VANADIUM OXIDES IN ELECTRODES FOR RECHARGEABLE LITHIUM CELLS

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Summary

In principle, vanadium pentoxide can be used as an active material for positive electrodes in rechargeable lithium cells. Cyclability is possible when the discharge is limited to a value of $y = 2.35$ (in $Li_y V_2 O_5$). The cycling behaviour is comparatively good up to a discharge level of $y = 1$.

Introduction

Substances with so-called "open crystal structures" are used as electrochemically active materials for insoluble positive electrodes in secondary lithium cells. The lattices of these substances have cavities that act as open, freely passable, channels for lithium ions. The compounds have channels in one, two or three directions, or a layer lattice. Insertion of lithium ions into such structures during discharge is observed for many of these compounds because the small size of the lithium ions and the comparatively low electrical field strength result in a good mobility of lithium. In order to make rechargeable lithium cells, however, it is essential that during the charging process the lithium ions can be removed from the lattice structure; to accomplish this the lithium bonding energy must not exceed a certain level. Additionally, the energetic or geometric conditions during positional displacements of lattice atoms must not be drastically changed.

Vanadium oxides are of special interest because of their comparatively low equivalent weight. Studies have been reported on the application of $V_6 O_{13}$ [1 - 5], $LiV_3 O_8$ [6 - 9] and $V_2 O_5$ [10 - 13] in secondary cells. The cycle life of most of these vanadium oxides is not sufficiently adequate, especially in the case of $V_2 O_5$, when the discharge proceeds down to the $+4$ state of vanadium. It is most important to discover the reason for this undesired behaviour.

The insertion of lithium ions into the lattice of oxide phase is considerably influenced by the crystal structure, the electronic structure, and

the thermodynamical stability. The structure of V_2O_5 contains intermediate layers ("gaps") and channels, as well as empty holes, where lithium ions can be inserted.

Experimental

The cycling behaviour of V_2O_5 in electrodes using carbon black as a conductive material and PTFE as a binding agent has been studied in glass cells having a lithium counter electrode, a lithium reference electrode, and an electrolyte solution of 1 M $LiClO_4$ in a 1:1 mixture of propylene carbonate and dimethoxyethane.

In order to characterize the electrodes for definite discharge or charge conditions at selected times, cyclic voltammograms were recorded and samples taken for analysis by photoelectron and IR spectroscopy. These samples were washed thoroughly in order to remove the $LiClO_4$; this involved the use of propylene carbonate and dimethoxyethane in dry argon atmosphere.

XPS data were obtained by a VG ESCA 3 photoelectron spectrometer excited by Al $K\alpha$ radiation (1486.6 eV). The vacuum in the analyser chamber was $\sim 5 \times 10^{-6}$ Pa. Thin layers of the samples were attached to double-sided adhesive tape. The bonding energies were standardized by the C 1s (285.0 eV) peak of the carbon contamination.

Infrared spectra provided a means of quickly inspecting samples after each stage of their treatment. The solids were ground and pressed into discs with TlBr [14] (in order to reduce interference from moisture and, eventually, metathetic and redox reactions). Spectra were recorded by a grating instrument (IR 75, Carl Zeiss Jena) from 4000 to 400 cm^{-1}.

Results and discussion

Discharge/charge curves

The discharge curve of the Li/V_2O_5 system (Fig. 1(a)) shows several voltage plateaus. By comparison with the potentials of some vanadium oxides of lower oxidation numbers, it can be concluded that the steps in the discharge curve do not correspond to low-valent vanadium oxide phases. The discharge curves of the oxides V_6O_{13}, VO_2, V_8O_{15}, V_3O_5 and V_2O_3 exhibit a different discharge behaviour and the plateau voltage values are not comparable with those of the V_2O_5 (Fig. 1).

