement is ascribed to an increase of the reversible capacity of the third and fourth steps of the electrochemical process. A change of the morphology or/and of the structure associated to the chemical oxidation and leading to an amorphous compound, could explain the better cycle life obtained. The lithiated compounds behaviour resembles the features of the weakly crystalline $Li_3V_2O_5$ ω-phase mentioned by Delmas et al. [15–18] or the behaviour of the new compound $Cr_{0.11}V_2O_{5.16}$ obtained by sol–gel process by Soudan et al. [19].

4. Conclusion

Chemically lithiated vanadium oxides $Li_xV_2O_5$, aged in air atmosphere, submit a chemical oxidation and present an amorphous feature probably due to morphological and structural changes. The reversibility of the third and fourth steps of the electrochemical process is improved and leads to a better stability of the cycling capacity. The smooth profile of discharge–charge curve allows a higher specific capacity to be accessed around 3 V. Indeed, the aged oxide $Li_{1.16}V_2O_5$ appeared to be very interesting for use as cathode in 3 V polymeric electrolyte rechargeable lithium batteries. For instance with the compound $Li_{1.16}V_2O_5$ aged for 48 days, a capacity of 300–280 Ah/kg is available after 20 cycles performed between 1.8 and 3.8 V and of 190 Ah/kg after 20 cycles performed between 1.8 and 3.2 V.

References

[1] M.S. Whittingham, M.B. Dines, J. Electrochem. Soc. 124 (1977) 1387.
[2] M.B. Dines, Mat. Res. Bull. 10 (1975) 287.
[3] M. Evain, U-Fit: A Cell Parameter Refinement Program, I.M.N., France, 1992.
[4] R.J. Cava, A. Santoro, D.W. Murphy, S.M. Zahurak, R.M. Fleming, P. Marsh, R.S. Roth, J. Solid State Chem. 65 (1986) 63.
[5] D.W. Murphy, P.A. Christian, F.J. Disalvo, J.V. Waszczak, Inorg. Chem. 18 (1979) 2800.
[6] P.J. Dickens, S.J. French, A.T. Hight, M.F. Pye, Mat. Res. Bull. 14 (1979) 1295.

[7] J.M. Cocciantelli, J.P. Doumerc, M. Pouchard, M. Broussely, J. Labat, J. Power Sources 34 (1991) 103.

[8] J. Galy, J. Solid State Chem. 100 (1992) 229.

[9] B. Pecquenard, Thése de l'Université Paris VI, 1995.

[10] J. Galy, A. Hardy, Acta Cryst. 19 (1954) 432.

[11] J.M. Cocciantelli, M. Ménétrier, C. Delmas, J.P. Doumerc, M. Pouchard, M. Broussely, J. Labat, Solid State Ionics 78 (1995) 143.

[12] J.P. Pereira-Ramos, R. Messina, C. Diolet, J. Devynck, Electrochim. Acta 33 (1988) 1003.

[13] J.P. Pereira-Ramos, R. Messina, J. Périchon, J. Power Sources 16 (1985) 193.

[14] J.M. Cocciantelli, M. Menetrier, C. Delmas, J.P. Doumerc, M. Pouchard, P. Hagenmuller, Solid State Ionics 50 (1992) 99.

[15] C. Delmas, C.R. Acad. Sci. Paris 310 (1990) 1425, série II.

[16] C. Delmas, S. Bréthes, M. Menetrier, J. Power Sources 34 (1991) 113.

[17] C. Delmas, H. Cognac-Auradou, J.M. Cocciantelli, M. Menetrier, J.P. Doumerc, Solid State Ionics 69 (1994) 257.

[18] C. Delmas, H. Cognac-Auradou, J. Power Sources 54 (1995) 406.

[19] P. Soudan, J.P. Pereira-Ramos, G. Gregoire, N. Baffier, Ionics 3 (1997) 261.