

## Thin-film vanadium oxide electrodes for lithium batteries

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### Abstract

Vanadium pentoxide films prepared by three techniques have been used as electrodes in solid-state batteries. The three types of films behave differently as host materials for lithium insertion. The electrochemical properties of sputtered films are very dependent on the oxygen partial pressure in the sputter gas, as is the sputter rate. The best electrochemical properties are obtained with a high oxygen partial pressure, whereas it is necessary to use lower oxygen pressures to reach acceptable sputter rates. Vanadium oxide films prepared by physical vapour deposition apparently forms compact layers that break under cycling. These films have a relatively low capacity for lithium insertion and the transport kinetics are slow. This material is not suited for electrode material. Vanadium oxide xerogels appear to be good alternatives to the sputtered films, although the capacity for lithium insertion is lower. The properties of these films can be varied by heat treatment, and good cycling performance has been demonstrated.

### Introduction

Solid-state lithium batteries have prospective applications as on-chip power sources for integrated circuit devices. These applications will benefit from the extremely low self-discharge of Li systems, and from the ability of batteries with intercalation electrodes to withstand prolonged periods of potentiostatic charge.

A large variety of thin-film deposition techniques are available for the fabrication of such batteries, techniques that are already well developed and in use for the manufacture of electronic devices. The properties of electrodes and electrolytes prepared by these techniques are not, however, trivial extrapolations of the results obtained with classical bulk materials. The resulting films often have very high defect concentrations, and the deposition technique will convey specific properties to electrode and electrolyte layers, making them different from layers deposited with other techniques.

In this work, electrode films prepared by radio frequency (RF) sputtering, physical vapour deposition (PVD) and solvent casting are compared with a bulk material, crystalline vanadium pentoxide.  $V_2O_5$  has been chosen as the basis material, as it meets the key requirements for electrode materials for this type of cells. It has a very high energy density and is, during the first deep discharge, converted to a modified form with a smoothly-sloping voltage characteristic, which easily lends itself to state-of-charge indication.

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Vanadium oxide electrodes were investigated in cells with poly(ethylene oxide)-based polymer electrolyte and a large excess of metallic Li as negative electrode. By using these well-characterized components, spurious effects from the other cell components are minimized.

## Experimental

The sputter deposition of vanadium oxide films was carried out at Risø National Laboratory using a CIT-Alcatel RF-apparatus (model SCM 451) with a 2 kW Dressler MGP power generator. Films were deposited on cleaned 11  $\mu\text{m}$  Ni foils using the following sputtering conditions: target-substrate distance: 5–9 cm; total pressure: 1 Pa Ar/O<sub>2</sub> mixture and total power: 150–250 W. The deposition rate was heavily dependent on the gas composition. The rate was approximately 10 times lower in pure O<sub>2</sub> than it was in Ar.

Vanadium oxide films were deposited on Ni foils using an Edwards SpeediVac Coating Unit. The starting material was 100–200 mg vanadium pentoxide in a Ni boat, resistance heated in a vacuum of  $0.5\text{--}1 \times 10^{-2}$  Pa. It was heated 2–5 min at a distance of 4–5 cm from the Ni foil. The source material lost 20–30 mg during evaporation, producing yellow-brown films of 0.5–1  $\mu\text{m}$  thickness.

The vanadium oxide xerogel was synthesized by the gel process developed by Lemerle *et al.* [1] and Livage *et al.* [2]. A decavanadic acid solution prepared by passing a NaVO<sub>3</sub> solution through a cation (H<sup>+</sup>) exchanger, polymerized spontaneously giving a clear, red-brown gel. This gel was spread manually on Ni foil, slowly dehydrated and finally heat-treated either at 100 °C in vacuum (<1 Pa) or at 300 °C in air.

Electrochemical characterization of the films was performed in solid-state cells with polymer electrolyte: Li|PEO–LiCF<sub>3</sub>SO<sub>3</sub>;  $\sim 12[\text{EO}]/[\text{Li}]|\text{Li}_x\text{V}_2\text{O}_5\text{--}y$ . The cells were cycled galvanostatically at 100 °C between preset voltage limits. The same current density was used during discharge and charge. At the end of charge the cell was kept potentiostatically at the upper voltage limit until the current had decreased by 90%. This was done to ensure that the electrodes were in well-defined states at the start of each discharge. By numerical differentiation the corresponding ‘differential capacity’,  $dx/dE$ , curves were obtained. For convenience the differential capacity during recharge is plotted as positive values. In this way, curves similar to cyclic voltammograms are obtained.

