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LITHIUM INSERTION INTO ORIENTED MICROCRYSTALS AND GELS OF ANHYDROUS AND HYDRATED VANADIUM PENTOXIDE

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Summary

Electrodes composed of pure crystalline orthorhombic V_2O_5 suitable for use as insertion cathodes can be prepared by electrolytic deposition of $(NH_4)_2V_6O_{16} \cdot H_2O$, or by spreading hydrated V_2O_5 gels on graphite cloth and subsequently heating to 350 °C. The insertion of Li into these electrodes can be followed by measurements of open-circuit potential, which show clearly the phase changes that accompany Li insertion. Maximum values of x in $Li_xV_2O_5$ are 1.49 for V_2O_5 made electrochemically and 1.23 for non-stoichiometric V_2O_5 made from a heated gel.

Introduction

Vanadium oxides have been studied recently for possible use as cathodes for rechargeable lithium batteries [1 - 3]. One oxide with promising characteristics is V_6O_{13}, which is prepared by thermal decomposition of NH_4VO_3. For use as electrodes, the oxide is mixed with an electronic conductor (commonly acetylene black) to enhance conductivity, and a polymer binder. However, homogeneous electrodes composed only of a thin layer of a pure vanadium oxide should give more reliable information about intrinsic electrochemical properties, and may also make possible the elimination of binders and electronic conductors. This paper is concerned with the properties of electrodes made from another oxide with promising characteristics, vanadium pentoxide, V_2O_5, on an inert substrate. The V_2O_5 has been prepared via two routes: from amorphous gels and from electrophoretic deposition.

Amorphous vanadium pentoxide gels have been known for many years [4]. Araki *et al.* [5] dried thin films of a xerogel ($V_2O_5 \cdot yH_2O$) on a conducting substrate and found that reversible insertion of lithium occurred. Heating the gel gave several different hydrates, and eventual transformation to orthorhombic V_2O_5 at 300 °C [6]. While the structure of these hydrates

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has been studied using X-ray and electron diffraction and IR [6 - 9], the mechanism of insertion and removal of lithium is not fully understood. Electrochemical deposition of salts with vanadium oxyanions has been described [10 - 13], and recently the preparation of useful electrodes has been achieved from deposits consisting of oriented microcrystals of ammonium hexavanadate monohydrate [13].

Experimental

Conducting supports (carbon cloth: Stackpole fibres-PWB6, platinum, SnO_2 coated glass, stainless steel, nickel sheet, glassy carbon, graphite) were cleaned, and other materials were purified, as described previously [13]. Electrodes of orthorhombic V_2O_5 were prepared by heating oriented microcrystalline deposits of $(NH_4)_2V_6O_{16} \cdot H_2O$ to 300 °C [13]. Amorphous vanadium pentoxide gels were prepared by polycondensation of metavanadate ion, which occurs when ammonium vanadate solutions are passed through a column of Dowex-50 ion exchange resin in hydrogen form [14]. Electrodes of amorphous, non-stoichiometric vanadium pentoxide with different hydration numbers were made by spreading the aged gel on various conducting substrates and allowing it to dry for several hours at room temperature and then briefly at specified higher temperatures.

Both types of deposit were analyzed by scanning electron microscopy (SEM), X-ray powder diffraction using Cu Kα radiation, $\lambda = 0.15405$ nm, differential scanning calorimetry (DSC; Perkin-Elmer DSC-1B), chemical analysis, and differential thermal, thermogravimetric, and differential thermogravimetric analysis (DTA, TGA and DTG; Mettler Recording Vacuum Thermoanalyser 127, using a medium-temperature furnace). Chemical analyses of V(IV) (which gives the amount of Li inserted) and V(V) were determined on samples using the two-step titration method described previously [13].

