Electrochemical lithium insertion in some nickel, zinc and cadmium vanadates

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Abstract

In this work we present a study of the electrochemical characteristics of lithium insertion in eight crystalline Ni, Zn and Cd vanadates. During the electrochemical study carried out down to 0.5 V vs. Li^+/Li, CdV_2O_6 and $Cd_2V_2O_7$ were found to be the compounds tested accepting the highest number of lithium atoms per metal atom ($Li/\Sigma M = 1.75$ and 1.63, respectively). The zinc and nickel vanadates tested accepted a smaller number of lithium atoms per formula unit. In situ X-ray diffraction experiments showed an almost complete amorphization of the cadmium vanadates at the end of the first discharge while nickel and zinc vanadates were not amorphous. Therefore, these results are in agreement with previous reports of larger lithium atom intake in amorphous than in crystalline materials. In any case, on cycling none of these vanadates perform as well as previously described vanadium compounds. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Lithium insertion; Vanadates

1. Introduction

Different crystalline and amorphous transition metal vanadates have been proposed recently as possible anodes for 'rocking-chair' or 'lithium-ion' batteries showing maximum specific capacities even higher than that of the graphite anodes normally used [1–3]. Sigala et al. reported [2] that when some crystalline lithium-transition metal vanadates are discharged to very low voltages, they become amorphous leading to new materials with very good cycling behaviour. For example, they reported capacities of about 600 Ah/kg for Li_8NiVO_4 after 100 cycles. Denis et al. [3] synthesised amorphous RVO_4 (R = In, Cr, Al, Y and Fe) and studied their electrochemical behaviour vs. lithium insertion finding out that $InVO_4$ and $FeVO_4$ showed reversible capacities as high as 900 A h/kg. It is within this context that we decided to carry out a study of the electrochemical characteristics of lithium insertion in seven crystalline vanadates of general formula $M_xV_2O_{5+x}$ (M = Ni and Zn, x = 1, 2, 3) and $Cd_yV_2O_{5+y}$ (y = 1, 2). As in situ X-ray diffraction cells are extremely effective when studying the correlation between electrochemical proper-

ties and structural changes as the insertion reaction proceeds, we built an electrochemical cell which could be fitted in our diffractometer Siemens D5000 based on similar designs reported in literature [4]. The performance of such a cell was tested studying structural changes taking place in the previously mentioned vanadates.

2. Experimental

2.1. Synthesis and characterisation

Starting materials were synthesised by a solid state reaction from stoichiometric mixtures of NH_4VO_3 (Alfa Aesar) and MO (where M = Ni, Cd and Zn, Aldrich Chem. and Baker Anal.). Reaction mixtures were taken to an electrical furnace and initially heated 2 h at 470°C to drive off NH_3 and then subjected to further grinding and annealing treatments at temperatures ranging from 650 to 1100°C depending on each compound. Phase identification and in situ X-ray diffraction experiments were carried out on a Siemens D5000 diffractometer using CuKα (1.5418 Å) radiation. Detailed structural information about these vanadates can be found in literature (see for example, Refs. [5–11]). Electrochemical experiments were carried

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out in a potentiostatic–galvanostatic multichannel system MacPile II (Biologic, Claix, France) using Swagelok™ type test cells [12]. Cell cathodes were prepared by mixing and pressing, a mixture of the transition metal vanadates being tested, carbon black and a binder (0.5% ethylene-propylene-diene terpolymer, EPDT, in cyclohexane) in a 88:10:2 molar ratio. An 1 M solution of $LiClO_4$ in a 50:50 mixture of ethylene carbonate (EC) and dimethylcarbonate (DMC) or of EC and diethoxy ethane (DEE) were used as electrolytes. Cells were assembled in a MBraun glove box under an argon atmosphere with continuous purge of water vapour and oxygen ensuring an inside concentration for both compounds below 1.5 ppm. Two different electrochemical experiments were carried out during this study, either in a current-controlled or in a potential-controlled mode. Intentiostatic experiments were carried out by applying continuously, a given current density to the cells and recording the evolution of cell voltage with composition (number of lithium atoms inserted). Potentiodynamic titrations were carried out by a stepwise technique also known as 'Step Potential Electrochemical Spectroscopy' (SPECS) [13]. In this technique, the potential is stepwise increased or decreased while recording charge increments vs. time at each potential level allowing, therefore, the study of insertion reaction kinetics and from there, the sequence of single phase and two phase domains which might be present on (de)insertion. Typical experimental conditions were set at ± 20 mV/2 h potential steps with a charge recording resolution of 8 μA h under a strict temperature control.