The vanadium content of the electrochemically investigated films was determined spectrophotometrically after completion of the cycling experiments. Due to the rather small amount of vanadium oxide present in each electrode (0.5–5  $\mu\text{mol}$ ), an appreciable uncertainty ( $\sim 10\text{--}20\%$ ) is associated with some of the results of these analyses. The amount of Li intercalated into the vanadium oxides, as given by the composition parameter  $x$ , can thus not be calculated exactly. The results presented are however judged to be fair representatives of a large number of cells.

## Results and discussion

Crystalline V<sub>2</sub>O<sub>5</sub> has been thoroughly characterized as electrode material in Li cells, see refs. 3 to 6. During the first discharge (Fig. 1) several plateaus in the discharge curve are seen. They show up even more clearly as peaks on the  $dx/dE$  plot. Each plateau corresponds to the formation of a new ordered Li <sub>$x$</sub> V<sub>2</sub>O<sub>5</sub> structure, and these features are retained in the subsequent recharges and discharges as long

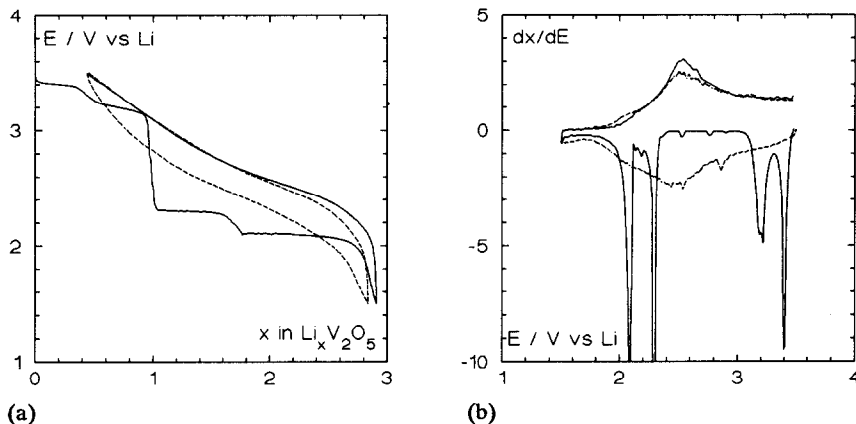


Fig. 1. (a) Potential ( $E$ ) vs. composition ( $x$ ), and (b) differential capacity ( $dx/dE$ ) vs. potential for lithium insertion into  $\text{Li}_x\text{V}_2\text{O}_5$  ( $50 \mu\text{A}/\text{cm}^2$ ). The first two cycles are shown, the second as broken line.

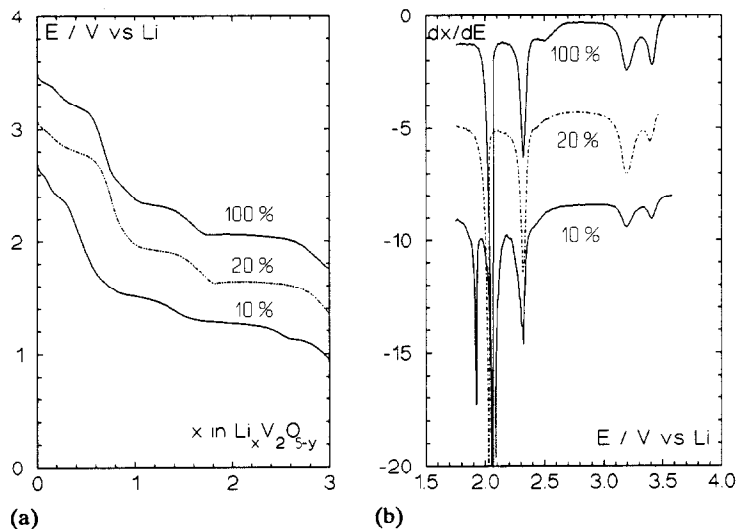


Fig. 2. (a) First discharge curves and (b) corresponding capacity curves ( $dx/dE$ ) for lithium insertion into vanadium oxide films sputtered in argon with 10, 20 and 100%  $\text{O}_2$  ( $10 \mu\text{A}/\text{cm}^2$ ). The 10 and 20% curves are displaced downward for clarity (10%: 400 mV and 4  $dx/dE$  units; 20% twice these amounts).