Open circuit potentials were measured for various values, x, of inserted lithium ions, according to the general formula $Li_x V_2O_{5-\delta} \cdot yH_2O$, using a cell containing counter, working, and reference electrodes of platinum, oxide, and Ag–AgCl, respectively. The electrolyte was 0.5 M lithium perchlorate in propylene carbonate (PC). All experiments were performed under purified nitrogen. Controlled currents were applied using a PAR Model 273 potentiostat interfaced to a microcomputer and graphics plotter. The programmed sequence of charge injection consisted of: pass constant current, density 0.1 - 1 mA cm^{-2}, for a measured time; turn off current; stir cell for 100 s to remove diffusion layers; stop stirring, wait 15 s; measure open circuit potential. Typically, 70 values of potential at intervals of 0.3 C were accumulated. The total value of x was determined from chemical analysis at the end of the experiment.

Results and discussion

Formation and nature of electrodes

The changes that take place in forming amorphous gels by polycondensation on an ion exchange column can be followed from the predominance diagrams of Baes and Mesmer [15] and the work of Lemerle et al. [14]. SEM of an electrodeposit and dehydrated gel are shown in Fig. 1. The uniformly-sized crystals of $(NH_4)_2V_6O_{16} \cdot H_2O$ are highly oriented and this, as well as the mechanism of electrodeposition, has been discussed elsewhere [13]. Chemical analysis of a gel before and after heating at 100 °C in air showed that the gel initially contains about 10 mol% V(IV), then loses water and oxygen. DTA, TGA, and DTG curves (Fig. 2) show that as the gel is heated, loss of weight occurs in three discrete steps. When heated in argon, these steps correspond to three endothermic DTA peaks at 160 °C, 180 °C, and 245 °C. In air the third DTA peak is offset by exothermic oxidation, and the rate of weight loss is slowed. Finally, chemical reduction of the sample heated in air stops at 315 °C and the weight increases rapidly.

X-ray diffraction experiments showed that the gel crystallizes after heating at 350 °C; in argon this crystallization gives a gradual exothermic shift, while in air the process is overwhelmed by the simultaneous oxidation, which gives rise to the very large exothermic peak in DTA. DSC experiments in both air and argon atmospheres have shown the same phenomena: first, endothermic water and oxygen loss, then exothermic oxidation and crystallization. DTA and DSC results showed that no amorphous, unhydrated phase exists; the transition from amorphous gel to crystalline $V_2O_{5-\delta}$ ($\delta = 0.9$) has $\Delta H = -3$ kJ mol^{-1} (from DSC) in an inert atmosphere. These results are similar to those reported by Aldebert et al. [6] if it is assumed that their results were obtained using samples heated in an inert atmosphere. They attributed all changes to loss of water except that at the highest temperature, which was attributed to crystallization. However, they failed to note that the gels have an initial content of V(IV), and that this increases on heating.
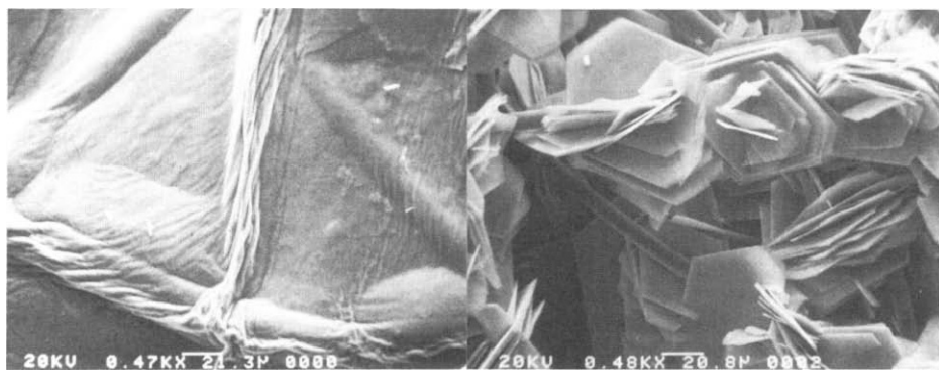

