

# Rechargeable lithium cells with modified vanadium oxide cathodes

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## Abstract

Modified vanadium oxide has been prepared by melting  $V_2O_5$  with additives of 3–3.5% of sodium orthosilicate at 690°C for 3 h followed by fast cooling to an ambient temperature. Charge–discharge characteristics of this oxide were studied as an active cathode material for lithium secondary batteries. The oxide undergoes irreversible transition to become essentially amorphous after first discharge to cut-off voltage of 2 V vs. Li, and then exhibits excellent rechargeability in the 1.5 to 3.9 V potential range. The coin type 2325 size secondary cells have been manufactured and tested with the modified vanadium oxide cathodes and Li–Al alloy anodes. Preliminary shallow cycling modifies the cells' performance and allows to obtain rating capacity 50 mA h in the voltage diapason of 2.0–3.9 V with draining current 0.5 mA. © 1999 Elsevier Science S.A. All rights reserved.

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## 1. Introduction

Vanadium pentoxide was among the first proposed rechargeable cathode materials for lithium batteries [1]. Since then, many researches have been performed in order to achieve higher specific energies, capacities and cycleabilities for these oxides [2]. The most promising results were obtained with some oxides of amorphous or near-amorphous structures [3–5].

Two major routes are presently in use to prepare such disordered structures—the low-temperature and high-temperature ones.

The low-temperature methods are based mainly on sol–gel processing [6–10]. Vanadium oxide gels are commonly made by hydrolysis of organic vanadyl alkoxides (e.g., vanadyl triisopropanoloxide,  $VO(OC_3H_7)_3$ ) in acetone–water solutions [6,11], or through ion exchange processing of sodium metavanadate and gelation of the resultant decavanadic acid [7,8,10,11].

The gels thus obtained are processed further either by drying in vacuo to obtain *xerogel* or by supercritical drying with liquid  $CO_2$  in autoclave that results in other product, *aerogel*. Both products exhibit excellent capacity (especially in thin-film electrodes), up to 3 moles Li per

mole  $V_2O_5$  in the potential range of 3.8 to 1.5 V vs. Li. [7,10]. These materials show sloping discharge curves typical for amorphous substances.

Beside sol–gel processing, two other low-temperature methods for preparation of amorphous vanadium oxides should be mentioned: electrochemical deposition from  $VOSO_4$  aqueous solutions [4,12] and hydrothermal reaction of vanadium pentoxide and lithium hydroxide in the presence of organic template cation [13].

The above-mentioned low-temperature oxides contain certain amount of residual water, commonly more than 0.5  $H_2O$  per  $V_2O_5$  unit. This water is chemically bound, thus supporting the porous and amorphous structure of the matrix. The structure breaks down when the lattice water is removed at the temperatures well above 300°C, and material crystallises losing its advantages in high capacity. Moreover, there are strong evidences for gradual extraction of this water from the cathode into the electrolyte in course of long-term cycling [14]. Evidently, this is harmful for efficient operation of anodic subsystem (lithium, lithium alloy, and carbon). Another significant drawback of such structures is their capability to absorb large quantities of organic solvent molecules [15] that should eventually result in partial dissolution of active cathode components, especially in the case of propylene carbonate-based electrolytes [16]. Thus, in spite of excellent laboratory results, the commercial use of 'low-temperature' amorphous vanadium oxides is still in question.

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The high-temperature routes for preparation of noncrystalline vanadium oxides use the melting of  $V_2O_5$  with some glassifying agents (so-called ‘glass-formers’), such as  $P_2O_5$  [17–20],  $B_2O_3$  [21],  $SiO_2$  and  $Al_2O_3$  [22]. Although less than the low-temperature oxides, such cathode materials still retain rather high specific capacity and long cycling stability [20]. The coin-type rechargeable cells with Li per carbon anodes of 2025 (25 mA h) and 2430 (50 mA h) size have been developed using near-amorphous  $V_2O_5$ – $P_2O_5$  (5 mass.%) composition. These cells were reported to have the excellent cycling characteristics (about 1000 cycles at 20% depth of discharge) and long-term reliability [23].