The reversibility of the Li/V_2O_5 system was investigated by cyclic voltammetry. The discharge took place to a certain extent (y in $Li_yV_2O_5$). The resulting discharge/charge curves are given in Fig. 2. Whereas at the beginning of the third plateau ($y \lesssim 2.35$) it was possible to recharge the system, at the end of this plateau ($y = 3$) the cycling behaviour was poor, and at values of $y > 3$ the system cannot be recharged. The duration of
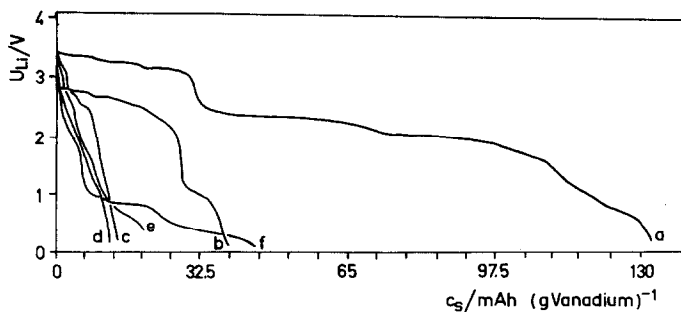
Fig. 1. Discharge curves of different vanadium oxides in cathodes of lithium cells with 1 M $LiClO_4$ PC/DME (1:1) solution (0.8 mA cm^{-2}). (a) V_2O_5; (b) V_6O_{13}; (c) VO_2; (d) V_3O_5; (e) V_8O_{15}; (f) V_2O_3.
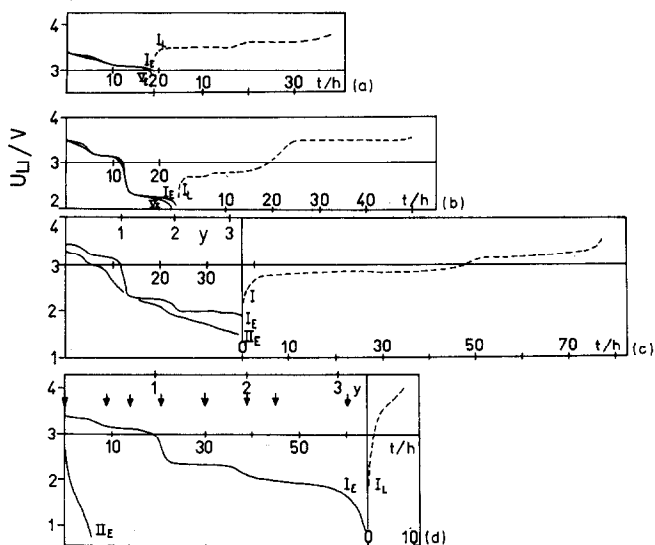
Fig. 2. Discharge and charge curves of Li/V_2O_5 cells ($i_{discharge}$ = 1.0 mA cm^{-2}; i_{charge} = 0.5 mA cm^{-2}); cycling to the end of the (a) first, (b) second, (c) third plateau, and (d) to 0.2 V. The Roman numerals indicate the cycle number; Index: E, discharging; L, charging; ↓, a potentiodynamic measurement being carried out (see Fig. 3) after a discharge time of (a) 0 h; (b) 9 h; (c) 14 h; (d) 21 h; (e) 30 h; (f) 39 h; (g) 45 h; (h) 60 h.

discharge was different for all curves. This was due to the different utilization coefficients and the different masses of the electrodes, which resulted from difficulties in the preparation of the small electrodes.

Voltammetry

The reversible, and irreversible, behaviour of the Li/V_2O_5 system at individual discharge steps is shown by the potentiodynamic ΔU–i curves for the V_2O_5 electrode obtained at different discharge and charge times (Fig. 3). The important influences are:
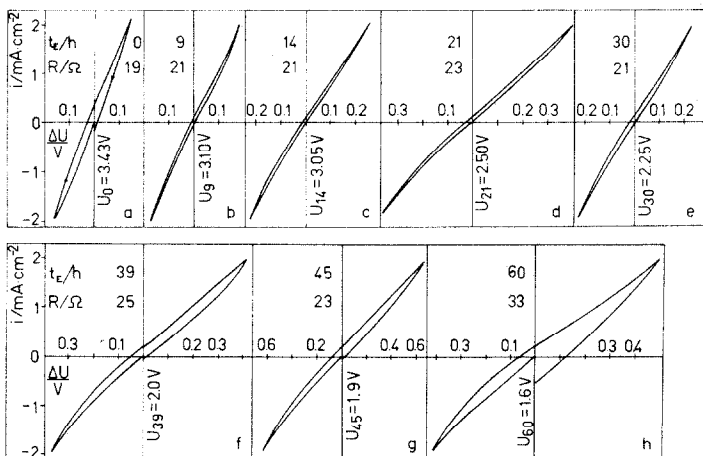
Fig. 3. Potentiodynamic potential–current density curves with ohmic voltage drop compensation after a discharge time t_E (see Fig. 2(d)) of Li/V$_2$O$_5$ cells with 1 M LiClO$_4$ PC/DME (1:1) solution (voltage sweep: 6.7 mV s^{-1}); R, ohmic resistance.