Fig. 1. Scanning electron micrographs of: (a) hydrated V_2O_5 gel, (b) electrodeposited $(NH_4)_2V_6O_{16} \cdot H_2O$, both on carbon fibre cloth. Magnification ×480, bar length 21 μm.
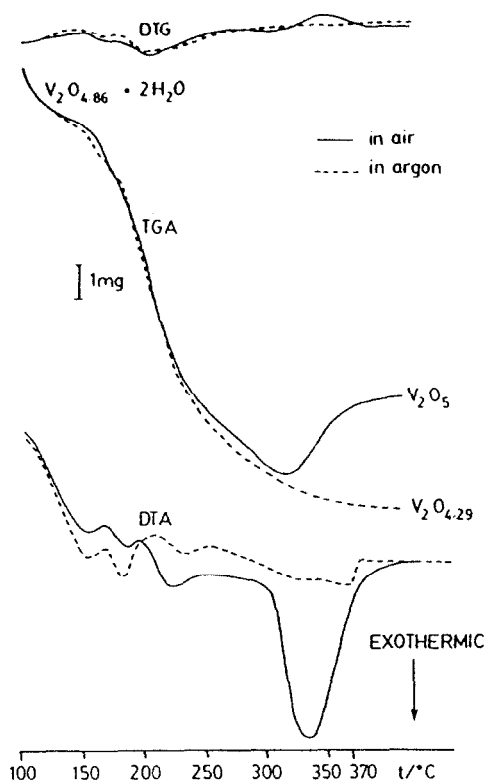
Fig. 2. Thermal analytical curves for hydrated V_2O_5 gels. Samples (70 mg) heated at 6 K min^{-1} to 370 °C, then held there for 10 min.

From the range of possible levels of hydration and oxidation for gels, three compositions were prepared for use as electrodes: dihydrated ($V_2O_{5-\delta} \cdot 2H_2O$, $\delta = 0.14$, by drying the aged gel from the ion exchange column at room temperature), hydrated ($V_2O_{5-\delta} \cdot 1.4H_2O$, $\delta = 0.42$, by drying the gel at 100 °C), and dehydrated ($V_2O_{5-\delta}$, $\delta = 0.07$, by drying the gel at 350 °C). The dry gel had a thickness of about 10 μm.

Insertion into electrodes: open circuit experiments

Carbon fibre cloth proved to be the substrate to which the gel adhered best without flaking during heating to various stages of hydration. Lithium ions were inserted into various electrodes to give lithium vanadium bronzes. Potassium and sodium ions could not be inserted in either the hydrated or the unhydrated V_2O_5 electrodes in non-aqueous solutions, probably because of their larger diameters. This was confirmed by X-ray diffraction, where no change in structure from the original V_2O_5 electrode was found.

The electrochromic behaviour of both the electrodeposits and the gel deposits was quite apparent. Starting from the orange-red of V_2O_5, insertion of Li^+ or H^+ caused a gradual colour change from light to dark

green to almost black as the limit of insertion was approached. The purple gels turned black on insertion of Li. These processes were reversible: for example, starting with a greenish-colored bronze, removal of Li^+ and electrons left a deposit with the same orange-red colour of V_2O_5. As the amount of inserted Li increased in electrodeposited V_2O_5, there was a corresponding reduction of V(V) to V(IV), as expected for the reaction given above. Lithium, therefore, can be readily inserted into pure V_2O_5 electrodes to form a ternary phase [16, 17].