Unfortunately, the phosphorus oxide as the glassifying agent is highly hygroscopic and electrochemically inactive compound that results in some inconvenience at processing and losses in achieved capacity. We have elaborated other high-temperature route to prepare near-amorphous electrochemically active vanadium oxide that combine small additives of sodium silicate with special thermal treatment. We report also the performance characteristics of coin-type cells with such cathode material and Li–Al anode.

## 2. Experimental

### 2.1. Modification of vanadium pentoxide

Powder of vanadium pentoxide of ‘pure’ grade (Ural Chemical Plant, Russia) with the additive of 3.5% sodium

orthosilicate,  $Na_4SiO_4$  (or equivalent mixture of sodium alkali and silica), was thoroughly ground in a mortar and put into alumina crucible. The resulting mixture was calcined in the muffle furnace at 680°C for 3 h and then the liquid melt was poured out onto the thick (5–8 mm) ambient temperature stainless steel sheet to obtain a layer of 2–3 mm thick. After cooling, the oxide was ground for 4 h in a mill with jasper balls.

The structures of the oxide were investigated by powder XRD method with DRON 3M diffractometer in  $CuK\alpha$  radiation. Three samples were studied: original  $V_2O_5$ , cathode mass before cells’ assembling, and cathode material after the first discharge–charge cycle. The last one was extracted from disassembled cell in the dry glove box, rinsed with propylene carbonate and dried in vacuo at 80°C.

### 2.2. Preparation of the cathode mass

Acetylene black (5 wt.%) and Lonza graphite powder (5%) was added into the mill and ‘dry grinding’ was performed for 2 h followed by ‘wet grinding’ with the addition of 5 wt.% (counting on dry substance) of aqueous suspension of Teflon F-4D binder for the next 2 h. The wet mass resulted was air-dried at ambient temperature for 4–6 h, and then vacuum-dried for 2 h at 300°C. The dried mass was then ground in the jasper mill for 1–2 h. Finally, the mass was sieved with 40  $\mu\text{m}$  mesh and used in the next experiments.

