

VANADIUM OXIDES AS ELECTRODE MATERIALS FOR RECHARGEABLE LITHIUM CELLS

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Summary

Lithium insertion has been studied in a number of vanadium oxides with special regard to their application as the active component in rechargeable lithium cells. Very high stoichiometric energy densities for lithium insertion are found for several of these materials. As these oxides are poor electronic conductors, however, the high energy densities are partially offset by the addition of conductive material necessary for practical electrodes. Cycling results are reported for the three-dimensional oxide V_6O_{13} , the layered $Li_{1+x}V_3O_8$, and the non-crystalline V_2O_5 xerogel.

Introduction

In a variety of ternary lithium-vanadium oxides, the lithium content can be varied between certain limits without major changes in the vanadium-oxygen lattice. This process is called lithium intercalation or lithium insertion, and can be described as the introduction/extraction of mobile lithium ions, together with their compensating electrons, as *guest species* into a rigid *host structure*.

Traditionally, oxides that are stable with variable lithium composition at high temperature (> 300 °C) are called *vanadium bronzes*. Many oxides which do not form these thermodynamically stable bronzes can still accommodate large amounts of lithium at ambient temperature, forming kinetically stable insertion compounds. These compounds owe their existence to the very high activation energy required to break vanadium-oxygen bonds, whereas lithium is easily introduced into these open structures.

Lithium insertion has been studied in a number of vanadium oxides, particularly with regard to their application as the active component in rechargeable lithium cells with a polymer electrolyte.

Experimental

The reversible composition interval and the potential *versus* composition relationships (e.m.f. curves) were studied by conventional electrochem-

ical techniques (*i.e.*, cyclic voltammetry and constant-current cycling) using thin-layer positive electrodes ($< 100 \mu\text{m}$) and metallic lithium as the negative electrode. The electrolyte was either a 1 M solution of LiAsF_6 in propylene carbonate (PC) for ambient temperature applications, or thin sheets ($30 - 50 \mu\text{m}$) of polymer electrolyte (LiCF_3SO_3 dissolved in poly(ethylene oxide) (PEO) in the molar ratio $\text{Li}:\text{O} = 1:15$) for measurements at $120 - 150^\circ\text{C}$. These cells were also used in cycling experiments. Cycling was performed with constant-current discharge, followed by current-limited potentiostatic recharge. To facilitate transport in the positive electrodes, the latter were made as composites of electrolyte, acetylene black, and insertion material.

In the screening of oxides for the ability to react with lithium and in the synthesis of larger amounts of lithium-inserted material for structural investigations, etc., lithiation was performed chemically with 0.5 M *n*-butyllithium (*n*-BuLi) dissolved in hexane at 25°C .

The oxides were synthesized according to the following procedures:

(i) $\alpha\text{-V}_2\text{O}_5$, V_6O_{13} , and $\text{VO}_2(\text{B})$ were prepared by thermal decomposition (425°C) of NH_4VO_3 in O_2 , N_2 , and H_2/Ar , respectively [1, 2].

(ii) $\beta\text{-Li}_{0.322}\text{V}_2\text{O}_5$ was synthesized by annealing the exact proportion of $\alpha\text{-LiV}_2\text{O}_5$ and $\alpha\text{-V}_2\text{O}_5$ in an evacuated, sealed ampoule at 500°C for 16 days [3].

(iii) $\text{Li}_{1+x}\text{V}_3\text{O}_8$ was prepared from LiCO_3 and $\alpha\text{-V}_2\text{O}_5$. After degassing the CO_2 at 400°C for 1 day, the mixture was melted (700°C) and cooled rapidly to avoid oxygen loss [4].

(iv) The layered LiVO_2 was synthesized by reaction of NH_4VO_3 and LiCO_3 in H_2/Ar atmosphere at 700°C for 2 days.

(v) V_3O_7 , V_4O_9 , and V_5O_{11} were prepared by equilibrating correct amounts of $\alpha\text{-V}_2\text{O}_5$ and V_6O_{13} in sealed ampoules at 500°C . $\text{LiV}_5\text{O}_{12}$ was produced similarly by reaction of a mixture of LiVO_3 , V_6O_{13} , and $\alpha\text{-V}_2\text{O}_5$ at 600°C .

