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e-V_2O_5: Relationships between synthesis conditions, material characteristics and lithium intercalation behavior

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Abstract

Electrolytic V_2O_5, called e-V_2O_5, are prepared by electrochemical oxidation of aqueous solutions of vanadyl ions. By using various electrodeposition parameters (electrodeposition current density, temperature) or by subsequent heat treatment it is possible to obtain various compounds differing in their V^{IV} concentrations, water contents and interlayer distances. After dehydration at 100°C under vacuum, the e-V_2O_5 compounds have the same water content and the same interlayer distance, but differ by their V^{IV} concentrations. Lithium insertion capacities depend on the V^{IV} content and on the annealing treatment at 180°C. Materials with the smallest V^{IV} contents present the highest reversible capacities and good cycling properties. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Vanadium pentoxide; Electrodeposition; Physico-chemical characterization; Electrochemical lithium intercalation

1. Introduction

The preparation of various oxides by an electrochemical oxidation of aqueous solutions is well known, and can be applied to battery cathode materials such as MnO_2 [1]. Vanadium pentoxides are among the most promising cathode materials for rechargeable lithium batteries. However further improvement of the electrochemical behavior of V_2O_5-based cathodes is still necessary. From this respect, the synthesis of poorly crystallized forms of vanadium pentoxides is attractive because these compounds intercalate important quantities of lithium [2].

Electrolytic V_2O_5, called e-V_2O_5, were recently prepared by electrochemical oxidation of vanadyl ions in aqueous solution [3,4]. They are poorly crystallized, hydrated, mixed valence compounds, with a $V_2O_{5-\delta/2} \cdot nH_2O$ formula [5,6].

Studies reported in this paper concern correlations between synthesis conditions (electrodeposition and annealing treatment), physico-chemical characteristics and lithium intercalation behavior of e-V_2O_5 compounds.

2. Experimental

Various e-V_2O_5 compounds were prepared by electrochemical oxidation of stirred 0.1 mol l^{-1} aqueous solutions of vanadyl sulfate (at 25°C or 60°C), in a three electrode cell connected to a PAR 273 potentiostat. The working electrode is a rotating Pt disc of 0.02 cm^2 (for current density vs. voltage curves) or a Pt foil of 60 cm^2 (for quantitative synthesis). Voltages are referred to a saturated calomel electrode (SCE). The counter electrode is a wide-surface area Pt foil. The oxide films were deposited by galvanostatic electrolyses at different current densities (varying from 1 to 12 mA cm^{-2}). The deposits were collected at the working electrode, washed with distilled water, and then dried for several hours in air at 60°C. Some of them were heated in air at 180°C for 3 to 30 h (hereafter called annealed compounds).

The V^{IV}/V_{total} atomic ratio was determined from redox potentiometric titrations. The water content was calculated from thermogravimetric analyses (TGA), and the interlayer distance inferred from X-ray diffraction experiments. These two last parameters strongly depend on the relative humidity (noted RH) [5], which was carefully controlled.

The materials, annealed or not, were dehydrated at 100°C under vacuum for 1 h prior to electrochemical tests

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in lithium batteries. Electrodes (3 mg of a mixture e-V_2O_5 (85%) carbon black (10%) and binder (5%) deposited on a 1 cm^2 aluminium foil) were tested in cells such as [Li/LiPF$_6$ (1 mol l^{-1}) in EC + DMC (2:1)/electrode] in galvanostatic or potentiodynamic mode. Voltages are referred to the lithium electrode.

3. Results and discussion

3.1. Physico-chemical characteristics of the compounds

Fig. 1 presents the current density vs. voltage curve plotted prior to the electrodeposition experiments. Oxidation of vanadyl cations, revealed by the current increase, occurs for $E \geq 0.5$ V/SCE, in accordance with thermodynamic data [4,7]. It is followed by water oxidation and simultaneous deposit formation at $E \geq 1$ V/SCE. The current observed for $E \geq 0.5$ V/SCE is more important during the reverse scan, due to the increase of electrochemically active surface of the electrode correlated to V_2O_5 deposition.