2.2. Electrochemical cell for in situ X-ray diffraction experiments

In order to carry out in situ X-ray diffraction studies, an electrochemical cell was built to fit in our diffractometer Siemens D5000. Such a cell consists of two metal parts built with stainless steel ASTM 1025: (i) a cell top which holds a beryllium window where cathode materials, prepared as described above, were deposited by spreading them as a slurry mixed with acetone and, (ii) a cell base. Metal lithium (negative and reference electrode) was placed on the cell base pasted on a nickel disk acting as a current collector. Two layers of S and S no. 25 glass fiber separator soaked on the electrolyte were placed between the electrodes. The cell also features a spring which ensures physical contact between the different parts and allows a tight seal.

3. Results and discussion

For reason of clarity, the electrochemical behaviour on lithium insertion of each one of the three family of vanadates (Ni, Zn and Cd), is described separately.
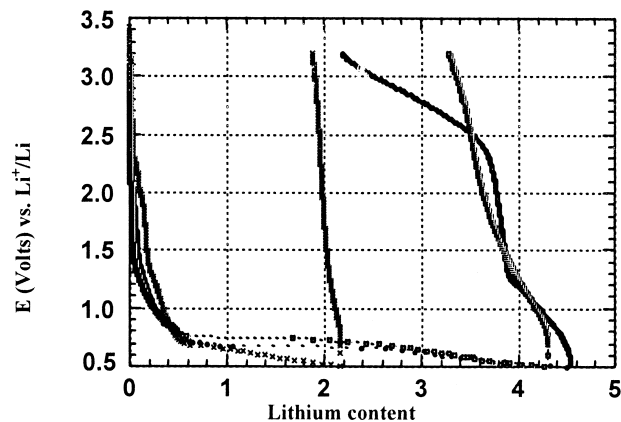

Fig. 1. Evolution of cell voltage vs. composition obtained when cycling (1 Li/50 h) three cells with the following configuration: $Li\|NiV_2O_6$ (open squares), $Li\|Ni_2V_2O_7$ (crosses) and $Li\|Ni_3V_2O_8$ (solid circles).

3.1. $Li\|Ni_xV_2O_{5+x}$ (x = 1, 2 and 3)

Fig. 1 shows the evolution of cell voltage vs. composition between 3 and 0.5 V of a complete charge–discharge cycle for the three nickel vanadates tested in this work. As can be seen, the compound accepting the largest intake of lithium atoms per metal atom is that with the molecular formula NiV_2O_6 (JCPDS 45-1053) where $Li/\Sigma M = 1.6$ vs. 0.6 and 0.9 for the other two compounds, $Ni_2V_2O_7$ (JCPDS 38-285) and $Ni_3V_2O_8$ (JCPDS 37-353), respectively. A general description of the three graphs would include the presence of slight slope changes down to approximately 0.75 V corresponding to the insertion of around 0.5 lithium atoms, and a large plateaux below that potential level. It was noticed on charging that lithium insertion in these nickel vanadates is not a reversible process since a large proportion of those atoms incorporated when discharging the cell remains in the structures after completing a charge–discharge cycle suggesting the existence of irreversible transformations. In fact, the large plateaux observed at 0.75 V according to SPECS data, might correspond not to a 'true' insertion reaction but to a transition metal reduction process. This observation is also in agreement with a gradual loss of crystallinity noticed in in situ X-ray diffraction experiments (not shown). Additionally, during further cycling the number of lithium atoms which can be extracted decreases rapidly.