(vi) The V_2O_5 xerogel, here named $\text{V}_2\text{O}_5(\text{X})$, was synthesized by polymerising an aqueous solution of decavanadic acid and then dehydrating at 230°C . The residual water content was $0.1 \text{ H}_2\text{O}/\text{V}_2\text{O}_5$ [5].

Results and discussion

In order that insertion materials may be used as active components in lithium cells, they must be able to accommodate appreciable amounts of lithium ions. Therefore, suitable materials are most likely to be found among those with an open structure and a relatively low density. The materials selected for this investigation were primarily oxides with a relatively low density compared with the rutile modification of VO_2 ($\rho = 4.67 \text{ g cm}^{-3}$) into which lithium ions are not inserted in appreciable amounts [6].

The composition intervals for lithium insertion in the investigated V oxides are shown in Table 1, together with stoichiometric energy densities calculated from e.m.f. curves. In some instances, there is an increase in the

TABLE 1
Physical properties of lithium–vanadium oxides

Substance	Density (g cm ⁻³)	Composition range	Stoichiometric energy density (W h kg ⁻¹)
Li _{1+x} V ₃ O ₈	3.49 (x = 0.5)	0.12 < x < 2 (25 °C)	440
		0 < x < 3 (120 °C)	650
α-Li _x V ₂ O ₅	3.40 (x = 0.0)	0 < x < 1 (25 °C)	460
		0 < x < 2 (120 °C)	750**
β-Li _x V ₂ O ₅	3.65 (x = 0.3)	0 < x < 1.33 (25 °C)	590
Li _x V ₂ O ₅ (Xerogel)	—	0 < x < 1.1 (120 °C)	430
Li _x V ₅ O ₁₂	—	0.73 < x < 4.45 (n-BuLi)*	
Li _x V ₃ O ₇	3.58 (x = 0.0)	0 < x < 4 (n-BuLi)*	
Li _x V ₄ O ₉	—	0 < x < 4 (n-BuLi)*	
Li _x V ₅ O ₁₁	—	0 < x < 5 (n-BuLi)*	
Li _x V ₆ O ₁₃	3.92 (x = 0.0)	0 < x < 8 (25 °C)	890
Li _x VO ₂ (B)	4.05 (x = 0.0)	0 < x < 0.6 (25 °C)	390
		0 < x < 0.82 (120 °C)	550
Li _{1-x} VO ₂	4.40 (x = 0.0)	0 < x < 1 (120 °C)	820**

*In these materials, the composition interval cited is determined from n-BuLi intercalation. Cyclic voltammetry has shown that lithium insertion is reversible in the major part of this interval.

**The host structure of these materials is not kinetically stable in the composition interval cited. Thus, the quoted stoichiometric energy density given cannot be attained on cycling.

reversible composition range at the higher temperature when compared with room temperature. This is due to improvements in kinetic performance, but as most of the intercalated V oxides are only metastable, further increases in temperature could lead to breakdown of the host structure. The consequence would be loss of reversibility and decrease in energy density, as displacement reactions generally proceed at lower potentials than insertion reactions.

E.m.f. data for a number of these oxides are collected in Fig. 1 as a function of the mean oxidation number of V. The e.m.f. curves for the kinetically stable compounds fall in a relatively narrow region, with some dependence on the oxidation number. This demonstrates that the magnitude of the e.m.f. is largely governed by the “chemistry” of the Li–V–O system, whereas the structure of the host lattice determines the magnitude of the composition interval and the shape of the e.m.f. curve.

Based on the data given in Fig. 1, the upper limit of the reversible stoichiometric energy density obtainable within the Li–V–O system is estimated to be 1200 W h kg⁻¹, assuming that the entire interval from V(5) to V(3) can be utilized for lithium insertion.