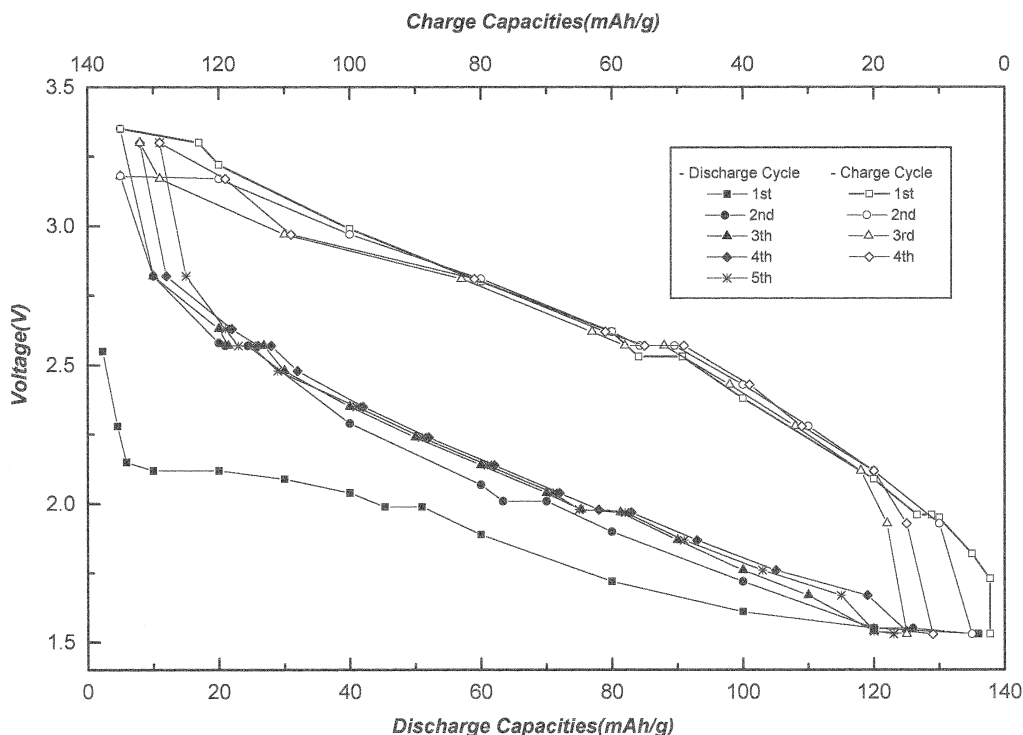


Fig. 1. Charge–discharge curves of the cathodes prepared from near-amorphous  $V_2O_5$  obtained in the laboratory cell with current density 0.5 mA/cm<sup>2</sup>.

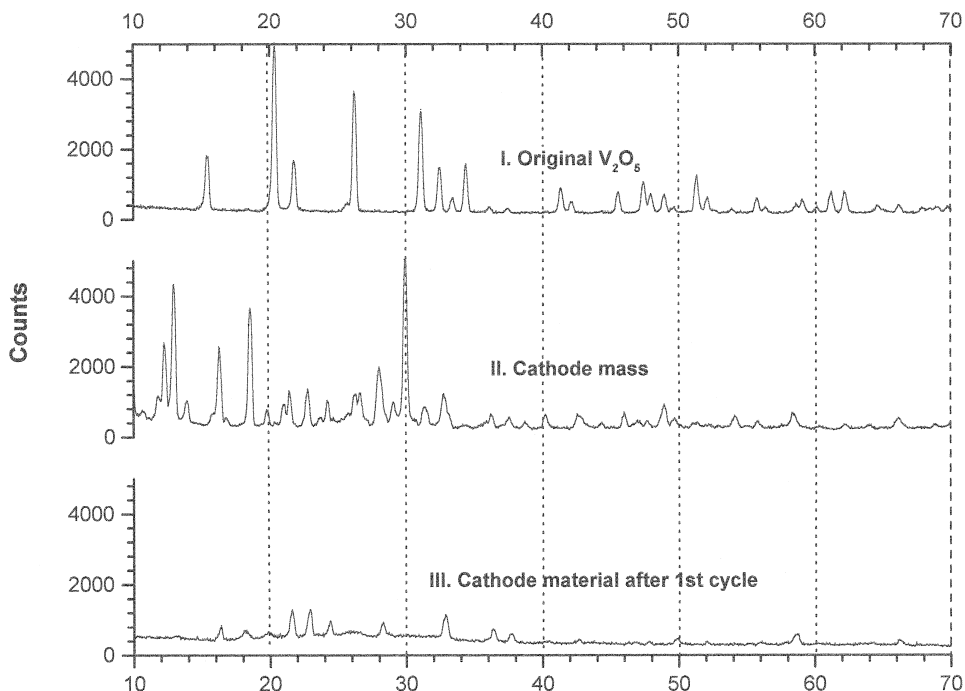


Fig. 2. XRD patterns of the original  $V_2O_5$  (I), modified cathode mass before use (II) and the cathode material after the first charge and discharge (III).

### 2.3. Electrochemical measurements

The conventional three-electrode electrochemical cell was used with lithium strips as the counter and the reference electrodes in the 1 M  $LiClO_4$  solution in mixed solvent propylene carbonate (70 vol.%) and dimethoxyethane. The working electrodes were of 3  $cm^2$  area and 0.2 mm thick. The active masses were pressed onto the nickel mesh current collector. Before introducing into the glove box, the electrodes were heated in vacuum oven at 300°C for 2 h. The composition of the cathode pellet was  $V_2O_5$ :graphite:acetylene black:binder = 85:5:5:5. The electrodes were cycled at constant current density of 0.5  $mA/cm^2$  in the range of 1.5 to 3.3 V.