The open circuit potentials plotted against x for the electrodes made from hydrated V_2O_5 gels and the electrodeposit $(NH_4)_2V_6O_{16} \cdot H_2O$ are shown in Fig. 3. As expected, the dihydrated gel shows no sharp potential changes to indicate any phase changes. As seen in Fig. 3, the maximum amount of lithium inserted for this particular electrode was $x = 1.23$. However, the highly reduced, hydrated gel electrode shows evidence of a distinct step, indicating that major restructuring and some crystallization of the gel is occurring. This was supported by X-ray diffraction of gel electrodes heated under similar conditions. The maximum amount of lithium inserted was found to be $x = 1.52$. The crystalline, hydrated $(NH_4)_2V_6O_{16}$ electrodeposit shows evidence of two phases at $x = 0.05$ and in the range $x = 0.1 - 0.35$, the maximum amount of lithium inserted being $x = 0.48$. Ammonium ions and water presumably are located between the vanadium–oxygen layers in hy-
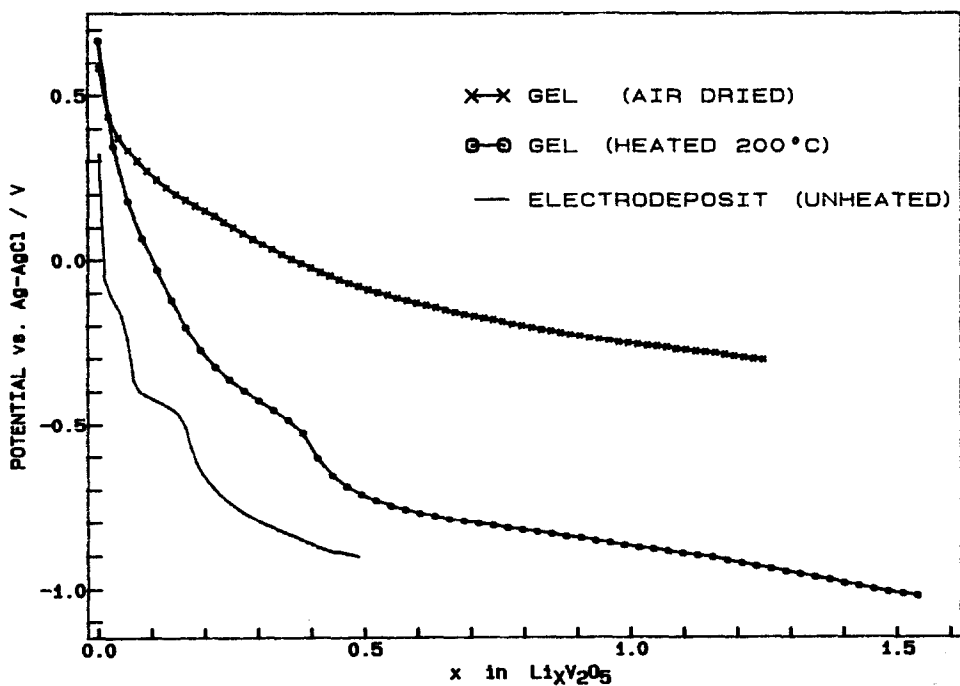