3.2. $Li\|Zn_xV_2O_{5+x}$ (x = 1, 2 and 3)

Fig. 2 shows a complete charge–discharge cycle for each one of the three zinc vanadates tested. In this case, the compound incorporating the largest number of lithium atoms per metal atom, is that with the molecular formula $Zn_2V_2O_7$ (JCPDS 38-251), $Li/\Sigma M = 1.1$. The main features of the curve obtained for this compound are two plateaux of approximately constant E values which are observed around 1.9 and another one starting at 0.8 V. The
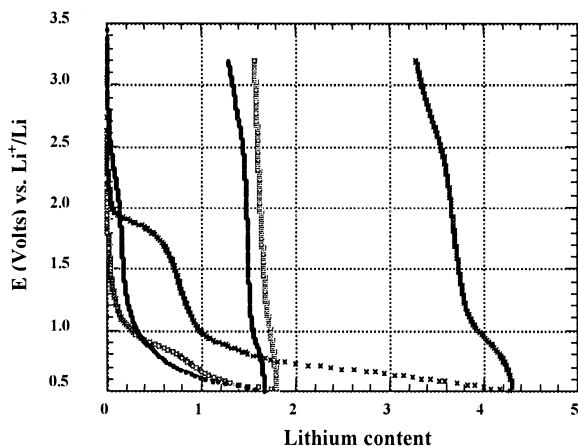
Fig. 2. Evolution of cell voltage vs. composition obtained when cycling three cells with the following configuration: Li‖ZnV$_2$O$_6$ (solid circles) (1 Li/40 h), Li‖Zn$_2$V$_2$O$_7$ (crosses) (1 Li/40 h) and Li‖Zn$_3$V$_2$O$_8$ (open squares) (1 Li/16 h).

plateaux at higher potential separate two solid solution regions with important changes in *E* values for small variations in composition. In situ X-ray diffraction experiments (not shown) showed that although this compound lost some crystallinity on discharge down to 0.5 V, it is not completely amorphous at this potential level and some peaks are still observed in its diffraction pattern. The other two zinc compounds tested present different electrochemical characteristics to the previous one on lithium insertion with a dramatic voltage drop down to 1 V and the beginning of what looks like a large plateaux at 0.6 V. Despite Zn$_3$V$_2$O$_8$ (JCPDS 34-378) being isostructural with its nickel homologous [5], a smaller number of lithium atoms is incorporated on discharge in the zinc vanadate, Li/ΣM = 0.36 for zinc vs. 0.9 for nickel. Since Zn^{2+} and Ni^{2+} have similar ionic radii (0.74 Å for Zn^{2+} vs. 0.69 Å for Ni^{2+} for coordination VI) [14], this result is probably related with the different reduction potential of each redox couple, Ni^{2+}/Ni vs. Zn^{2+}/Zn (−0.25 and −0.76 V, respectively), and suggests an active role in the insertion reaction for the transition metal present in these type of
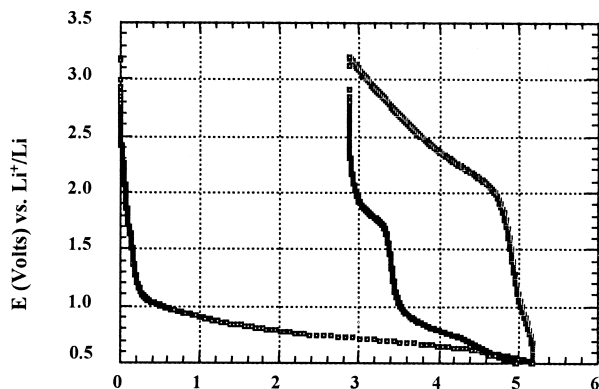
vanadates. The third zinc vanadate tested, ZnV$_2$O$_6$ (JCPDS 23-757), does not show any interesting electrochemical characteristic on lithium insertion. The three compounds tested showed poor cyclability on charging suggesting that, again, major structural changes are taking place during their insertion induced reduction reaction.