(i) the polarization of the electrode (polarization resistance);

(ii) the ohmic resistance;

(iii) the size of the area enveloped by the hysteresis of the cyclic voltammogram.

A considerable change in these factors was observed by means of potentiodynamic curves recorded at the point where transfer from one voltage plateau to the other took place (voltage step). For example, on transfer from the first to the second plateau ($t_E = 21$ h) an increase was observed in the polarization, the ohmic resistance, and the hysteresis envelope. At each transfer from a higher to the next lower potential level, because of the reduction of vanadium in the oxide, the lattice is more or less rearranged or the insertion of lithium ions into new lattice locations is complicated. During discharge at the plateau, this phenomenon disappears. Towards the end of the discharge, the initial structure is completely destroyed and the factors mentioned above markedly increase on transfer from the system's "reversible" state to the irreversible state.

In the ΔU–i curve, the increase in irreversibility is demonstrated by:

(i) the increase in polarization (by 0.1 V at 1 mA cm^{-2});

(ii) the increase in ohmic resistance (by 10 Ω);

(iii) the 10 - 15 fold extension of the hysteresis envelope.

At given stages of the recharging process, the voltammograms reflect the reversibility or irreversibility of the process.

XPS

In the photoelectron spectra (XPS) of the discharge products, the shift of the electron energy levels (V 2p$_{3/2}$; O 1 s; Li 1 s) demonstrates that V^{5+}

Probe	Li 1S	C 1S	V 2P$_{3/2}$	O 1S	F 1S
a (y=0)	20;c/%	50; c/%	5;c/%	c/% 20;	5;c/%
b (y=1)					
c (y=2)					
d (y>3)					
e	53 55 57(?)	284 288 292	516 518	532 534	E_B/eV 689 691
f					
g					
h					

Fig. 4. Diagrams of ESCA patterns of V_2O_5 electrodes after discharge and charging process in a lithium cell. (a) V_2O_5 with carbon black and PTFE; (b) discharge to the first voltage plateau; (c) discharge to the second voltage plateau; (d) discharge to 0.2 V; (e) after charging from the end of the first plateau; (f) after charging from the end of the second plateau; (g) after charging from the third plateau ($y = 2.35$); (h) charging after complete discharge.
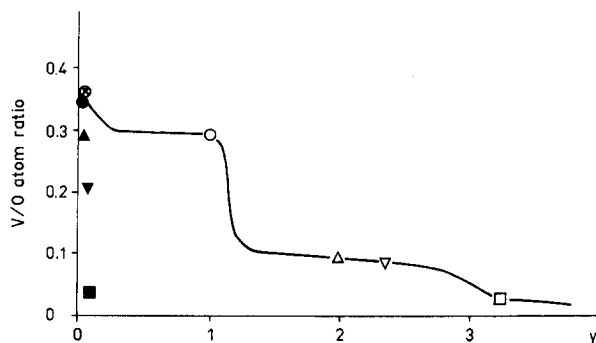

Fig. 5. Atomic ratio V/O in V_2O_5 electrodes as a function of the discharging degree, y (in $Li_yV_2O_5$), during discharge and charge in a lithium cell. ○, △, ▽, □, Discharge; ●, ▲, ▼, ■, after charging from the corresponding point of the discharge curve.

is reduced to the lower oxidation states of V^{4+} and V^{3+} and the chemical bond between the inserted lithium and the oxygen of the oxide is more ionic than that for the Li_2O.

Figure 4 shows XPS data for the elements present in samples taken at different stages of discharge and charge. There is a change in the electronic structure and bonding energies in the V_2O_5 due to the insertion of lithium during discharge. After recharging, the initial state (Fig. 4 (a)) is again achieved when the system is discharged only up to the beginning of the third plateau (curves (e) (f) and (g)). At the beginning of the third plateau (where y in $Li_yV_2O_5$) is $2 < y \leqq 2.35$, recharging is still possible (curve (g)), though the XPS data show an oxygen state which is due to an Li—O bond and corresponds to that in Li_2O. At values of $y \geqq 2.35$ an irreversible structure change occurs.