as the discharge is limited to 2.2 V. At this voltage 1.8 Li per  $\text{V}_2\text{O}_5$  unit has been inserted. When  $\text{V}_2\text{O}_5$  is further discharged as in Fig. 1, the structure of the host lattice breaks down and the cell voltage in subsequent recharges and discharges follows a smoothly-sloping curve with no sudden changes in gradient. This is indicative of an amorphous host material.

Good cycling performance has been obtained with such converted electrodes [6] and the stoichiometric energy density is high: 790 W h/kg has been calculated for the second cycle in Fig. 1, only for pure cathode material. The smooth-voltage characteristic

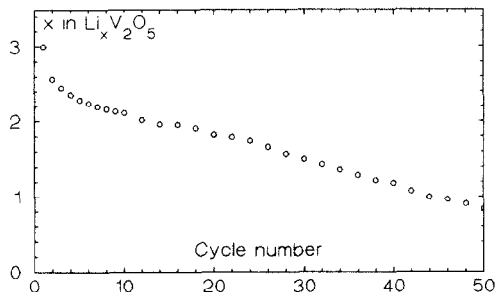


Fig. 3. Discharge capacity as function of cycle number for lithium insertion into a vanadium oxide film sputtered in 10%  $O_2$ . The cell load is  $50 \mu A/cm^2$ ,  $C/15$  h.

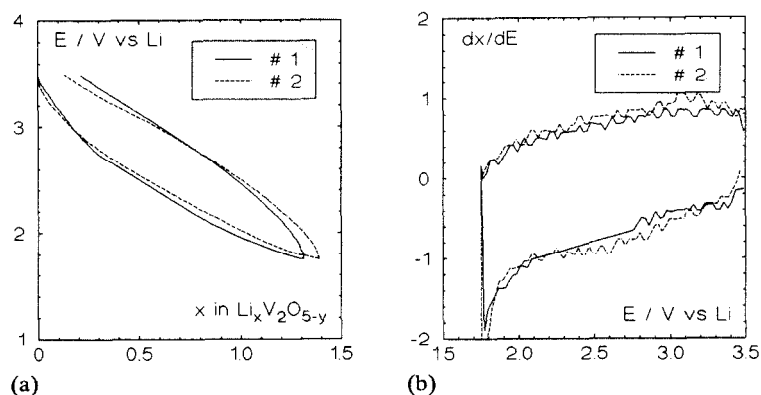


Fig. 4. (a) Potential vs. composition, and (b) differential capacity ( $dx/dE$ ) vs. potential for lithium insertion into a vanadium oxide film made by physical vapour deposition ( $10 \mu A/cm^2$ ).

is well suited for micropower sources in 'intelligent' devices as the cell voltage directly indicates the state-of-charge of the battery. The volume changes of the electrode during cycling are also expected to be more uniform when using the amorphous material instead of crystalline  $V_2O_5$ .

The electrochemical properties of a series of three sputtered vanadium oxide films prepared with 10, 20 and 100%  $O_2$  in the sputter gas are compared in Fig. 2 where the voltage-composition curves and the corresponding differential capacity obtained during the first discharge are shown.