3.3. Li‖Cd$_y$V$_2$O$_{5+y}$ (y = 1, 2)

Figs. 3 and 4 show the evolution of cell voltage vs. composition between 3 and 0.5 V, for the two cadmium vanadates tested in this work. These compounds are by far the ones from those tested, accepting the largest intake of lithium atoms on discharge. Thus, Li/ΣM = 1.75 for CdV$_2$O$_6$ (JCPDS 22-133) and 1.63 for Cd$_2$V$_2$O$_7$ (JCPDS 38-250). The compound CdV$_2$O$_6$ which presents a Branerite type structure with three and four-sided tunnels along the *Y* axis [7], incorporates 5.2 lithium atoms per formula unit but only around two can be extracted at the end of a complete charge–discharge cycle. The main features of the discharge curve are: (i) an important voltage drop down to 1 V and (ii) a large plateaux below this potential level. As

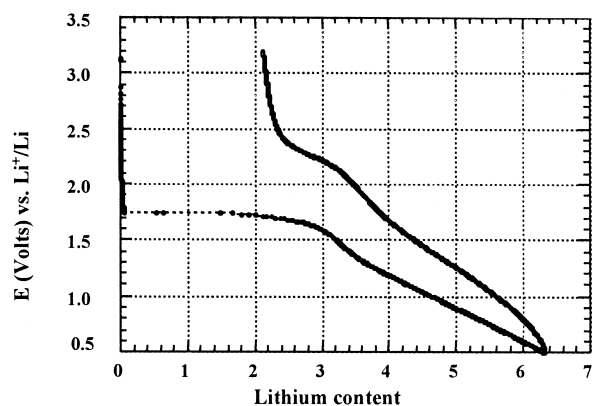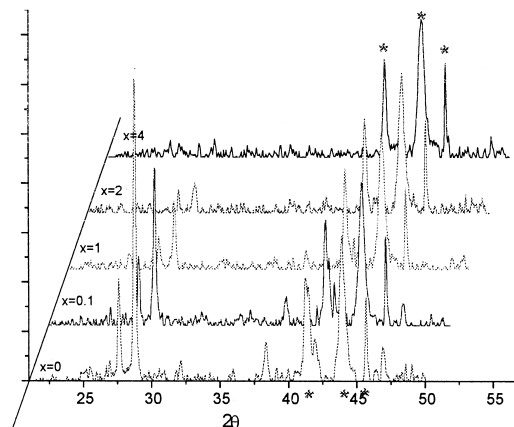
Fig. 4. Evolution of cell voltage vs. composition obtained when cycling (1 Li/40 h) a cell with the following configuration: Li‖Cd$_2$V$_2$O$_7$.

Fig. 3. Evolution of cell voltage vs. composition obtained when cycling (1 Li/40 h) a cell with the following configuration: Li‖CdV$_2$O$_6$.

Fig. 5. X-ray diffraction patterns of Li$_x$CdV$_2$O$_6$ obtained when discharging a cell with the following configuration Li‖CdV$_2$O$_6$.
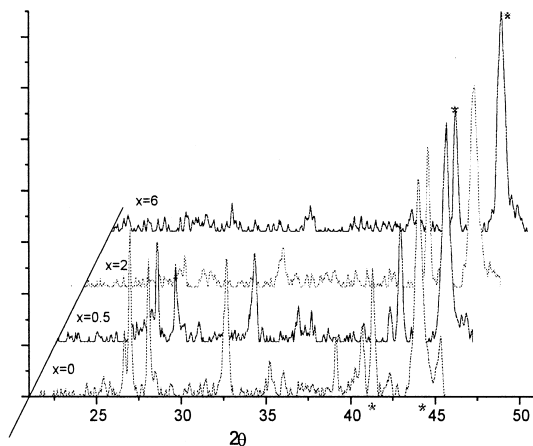
Fig. 6. X-ray diffraction patterns of Li$_x$Cd$_2$V$_2$O$_7$ obtained when discharging a cell with the following configuration Li‖Cd$_2$V$_2$O$_7$.