Various e-V_2O_5 were obtained by maintaining the oxidation current density at a constant value during several hours. Chemical analyses reveal that the obtained compounds are hydrated mixed valence compounds (i.e., containing V^{IV} and V^V). Moreover, they bear exchangeable protons and can be written more correctly as H$_x$V$_2$ $\times$O$_{5-\delta/2+x/2} \cdot nH_2$O with $x = 0.4$, $0 < \delta < 0.4$ and $0 < n \leq 1.8$.

X-ray diffraction patterns of these compounds are similar to already reported diagrams of compounds prepared by chemical oxidation of V metal (2D-V_2O_5) [8], hydrothermal synthesis from VOSO$_4$ [9], or sol heating [10]. The X-ray diffraction diagrams of all these compounds present a first intense peak, related to the water content of the corresponding sample; e-V_2O_5 are therefore layered compounds, in which the most important part of water
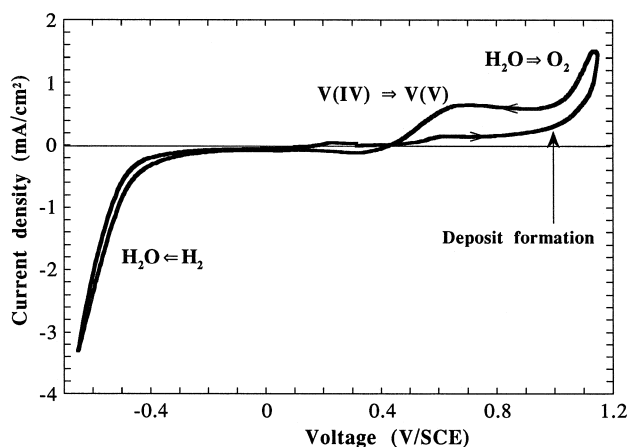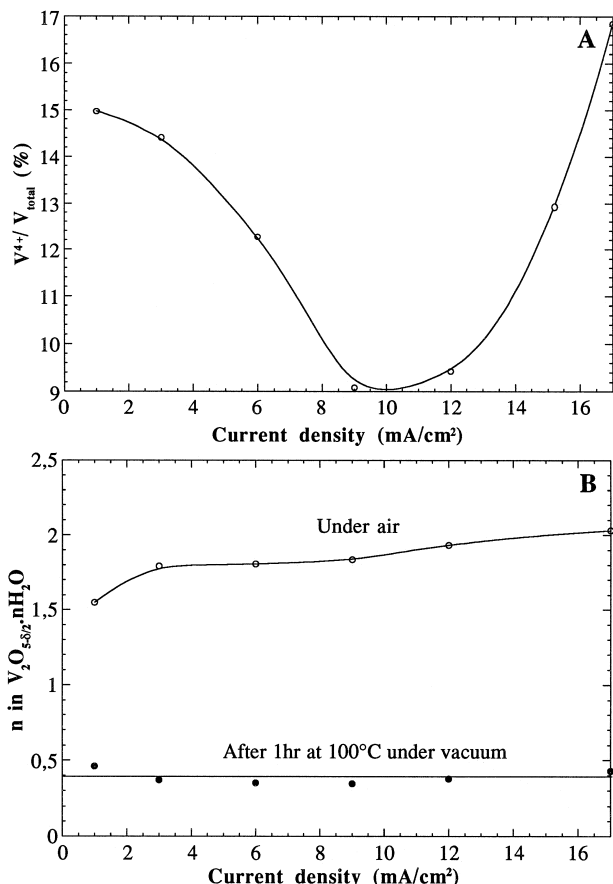

Fig. 2. Influence of the electrodeposition current density on the V^{IV}/V_{total} ratio (A) and on the water content (B) of the compounds synthesized at 25°C.

molecules and perhaps VO^{2+} ions are situated in the interlayer space. Although they present similarities with xerogels, they exhibit nevertheless small differences with these compounds [11,12]. Preferential orientation effects are less important for e-V_2O_5 than for xerogels, as it is the case for V_2O_5 aerogels. Nevertheless the BET surface of e-V_2O_5 never exceeds 1 m^2 g^{-1}, demonstrating that these compounds cannot be considered as aerogels [11]. In conclusion, e-V_2O_5 can be described as bi-layers containing structural units of the α-V_2O_5 structure [6,8–10], with perhaps some additional structural defects.