The film sputtered in pure  $O_2$  behaves similarly to crystalline  $V_2O_5$ : two capacity peaks between 3.0 and 3.5 V and two narrow peaks (potential plateaus) at 2.4 and 2.1 V are observed. A small 'nucleation overvoltage' is seen as a minimum in the discharge curve close to  $x=1.7$ , indicating that some degree of long range order must exist in this material. In the high voltage region there are, however, some notable differences between the behaviour of this film and crystalline  $V_2O_5$ ; the capacity peaks are broader and cover a more narrow composition range,  $0 < x < 0.8$  compared with  $0 < x < 1$  for crystalline  $V_2O_5$ . The voltage curve is also less steep in the transition between the two plateau regions. These differences show that the oxide of this film might contain some (less than 20%) reduced vanadium, V(IV), and that this oxide is certainly less crystalline than bulk  $V_2O_5$ . The film sputtered in 20%  $O_2$  behaves in

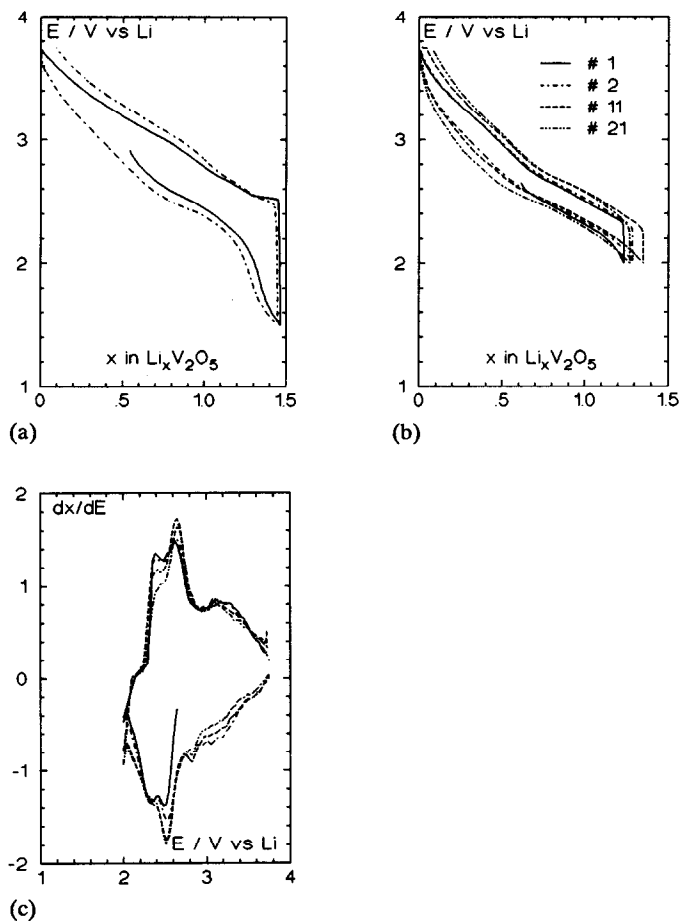


Fig. 5. Potential vs. composition, and differential capacity ( $dx/dE$ ) vs. potential for lithium insertion into a vanadium oxide xerogel film (heat treated at 100 °C); (a) discharge to 1.5 V, (b) and (c) discharge to 2.0 V; current density 50  $\mu\text{A}/\text{cm}^2$ .

a very similar way, but the film sputtered in 10%  $\text{O}_2$  is different; it still has the same peaks as the two other films, but the area under the high-voltage peaks is now much smaller and a new peak at 1.9 V has emerged. With films sputtered in pure Ar, nearly all the capacity in the first discharge is accessed in the plateau at 1.9 V.

Recharge of these films after the initial discharge to 1.5 V leads to a smooth and featureless voltage curve, as was seen with bulk  $\text{V}_2\text{O}_5$ . In Fig. 3, the capacity evolution of a cell operated between 3.5 and 1.75 V is shown. The average of the cycling efficiency, defined as the ratio between the discharge capacities of two subsequent cycles, is 97.5%.

The vanadium oxide films prepared by PVD were apparently completely amorphous as no inflexions or plateaus appeared in the discharge curves, Fig. 4. When discharged to 1.75 V, the highest amount of Li inserted was never more than approximately 1.5 Li per  $\text{V}_2\text{O}_{5-y}$  unit. The cycling behaviour was erratic; some cells only attained the maximal capacity after tens of deep cycles, whereas other cells — as that shown