Common to most of these oxides is a tendency for the inserted lithium ions to condense in several phases during discharge. Because of this phase separation, the e.m.f. curve shows steps, or plateaux, as the e.m.f. is com-

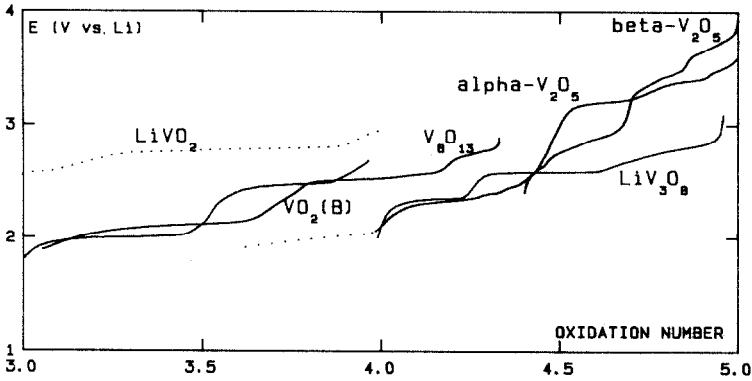


Fig. 1. E.m.f. curves for Li insertion in various Li-V oxides (at 25 °C or 120 °C) as a function of the mean oxidation state of vanadium. Dotted lines indicate that these reactions lead to changes in the host lattice.

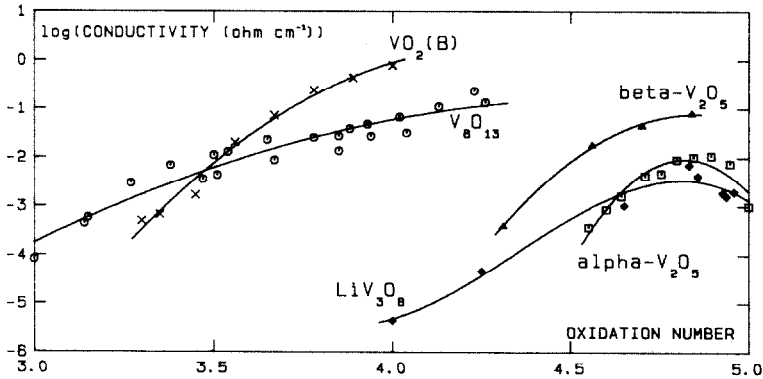


Fig. 2. Electronic conductivity of compressed powders (at 70 MPa) of various Li-V oxides as function of the mean oxidation state of vanadium.

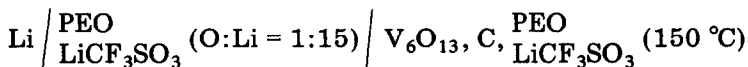
position-independent within a two-phase region. The phase shifts are accompanied by abrupt changes in the unit-cell dimensions, typically an expansion of a few percent. These volume changes could be one of the causes of the capacity deterioration observed during cell cycling, breaking the integrity of the electrode composite.

The electronic conductivity (σ_e) was measured on the compressed powders (at 70 MPa) of a number of lithium-inserted vanadium oxides. The measured conductivity was not corrected for porosity or intergranular resistances, but a general trend is still clear from the results shown in Fig. 2: the electronic conductivity decreases by orders of magnitude upon lithium insertion, except at oxidation states close to V^{5+} where an initial increase is seen. Because of the low electronic conductivity of the fully lithiated oxides, conductive material must be added to electrodes using vanadium oxides as the active material.

Cell cycling

Among the vanadium oxides with 3-dimensional crystal lattices, V_6O_{13} has by far the highest reversible stoichiometric energy density (890 W h kg^{-1} , 25°C), and this material has been the subject of many investigations [7, 8].

In Fig. 3, the discharge capacity of a cell of the following type:



is shown as a function of the cycle number. Initially, the cell was discharged with a current corresponding to a stoichiometric discharge time of 4 h. During the first 10 cycles, the material utilization falls from 8 $\text{Li/V}_6\text{O}_{13}$ to 3.6 $\text{Li/V}_6\text{O}_{13}$, but during the next 300 cycles, the capacity remains fairly constant. In cycle 200, the current density is decreased by a factor of 10, causing a larger part of the original capacity, namely, 5 $\text{Li/V}_6\text{O}_{13}$, to be utilized. During cycles 350 - 575, where the cell capacity drops to 1.3 $\text{Li/V}_6\text{O}_{13}$, there is still 5 - 6 $\text{Li/V}_6\text{O}_{13}$ available for discharge when the load is decreased by a factor of 10. After cycle 575, all cycles are carried out with the decreased load ($C/40 \text{ h}$). The capacity now decreases to 0.02 $\text{Li/V}_6\text{O}_{13}$ in cycle 730. In the last cycle, however, when the load is further decreased by a factor of 10 ($C/400 \text{ h}$), there is still a capacity of 4.7 $\text{Li/V}_6\text{O}_{13}$ available for discharge. The cell had then been in continuous operation for 10 months. X-ray diffraction showed that the electrode still contained V_6O_{13} and that no new Li-V-O compounds had been formed, although broadening of the XRD peaks indicates some loss of crystallinity.