Fig. 2A shows the variations of the V^{IV}/V_{total} atomic ratios of the different compounds with the current densities used during electrodeposition. The V^{IV}/V_{total} atomic ratio first decreases with the current density, reaches a minimum value of 9% for 10 mA cm^{-2} and then increases to 17% for 17 mA cm^{-2}. This behavior (decrease followed by increase), was also observed at higher temperatures. Working at higher temperatures enables one to prepare more oxidized compounds: a compound containing 4% of V^{IV} has been prepared at 60°C for a current density of 5 mA/cm^2.

When heating the compounds at 100°C under vacuum, the V^{IV}/V_{total} atomic ratios of the compounds remain
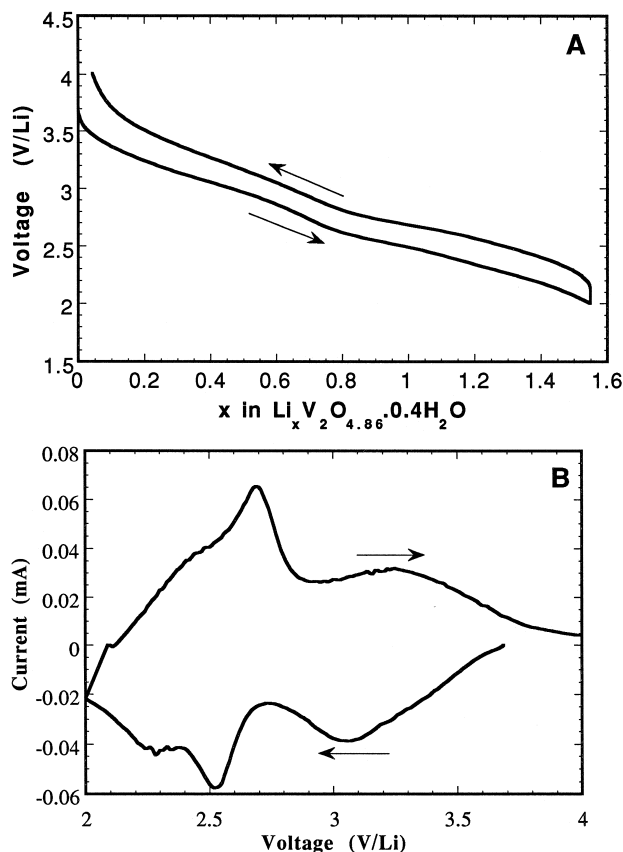

Fig. 1. Typical voltammogram obtained at a Pt rotating (360 rot. min^{-1}) disc electrode in a desaerated 0.1 mol l^{-1} VOSO$_4$ solution at 25°C.

Fig. 3. Typical first discharge and first charge curves of e-V_2O_5 ($V_2O_{4.86}$ ·$0.4H_2O$; V^{IV}/V_{total} ratio of 14%) in the 4–2 V/Li voltage range, recorded in potentiodynamic mode at 5 mV/h (A: voltage vs. intercalation rate; B: current density vs. voltage curve).