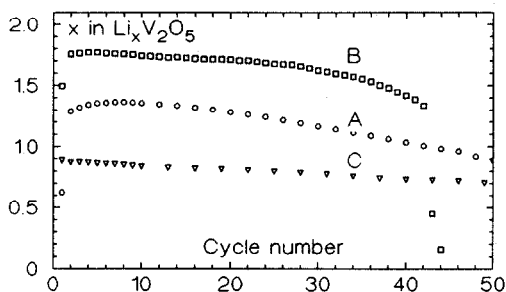


Fig. 6. Discharge capacity as function of cycle number for lithium insertion into vanadium oxide xerogel films. The cell load is  $50 \mu\text{A}/\text{cm}^2$  ( $C/2$  h). (A) film heat-treated at  $100^\circ\text{C}$ , discharge to  $2.0$  V; (B) film heat-treated at  $300^\circ\text{C}$ , discharged to  $1.5$  V; (C) film heat-treated at  $300^\circ\text{C}$ , discharged to  $2.5$  V.

in Fig. 4 — delivered full capacity from the first few cycles. This behaviour, together with the rather larger hysteresis between charge and discharge curves, indicates that vanadium oxide films deposited by PVD are dense and only allow slow diffusion of Li ions. Apparently, the formation of cracks and defects is necessary in order to utilize the Li capacity. Such a material will not be well suited for single-phase electrodes as these processes also leads to electrode deterioration. All the cells tested failed within few tens of cycles after the maximum capacity was reached.

Vanadium pentoxide xerogel films have been shown to possess an unique turbostratic structure, with layers parallel to the substrate [7, 8]. The layers are made up of ribbon-like particles and the structure is stabilized by physisorbed and chemically-bound water. The amount of water in the air dried gel,  $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ , can be varied reversibly from  $n \approx 1.6$  at ambient conditions to  $n \approx 0.6$  at low vapour pressures or in vacuum [9]. Below  $n = 0.6$  the dehydration is less reversible. The remaining water can gradually be removed upon heating above  $100^\circ\text{C}$ ; by heat treatment at temperatures above  $350^\circ\text{C}$  all water is removed and the gel is converted to orthorhombic vanadium pentoxide.

In order to comply with the strict anhydrous conditions in a Li battery, all reversibly-bound water should be removed from the xerogel electrode films before use. In this work this was ensured by heating to  $100^\circ\text{C}$  in vacuum ( $< 1$  Pa) overnight. In a second set of experiments, the films were further dehydrated by heat treatment at  $300^\circ\text{C}$  in air.

Consistent with previous reports [8] of spontaneous reduction of dried xerogel films, the initial discharge often started at a lower potential than the following discharges, and the first discharge capacity was in these cases considerably smaller than the corresponding recharge capacity. This is seen in the voltage-composition curve in Fig. 5(a) for the first two cycles of a cell with xerogel electrode dried at  $100^\circ\text{C}$ . To facilitate comparison, the first cycle is drawn with  $x$  set to zero at the end of recharge. The cycling curve is rather smooth compared with crystalline vanadium oxides, and there is no evidence of structural rearrangements due to Li cycling. When the discharge is continued down to  $1.5$  V, a large jump in potential is observed when the current is reversed, much larger than that hysteresis at higher potentials. Some electrodes even show a small local maximum in potential immediately after the current reversal. This indicates that the discharge is limited by the number of electronic states and that the electronic conductivity of the xerogel decreases rapidly when the electrode is discharged to this depth. The capacity retention is not very good, only 40% of the maximum capacity is available in cycle 20. This is consistent with previous results for