Figure 5 represents the atomic ratio V/O determined by XPS inves- tigations at different stages of the discharge process, taking into account that the method used provides information concerning the surface of the samples only. Surprisingly, the initial ratio, 0.35 (theoretical value for V_2O_5 = 0.4), decreases during the discharge, *i.e.*, an enrichment of oxygen atoms occurs at the surface. With reversible charging, this ratio returns to a higher value, whereas it remains low for irreversible charging. This result cannot be easily interpreted. The relative enrichment of the oxygen at the surface cannot be completely attributed to transport of oxygen from the V_2O_5 lattice to the surface, but possibly may be explained by a movement of the oxygen nearer to the vanadium. It is also possible, however, that even from the beginning of discharge, Li_2O, as well as Li_2CO_3, is formed in the electrochemical process by a decomposition reaction with propylene carbonate.

IR spectra

Figure 6 shows the IR spectra of samples in the same discharge and charge states as for the XPS data (*i.e.*, Fig. 4). In agreement with the V_2O_5 spectra, the simultaneous appearance of a narrow band at about 1000 cm^{-1} and of a broader band at 800 cm^{-1} is recognized as being characteristic of vanadium(V)–oxygen vibrations. Barraclough *et al.* [15] assign the higher
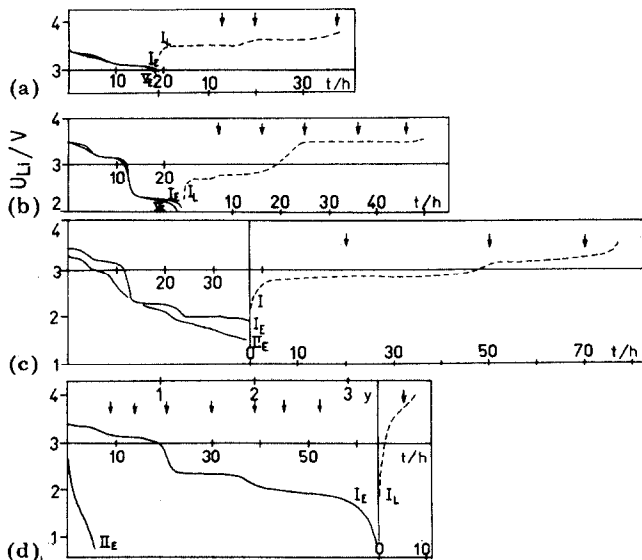

Fig. 6. IR spectra of V_2O_5 electrodes after the discharging or charging process in a lith- ium cell. (a) V_2O_5 + carbon black + PTFE; (b) discharging up to the end of the first voltage plateau; (c) discharging up to the end of the second voltage plateau; (d) dis- charging up to the end of the third voltage plateau; (e) after charging from the end of the first plateau onward; (f) after charging from the end of the second plateau onward; (g) after charging from the third plateau (y = 2.35) onward; (h) after charging when the system was discharged to 0.3 V.

band to a V–O stretching vibration, and the lower band to a V–O vibration. However, the lower band can also correspond to a different type of movement of the V–O bonding.

During the discharge process, the intensity and the number of bands corresponding to the vanadium–oxygen vibrations decrease. This could be due to the greater symmetry of the lattice, or to a lower number of vibrating atoms, *i.e.*, oxygen has entered the Li–O bonds. In samples obtained after discharge, from $y = 1$ (in $Li_yV_2O_5$) no band at 800 cm^{-1} occurred in the IR spectrum, and from $y = 2.35$ the band at 1000 cm^{-1} had disappeared. The newly formed band at 600 cm^{-1} follows from a disarranged crystal structure because of a new arrangement of the vanadium–oxygen bonding. The occurrence of bands between 1000 and 800 cm^{-1} (spectrum (c); $y = 2$) is caused by lithium vanadate LiV_2O_5.

The spectra (e) - (h) correspond to samples obtained after the Li/V_2O_5 system was discharged to definite y values ($y = 1$; 2; 2.35; > 3) and then charged. When the system was discharged only to $y = 2$, the band at 800 cm^{-1} was again present after charging. However, the band was absent when the system was discharged to $y \geq 2.35$. After discharge to this value, subsequent charging results in the sample having LiV_2O_5 (spectrum (g)). No further changes in the IR spectrum were observed at discharge depths to $y > 2.35$. This means that the crystal structure obtained cannot be electrochemically transferred again into the initial structure and the vanadium reduced to V^{3+} cannot be oxidized back to V^{4+} or V^{5+}.

Acknowledgements

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