unchanged. On the contrary, a thermal treatment at 180°C induces a decrease of the V^{IV} concentration of all samples. On account of these results showing that experimental
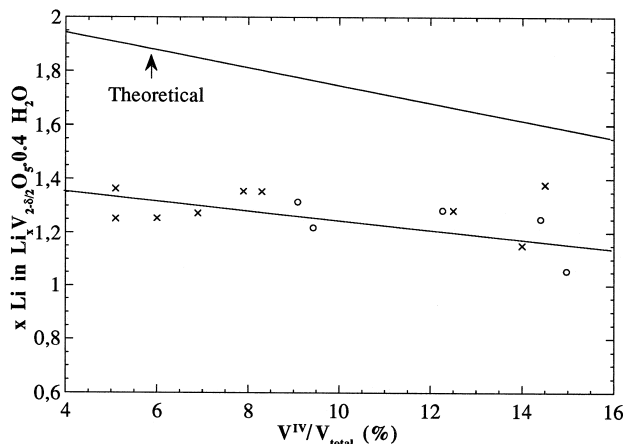

Fig. 4. Variations of the reversible specific capacities recorded during the second discharge (galvanostatic mode, C/50) with the V^{IV}/V_{total} ratio, for samples dehydrated at 60°C in air then at 100°C under vacuum (×), and annealed at 180°C in air then dehydrated at 100°C under vacuum (○). Theoretical capacities, calculated considering the total reduction $V^V \rightarrow V^{IV}$, are given for comparison.

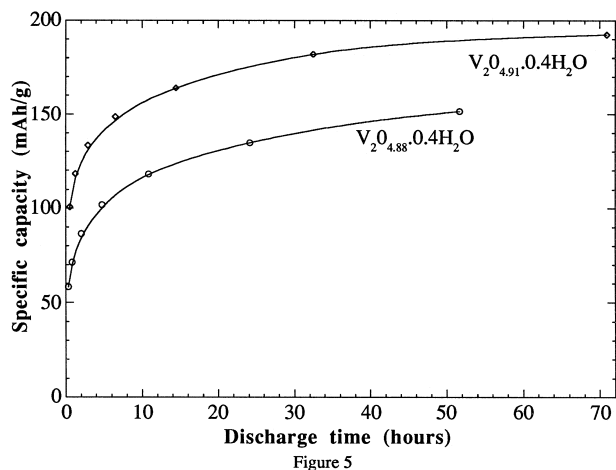Fig. 5. Variations of the specific capacity with the discharge time for $V_2O_{4.88} \cdot 0.4H_2O$ ($V^{IV}/V_{total} = 12\%$) and $V_2O_{4.91} \cdot 0.4H_2O$ ($V^{IV}/V_{total} = 9\%$).

conditions (electrodeposition current density or heat treatment temperature and/or duration) enables one to tune the V^{IV} concentration in e-V_2O_5 materials, various compounds were prepared with a V^{IV}/V_{total} ratio ranging from 3 to 15%.

Fig. 2B presents the evolution of the water content of the different samples with the electrodeposition current density. This content was measured either after drying at 60°C and equilibration in air for RH = 30% (TGA carried out in air for RH = 30%) or after dehydration at 100°C for 1 h under vacuum (TGA carried out under vacuum). The water content measured in air increases with the electrodeposition current density. This feature indicates that compounds with the same V^{IV} content but obtained at different current densities have different water contents in accordance with small differences in the corresponding X-ray diagrams. All compounds have the same water content after dehydration at 100°C under vacuum. A complete dehydration requires a heat treatment at temperatures higher
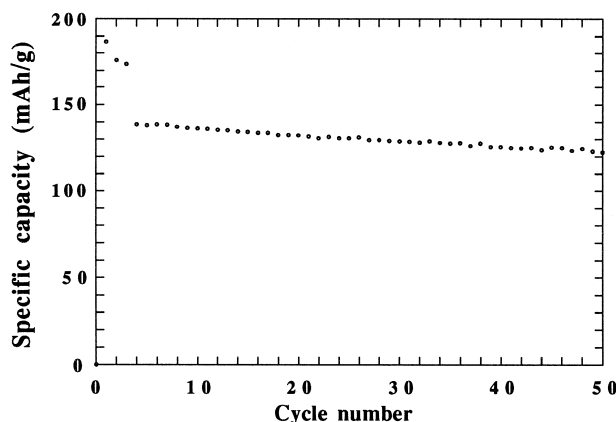

Fig. 6. Evolution of the specific capacity for $V_2O_{4.86} \cdot 0.4H_2O$ ($V^{IV}/V_{total} = 14\%$) during cycling at C/75 rate (first three cycles) and at C/4 rate (following cycles).

than 260°C, and leads to the irreversible formation of α-V_2O_5 [5,6].