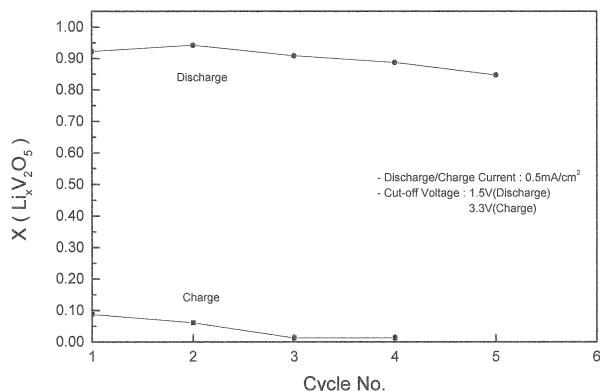


Fig. 3. The amount of Li inserted at discharge and remained at charge in the conditions corresponding to that in Fig. 1.

### 2.4. Fabrication and testing of the coin cells

The cells were manufactured of 2325 size. The anode was made of Li–Al alloy. The samples of the cathode mass of 0.6 g each were pressed into the cells' cans with the 3.0 metric tons pressure. To remove residual moisture, the cathodes were treated in vacuum at 300°C for 2 h. The cells were assembled in a dry glove box. The electrolyte (0.005 wt.% of water) was of the same composition as above. The separators were made from nonwoven porous polypropylene of 100  $\mu m$  thick.

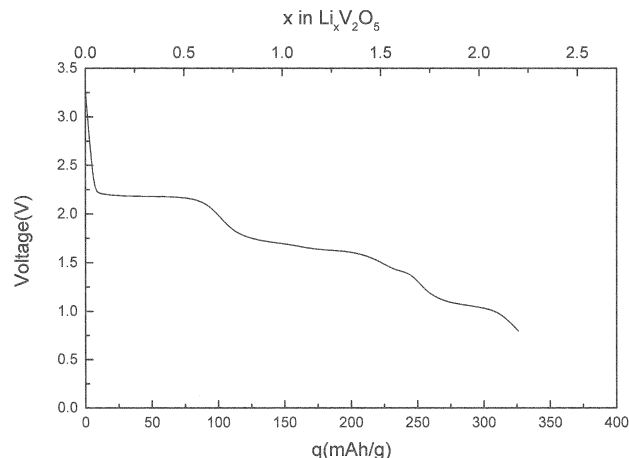


Fig. 4. The first deep discharge curve of 2325 coin-type cell with constant load of 5.6  $k\Omega$ .