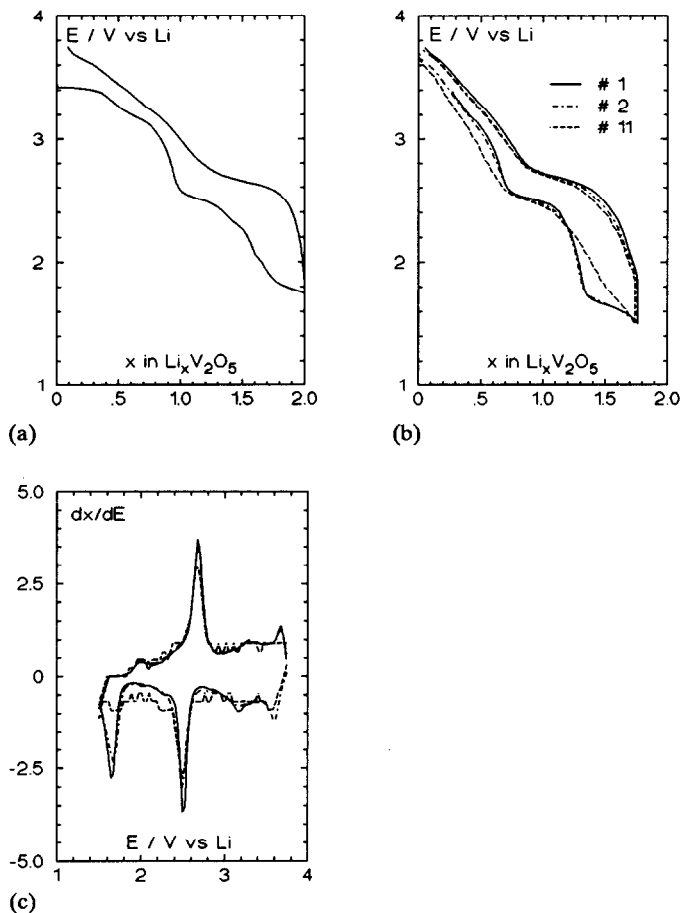


Fig. 7. Potential vs. composition for lithium insertion into a vanadium oxide xerogel film (heat treated at  $300^\circ C$ ): (a) and (b) electrodes prepared from different gels, and (c) differential capacity ( $dx/dE$ ) vs. potential corresponding to (b). The current densities are (a)  $25 \mu A/cm^2$ , and (b)  $50 \mu A/cm^2$ .

cells with liquid organic electrolytes [10]. If however, the discharge is limited to 2.0 V as in Figs. 5(b) and 5(c), the cycling efficiency is greatly improved, and more than 50 cycles can be realized with little or no change in the shape of the differential capacity curves. The evolution of the discharge capacity with cycle number is shown in Fig. 6 curve (A), from which an average cycling efficiency of 99.2% is calculated.

The films heat treated at  $300^\circ C$  show pronounced plateaus and a higher capacity than the films dried at  $100^\circ C$ . Some variation is seen between different film batches, see Figs. 7(a) and 7(b). The main features of the voltage curves are however the same and the differences in electrode utilization is within the experimental uncertainty. The Li ions inserted in this material are apparently accommodated on sets of well-defined sites, but these sites are not equal to the sites found in orthorhombic vanadium pentoxide as evident from comparison of Figs. 1(b) and 7(c). The cycling efficiency of these electrodes is high (99.4%) as seen from Fig. 6 curve (B) and can be raised to 99.5% if the discharge is limited to 2.5 V, Fig. 6 curve (C).

## Conclusions

Vanadium pentoxide films prepared by three different techniques have been demonstrated to behave very differently as host materials for Li insertion.

The electrochemical properties of sputtered films are very dependent on the oxygen partial pressure in the sputter gas, as is the sputter rate. The best electrochemical properties are obtained with a high oxygen partial pressure, whereas it is necessary to use lower oxygen pressures to reach acceptable sputter rates. The cycling properties of the sputtered oxide films are inferior to those obtained with traditional composite electrode films, probably because they do not possess the necessary compliance to accommodate changes in volume of the electrode material during deep cycling.

Vanadium oxide films prepared by PVD apparently form compact layers that break under cycling. These films have a relatively low capacity for Li insertion and the transport kinetics is not as fast as in other vanadium oxides used as host materials for Li insertion. This material is thus not suited as electrode material.

Vanadium oxide xerogels appear to be good alternatives to sputtered films, although the capacity for Li insertion is lower. The properties of these films can be varied by heat treatment and good cycling performance has been demonstrated even in the rather nonuniform films obtained by manual casting. Preliminary results at our laboratory show that the cycling properties are further improved in homogeneous films prepared by spin-coating.

## Acknowledgements

Support from the Danish Ministry of Energy, contracts 1443/87-3, 1443/88-3 and 1443/89-3 is gratefully acknowledged.

Prof. F. W. Poulsen, Risø National Laboratory is thanked for providing the sputtered samples.

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