It is thus concluded that V_6O_{13} is fully capable of withstanding a large number of deep-discharge cycles, but that improvements in the electrode preparation technique are necessary in order to avoid degradation of the electrode's kinetic performance upon cycling.

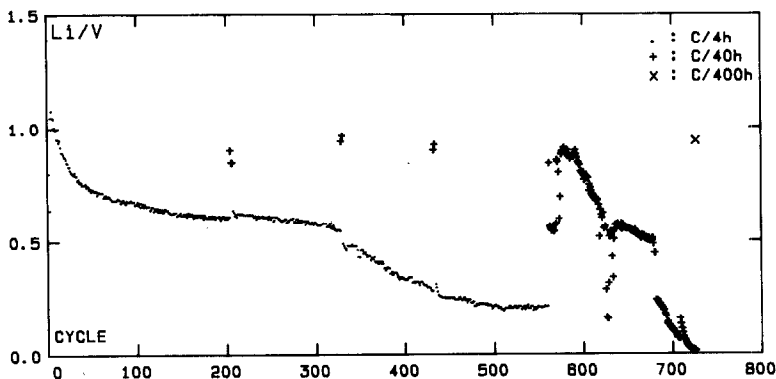


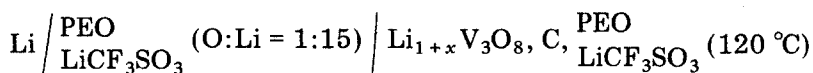
Fig. 3. Discharge capacity vs. cycle number for V_6O_{13} cell. Discharge rates: \cdot , $C/4 \text{ h}$; $+$, $C/40 \text{ h}$; \times , $C/400 \text{ h}$.

Two oxides with layered (two-dimensional) structures have been investigated, namely, $\text{Li}_{1-x}\text{VO}_2$ and $\text{Li}_{1+x}\text{V}_3\text{O}_8$. The structure of $\text{Li}_{1-x}\text{VO}_2$ is analogous to lithium-intercalated TiS_2 . Lithium ions can be extracted from this compound electrochemically, but because of strong electrostatic O-O interaction, the host structure becomes unstable upon lithium-deintercalation, leading to irreversible changes in the structure [9]. This is reflected by the very high potential at which lithium is initially extracted from this material (Fig. 1), but subsequent cycling proceeds at a lower potential and in a smaller composition interval ($\Delta x \cong 0.5$).

However, even in its non-intercalated form, the $\text{Li}_{1+x}\text{V}_3\text{O}_8$ structure is stabilized by interlayer lithium ions. Although mobile, these ions cannot be removed, as this would require oxidation beyond V(5). This compound reacts with n-BuLi yielding $\text{Li}_4\text{V}_3\text{O}_8$. X-ray diffraction analysis shows that the unit-cell parameters do not change significantly up to the composition $\text{Li}_3\text{V}_3\text{O}_8$. Further insertion leads to an increase in the crystallographic *b*-axis and to a slight increase in the interlayer spacing. The net volume expansion is 9%.

In organic electrolyte at ambient temperature, only 2 Li/ V_3O_8 can be cycled, and the potential *versus* composition curve shows pronounced hysteresis. However, with a polymer electrolyte at 120 °C, 3 Li/ V_3O_8 can be cycled reversibly.

In Fig. 4, the discharge capacity of cells of the type:



is shown as a function of the cycle number. To test the influence of volume expansion on the insertion material, two identical cells were cycled over different potential intervals: (a) 3.5 - 2.5 V *versus* Li (2 Li/ V_3O_8); and (b) 3.5 - 2.0 V *versus* Li (3 Li/ V_3O_8). The cells were discharged with a current corresponding to a stoichiometric discharge time of 4 h per Li/ V_3O_8 (*i.e.*, 25 μA