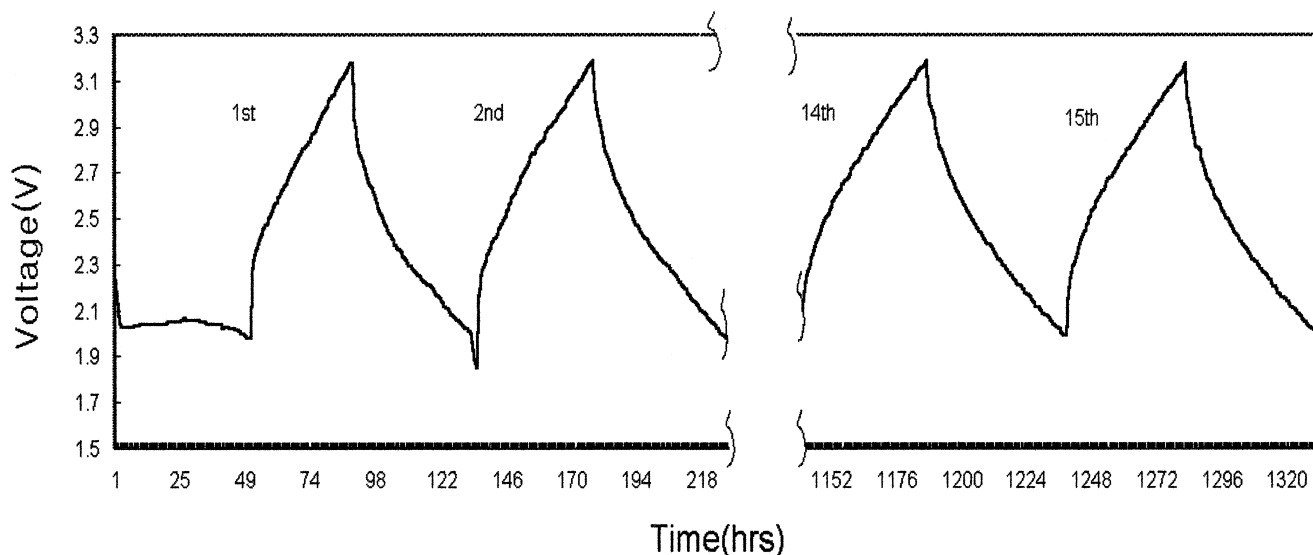


Fig. 5. Profiles of charge–discharge curves of the cells at shallow cycling conditions: voltage range, 2.0 to 3.2V; current, 0.5 mA.

The cycling tests were performed in galvanostatic conditions in the range of 2.0 to 3.2 V and 2.0 to 3.9 V, charge and discharge current being equal to 0.5 mA. Several cells were deeply discharged to 0.9 V with constant load of 5.6 k $\Omega$ .

### 3. Results and discussions

The stepwise shape of the first discharge curve (Fig. 1) points to some crystalline structure of the modified oxide. Indeed, the XRD pattern (Fig. 2II) shows the crystal structure of the oxide other than the one for the original V<sub>2</sub>O<sub>5</sub> precursor.

However, the subsequent charge and discharge curves transform completely acquiring the form with continuous voltage variation (with only minor steps at 2.6 V) that is typical for amorphous substances (Fig. 1). This is evident for the rapid electrochemically induced transition toward the amorphous state, similar to that reported for some deeply discharged vanadates, although the transition was

observed there at significantly lower voltages, below 1 V [24,25]. The amorphization of the structure is clearly seen in XRD pattern, Fig. 2III.

The galvanostatic charge and discharge data obtained in electrochemical cell demonstrate good reversibility of the process (Figs. 1 and 3). The amount of lithium in Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub> varies reversibly from 0.9 to 0 when cycling between 1.5 and 3.3 V vs. Li with current density 0.5 mA/cm<sup>2</sup> offering the cycleable capacity of about 130–140 mA h/g at average voltage 2.6–2.7 V.

The results of these previous electrochemical investigations were used to develop the rechargeable coin cells of 2325 size for applications as backup power sources for CMOS-RAM memories, real-time clocks, and other uses. The nominal capacity of 50 mA h and operation voltage about 2.7 V were intended. The performance and some characteristics of these cells are reported below.

The curve that corresponds to the first deep discharge of a freshly prepared cell on constant load of 5.6 k $\Omega$  is shown in Fig. 4. One can see from this curve that deeply

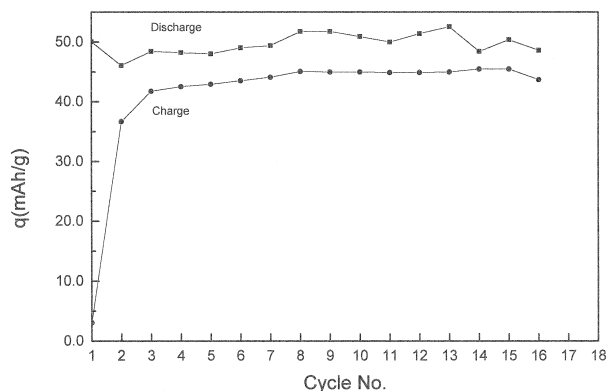


Fig. 6. Cells' capacities achieved in charge and discharge at the conditions as those in Fig. 5.

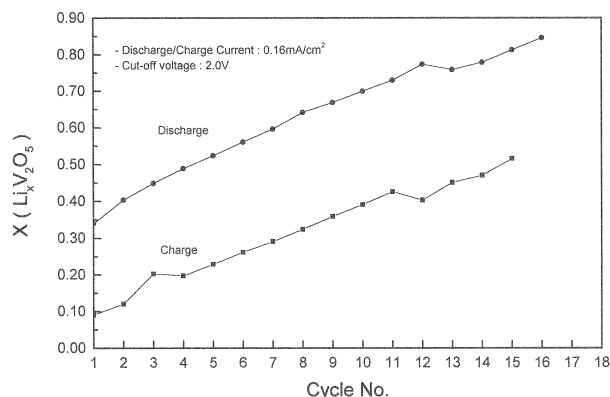


Fig. 7. The amount of inserted Li in discharged and charged state of the cathode material.