further cycling suggests, the original material transforms itself during the first discharge so that successive charge–discharge cycles have different characteristics with a new plateaux showing up at around 1.7 V. This new material can reversibly incorporate two lithium atoms. As can be seen in Fig. 5, a gradual loss of crystallinity is observed as the insertion reaction proceeds so that the diffraction pattern of the material obtained at 0.5 V is almost featureless.

The electrochemical behaviour of Cd$_2$V$_2$O$_7$, a thortveitite type structure [11], is completely different from that shown by CdV$_2$O$_6$.

A large plateaux at approximately 1.75 V and a succession of slight slope changes below that potential level are the main characteristics of this discharge curve. On charging, 2.5 lithium atoms remain in the structure and are not removed at the end of a complete cycle. A gradual fade on capacity is observed when an electrochemical cell containing this phase as active material of the positive electrode, is cycled. However, a certain reversibility is observed when cycling the cell between 2 and 0.5 V suggesting that the transformation which gives origin to the plateaux seen at 1.75 V, is an irreversible process. The new material formed at that voltage can reversibly incorporate 2.5 lithium atoms between 1.75 and 0.5 V. In situ X-ray diffraction experiments, Fig. 6, show that as observed with the previous cadmium vanadate, the amorphization of the fully lithiated material is almost complete and no peaks but those corresponding to the Be window, are evident.

4. Conclusions

A study of lithium insertion in 8 nickel, zinc and cadmium vanadates have been presented in this work. Cadmium vanadates were the compounds which incorporated the largest number of lithium atoms per metal atom and showed some cyclability on lithium insertion. In situ X-ray diffraction experiments showed that these materials were the only ones reaching a high degree of amorphization at the lowest voltage limit used in this work. Therefore, these results are in agreement with previous reports of better cyclability on lithium insertion in amorphous than in crystalline materials. On cycling, the compounds tested do not perform as well as other previously described vanadates. Further studies are underway at this moment for some of the vanadates mentioned in this work, to determine the nature of the processes observed during the electrochemical experiments.

Acknowledgements

References

[1] Y. Idota, Eur. Pat. 0 567 149 A1, 1993.
[2] C. Sigala, D. Guyomard, Y. Piffard, M. Tournoux, C.R. Acad. Sci. Paris 320 (1995) 523, Serie II b.
[3] S. Denis, E. Baudrin, M. Touboul, J.-M. Tarascon, J. Electrochem. Soc. 144 (1997) 4099.
[4] Y. Chabre, NATO ASI Series 305 (1993) 181.
[5] R. Gopal, C. Calvo, Can. J. Chem. 49 (1971) 3056.
[6] R. Gopal, C. Calvo, Can. J. Chem. 51 (1973) 1004.
[7] J.C. Bouloux, J. Galy, Bull. Soc. Chim. Fr. 3 (1969) 736.
[8] Hk. Müller-Burschbaum, M. Kobel, Z. Anorg. Allg. Chem. 596 (1991) 23.
[9] E.E. Sauerbrei, R. Faggiani, C. Calvo, Acta Cryst. B 29 (1973) 2304.
[10] J. Angenault, A. Rimsky, C.R. Acad. Sci. Paris C 267 (1968) 227.
[11] P.K.L. Au, C. Calvo, Can. J. Chem. 45 (1967) 2297.
[12] J.-M. Tarascon, J. Electrochem. Soc. 132 (1985) 2089.
[13] Y. Chabre, J. Electrochem. Soc. 138 (1991) 329.
[14] R.D. Shannon, Acta Cryst. A 32 (1976) 751.