Fig. 3. Potential–x curves for electrodeposited $(NH_4)_2V_6O_{16} \cdot H_2O$ and $V_2O_{5-\delta} \cdot yH_2O$ gels. Air-dried gel, $\delta = 0.14$, $y = 2$; heated gel, $\delta = 0.42$, $y = 1.4$.
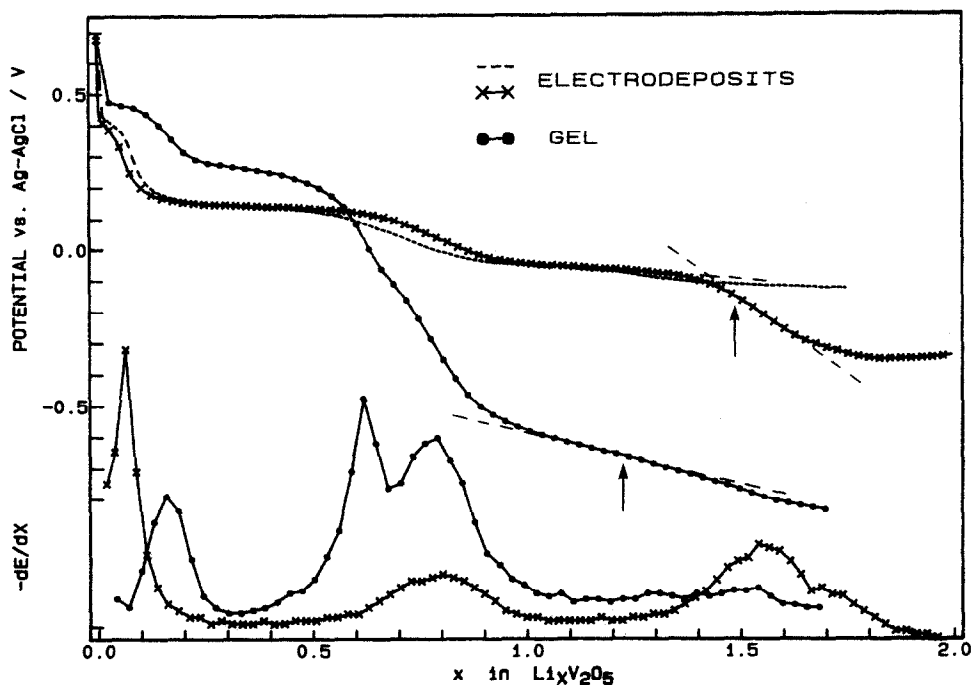
Fig. 4. Potential–x and dE/dx–x curves. Electrodeposits (V_2O_5) heated at 320 °C: x, current density 0.75 mA cm^{-2}; — — —, current density 0.25 mA cm^{-2}. Gel ($V_2O_{4.93}$) heated at 350 °C: current density 0.3 mA cm^{-2}. Arrows show maximum x from chemical analysis.

drated V_2O_5, and have a definite influence on the amount of Li$^+$ that can be inserted.

The open circuit potentials, E, and also dE/dx, are plotted against x in Fig. 4 for the electrodes made from electrodeposited material heated to form orthorhombic V_2O_5, and from gels heated to form non-stoichiometric V_2O_5. The three phases for lithium insertion into V_2O_5 to form $Li_1V_2O_5$ are clearly observed, and lie within the ranges for α, ϵ and δ bronzes given in other work [16 - 19]. It has been proposed that additional lithium present at $x > 1$ causes disproportionation into V_2O_3 and $LiVO_3$ [20]. Liaw et al. [21] mention a phase change occurring at $x = 1.33$ with the two plateau voltages close together, indicating low stability of $LiVO_3$; at this point more V_2O_3, as well as Li_3VO_4, is formed. From chemical analysis our results yield the maximum values of lithium inserted to be $x = 1.49$ for V_2O_5 made electrochemically and $x = 1.23$ for the non-stoichiometric V_2O_5 from a heated gel. These values agree very well with the actual charge injected if the two linear portions of the final potential drop are extrapolated, as shown in Fig. 4. Hence, the final phase change for these electrodes of pure V_2O_5 appears to be similar to that found by Liaw et al. [21] at $x = 1.33$ but lithium insertion with the reduction of V(V) to V(IV) does not occur after

this phase change. The potentials for $x > 1.33$ depend on the current density for insertion, and perhaps on the sample size, and the reasons for this behaviour are being investigated.

Conclusion

Electrodes composed of pure, crystalline, orthorhombic V_2O_5 deposits and suitable for use as insertion cathodes can be prepared on suitable substrates either by electrophoretic deposition of $(NH_4)_2V_6O_{16} \cdot H_2O$ or by spreading hydrated V_2O_5 gels, followed by heating to 350 °C. Lithium insertion into the unheated deposits depends strongly on the presence of water or ammonium ions, which suggests that these substances, even in contact with non-aqueous solvents, remain in place in interlayer positions in the lattice and block insertion of lithium ions. Values of the number of lithium ions per vanadium in the lattice support this view. Lithium insertion in the crystalline deposits of pure V_2O_5 occurs in three stages, each characterized by a specific coordination number for the inserted ion, and a range of values for the interlayer lattice spacing.

Acknowledgements

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