Table 1  
Rechargeable lithium aluminium/modified vanadium pentoxide coin cells

Model	VL2325	VL2325c <sup>a</sup>
Nominal voltage, V	3	3
Rated capacity, mAh	25	50
Standard discharge, mA	0.5	0.5
Discharge end voltage, V	2.0	2.0
Charge end voltage, V	3.2 to 3.3	3.8 to 3.9
Working temperature range, °C	−20 to +60	−20 to +60
<i>Dimensions:</i>		
Diameter, mm	23.0	23.0
Height, mm	2.5	2.5
Weight, g	3.2	3.2

<sup>a</sup>Modified by preliminary cycling, see text.

discharged oxide accumulates the surprisingly high amount of lithium, more than 2 moles per V<sub>2</sub>O<sub>5</sub> unit.

The cycleability of the cells was first tested in the shallow depth conditions, with voltage limits of 2.0–3.3 V and current 0.5 mA, which correspond to nominal capacity 25 mA h. The lower cut-off voltage of 2.0 V was chosen as optimal following the data of [26].

The charge–discharge curves of these coin type cells (Fig. 5) are very similar to those obtained in the laboratory cell (Fig. 1)—the first discharge is stepped, and the next are continuously sloping charge and discharge curves.

The plot of achieved capacity vs. cycle number (Fig. 6) shows no significant fade of capacity of the cells on cycling. There is, however, a gap between the discharge and charge capacities, which tends to decline with the increase of cycle number. Since the discharge capacities are invariably higher than the charge ones, one can conclude that discharged (to the same 2.0 V voltage) oxide becomes more enriched with lithium in course of cycling. This tendency, shown in Fig. 7, is apparently caused by certain rearrangement of the oxide structure. That is believed to create additional active sites with energies more than 2 eV during the shallow cycling from 3.2 to 2 V. The inner cause of such behavior remains unclear, although one practically important conclusion can be drawn: the reversible capacity should at least be doubled by applying higher (about 3.8–3.9 V) cut-off voltage on charge after the first few dozens of cycles are processed. Indeed, the more deep charge of the cells after the first 20 shallow cycles (such as in Fig. 5) permitted us to achieve the reversible capacity of 50 mA h (or more than 100 mA h/g of active cathode material) in several cycles performed with 0.5 mA current. Further investigations on long-term cycling with such operating modes are still in progress, and about 90 cycles are already achieved with no significant capacity fade.

Some specifications of coin cells with modified vanadium pentoxide cathodes are given in Table 1. Comparison with commercially available analogues [27] demonstrates the superiority of the developed cells in capacity, energy density, and operating current.

## 4. Conclusions

Small additives of sodium ortosilicate, Na<sub>4</sub>SiO<sub>4</sub>, to vanadium pentoxide combined with melting the mixture at 680°C for 3 h and subsequent fast cooling result in modified vanadium oxide being able to uptake more than 2 moles of Li per V<sub>2</sub>O<sub>5</sub> unit during the deep electrochemical discharge. About half of this quantity shuttles reversibly, providing stable charge discharge capacity near 140 mA h/g, the structure of the material being changed irreversibly to almost amorphous after the first operation cycle.

The coin-type cells of 2325 size of 25 mA h rating capacity were manufactured with the modified oxide as the cathode and Li–Al alloy as the anode. In the course of long-term cycling between 2.0 and 3.2 V (25 mA h), the performance of these cells is gradually enhanced due to a structural rearrangement of the oxide that creates additional occupational sites in the host structure for inserted Li at potentials above 2 V. Thus, the preliminary cycling of the cells for 10–20 times at 2.0 to 3.2 V results in increasing the rating capacity to 50 mA h when cycling in 2.0 to 3.9 V range.

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