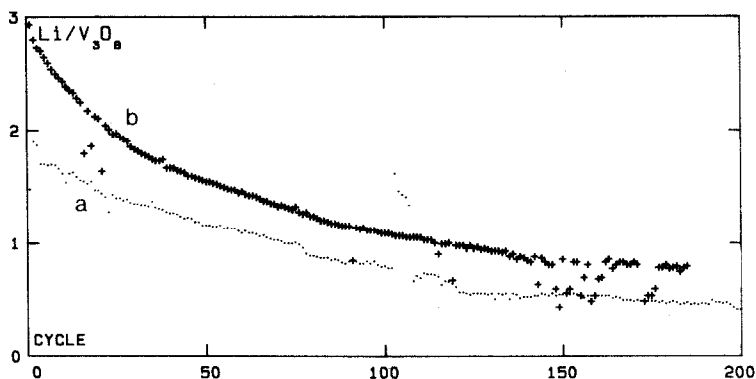


Fig. 4. Discharge capacity *vs.* cycle number for $\text{Li}_{1+x}\text{V}_3\text{O}_8$ cell in potential intervals (a) 3.500 - 2.500 V; (b) 3.500 - 2.00 V. Cell (a) was discharged to 2.0 V in cycles 103 - 107.

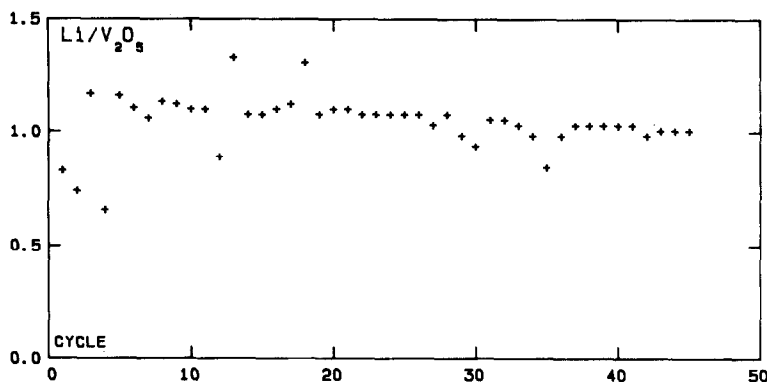
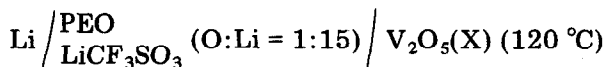


Fig. 5. Discharge capacity vs. cycle number for $V_2O_5(X)$ cell.

cm^{-2}). Initially, the capacity of cell (a) decreases more rapidly than that of cell (b), but after ≈ 50 cycles this difference vanishes, and the capacity loss per cycle corresponds to a cycling efficiency of 99.1% for both cells.

Non-crystalline $V_2O_5(X)$ has also been investigated. After careful dehydration at 230°C , the resulting films were applied directly in lithium cells without addition of conductive diluent. The water remaining in the films appears to be strongly bound, as no adverse effect on the lithium counter electrode was detected in the limited number of cycles carried out with these cells. In Fig. 5, the discharge capacity of a cell of the type:



is shown as function of the cycle number. This cell was cycled in the potential interval $3.5 - 2.2$ V versus Li ($50 \mu\text{A cm}^{-2}$). The discharge curve is nearly linear in this potential region, with none of the inflections and plateaux characteristic of the other V oxides. Despite the scattering of the results, it is clear that cycling of this electrode only causes minor capacity losses. The average cycling efficiency during the first 46 cycles is 99.7%. However, this good performance is accompanied by a modest energy density: 420 W h kg^{-1} for insertion of $1.1 \text{ Li/V}_2\text{O}_5$.

Conclusion

Vanadium oxides offer some of the highest known stoichiometric energy densities for lithium insertion. However, the oxides investigated are rather poor electronic conductors; the conductivity decreases with increase in the lithium content. Thus, the energy densities are offset by the need for the addition of conductive material to practical electrodes.

Even though the lithium-inserted oxides are only metastable, no signs of precipitation of thermodynamically stable Li-V-O compounds are seen, even after prolonged cycling at 150°C . Experiments on $\text{Li}_{1+x}\text{V}_3\text{O}_8$ cells

show that the lattice expansion of the host is not the only cause of the deterioration of the kinetics of the electrode composites on cycling, leading to loss of available capacity for a given load. Improvements in the electrode fabrication technique are needed to alleviate this problem.

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