The variations of the interlayer distance of the different samples present the same features than the variations of the water content measured in the same conditions, suggesting that the two parameters are correlated. When the electrodeposition current density increases from 1 to 17 mA cm^{-2}, the interlayer distance measured in air for RH = 30% varies from 11.5 Å to 13.5 Å, in two consecutive steps of 1 Å. The volume increase associated to these two steps is too important to be due only to water intercalation and concerns also other cationic species [6]. After dehydration at 100°C under vacuum, all compounds have the same interlayer distance of 9.8 Å.

3.2. Electrochemical intercalation of lithium

The electrochemical lithium intercalation behavior presented in Fig. 3 is representative of the different samples that were studied. Three intercalation steps are revealed by peaks on the current density vs. voltage curve (Fig. 3B) near 3.10 V/Li, 2.50 V/Li and 2.30 V/Li, respectively. These three intercalation steps are visible on the voltage vs. intercalation rate curve (Fig. 3A) as badly defined plateaus, in accordance with the poor crystallization state of the compounds. The three intercalation steps correspond to the intercalation of more than 1.5 Li per e-V_2O_5 in the 4–2 V range. The difference measured between the first discharge and first charge capacities is equal to the irreversible capacity, and corresponds to the small quantity of lithium irreversibly trapped in the structure after the first discharge. The capacity measured during the following cycle are the same in discharge and in charge, and is called hereafter reversible specific capacity.

After dehydration at 100°C, i.e., in the conditions in which the materials are tested in batteries, the various compounds just differ by their V^{IV}/V_{total} atomic ratio. Fig. 4 presents the variations of the reversible specific capacities, measured in galvanostatic mode during the second discharge for a discharge duration of 50 h (noted C/50 rate), with the V^{IV}/V_{total} atomic ratio, for two series of compounds (dehydrated at 60°C in air then at 100°C under vacuum, and annealed at 180°C in air then dehydrated at 100°C under vacuum). Results are compared to the theoretical variations obtained by considering the total reduction of V^{V} into V^{IV}. The largest capacities are obtained for small V^{IV}/V_{total} atomic ratios, with no significant differences between compounds annealed or not.

Experiments were also carried out at different discharge currents. As shown in Fig. 5, the variations of the capacities are very important when the discharge time varies between 0 and 10 h, and less important for higher discharge durations. Moreover, we can notice that the largest

capacities are always obtained with the highest V^{IV}/V_{total} atomic ratio independently of the discharge time, confirming the results described previously for a discharge duration of 50 h (Fig. 4).

Compounds were subjected to 50 cycles at C/4 rate. Typical results are presented in Fig. 6. They reveal very good cycling properties with a weak capacity loss, never exceeding 0.35 mA h/g per cycle. This capacity loss occurs on the 2.5 V/Li intercalation phenomenon mainly. It is responsible for the small increase of the average intercalation voltage from 2.7 to 2.85 V/Li.

4. Conclusion

Various e-V_2O_5 compounds, differing by their V^{IV} concentrations and water contents (and consequently their interlayer distances), can be prepared by adjusting the electrodeposition current density and temperature, and the duration of a subsequent thermal treatment at 180°C. Materials tested in batteries were heated for 1 h at 100°C under vacuum, a treatment which leads to the same water content of 0.4 H_2O per formula unit and the same interlayer distance of 9.8 Å for all materials. The lithium intercalation occurs in three steps spread on large voltage ranges, and largest capacities are obtained for compounds with the highest V^{IV}/V_{total} atomic ratios. The last intercalation step (2.50 V/Li) is mainly responsible for the capacity losses observed upon cycling. However these capacity losses remain very weak, and e-V_2O_5 materials present very good cycling properties.

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