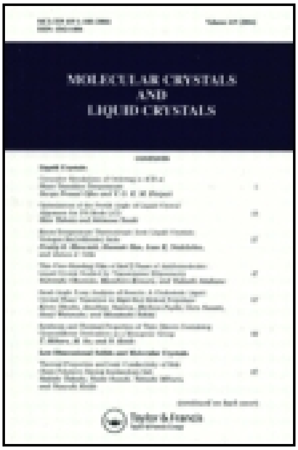

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Synthesis, Characterization and lithium Intercalation behavior of electrodeposited V_2O_5

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Synthesis, Characterization and lithium Intercalation behavior of electrodeposited V_2O_5

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Vanadium pentoxide deposits have been prepared by electrochemical oxidation of vanadyl ions in aqueous solution. They were characterized with the use of a combination of techniques including: X-ray diffraction, TGA, SEM, chemical titration... They exhibit a 2D structure similar to that of V_2O_5 gels and contain the same number of exchangeable protons and water molecules per formula unit. However clear differences are also observed, mainly related to the V^{4+} content, the interlayer distance and their evolution with thermal treatments.

The electrochemical behavior of as prepared and heat treated electrodeposited materials was investigated with respect to lithium intercalation. A thermal treatment at T>140°C induces an irreversible decrease of the V^{4+} content and leads to a higher specific capacity.

Keywords: Vanadium pentoxide; electrodeposition; physico-chemical characterization; electrochemical Li intercalation.

INTRODUCTION

Vanadium pentoxides are good positive electrode materials for rechargeable lithium batteries. Many attempts were made to modify their structure in order to further improve their electrochemical performances, like amorphisation or preparation of gel materials [1-6]. Studies reported in this paper concern the preparation of electrolytic V_2O_5, noted e-V_2O_5, by oxidative electrodeposition from an aqueous solution of vanadyl sulfate, its physico-chemical characterization and preliminary investigations of the electrochemical Li intercalation properties.

EXPERIMENTAL

The e-V_2O_5 compound was prepared at ambient temperature by electrochemical oxidation of a 0.1M aqueous solution of vanadyl sulfate under a fixed voltage of +1V/S.C.E.. The deposits were collected at the Pt electrode, washed with distilled water and dried at 50°C.

The samples were characterized by a combination of techniques. A Quantasorb Junior equipment was used to measure the surface area (single point B.E.T. technique). X-Ray Diffraction patterns (XRD) were collected on a Siemens D5000 diffractometer. The water content was inferred from two TG experiments: one under air up to 500°C at 2K/min (Setaram TG-DSC111) and the other under argon at 5K/min, in order to identify the gaseous species released, with the use of a mass spectrometer (Leybold Transpector H300cis). The adsorption isotherm was determined from powder samples equilibrated at different partial pressures of water vapor. The starting water content was determined from TGA. The V^{4+}/V_{total} atomic ratio was determined from a redox potentiometric titration. Battery preparation and testing were made as previously described [7]. All voltages given in the text, are reported versus the Li/Li^+ (1 mol l^{-1}) reference system.

RESULTS AND DISCUSSION

e-V_2O_5 samples prepared are microscopically homogeneous. They are green black, thus indicating that they could contain a non negligible amount of V^{4+}. The V^{4+}/V_{total} molar ratio inferred from a redox potentiometric titration is equal to 16(±2)%. Accordingly, the chemical formula will be considered as $V_2O_{5-\delta}$, nH_2O with $\delta=0.16$. This V^{4+}content is much larger than that of V_2O_5 xerogels (1%).

V_2O_5 gels are known to be polyvanadic acids containing exchangeable protons [8]. The H^+/Na^+ ion-exchange reaction on e-V_2O_5 shows that it contains ≈15% of exchangeable protons, therefore, a more correct chemical formula is $H_{2y}V_2O_{5-\delta+y}$, $n'H_2O$, and as $\delta \approx y$, it becomes $H_{0.3}V_2O_5$, $n'H_2O$.

The water content starts for RH≈0% is n≈0.6 and n=1.3 for RH≈10%. Then a continuous, but slow, increase is observed leading to n≈2.6 for RH=80%. When RH becomes greater than 90%, the water content increases rapidly reaching n≈7 at RH=100%. This rather flat sigmoïd-like evolution is quite different from that observed for V_2O_5 gels [8].

The XRD pattern of e-V_2O_5 (fig. 1) is very similar to that reported for 2D V_2O_5 prepared either by reaction of V metal with H_2O_2 [3] or the sol gel route followed by mixing in a graphite dispersion [9]. However the interlayer distance is 13.5Å for e-V_2O_5 (without thermal treatment) and 11.5Å for V_2O_5 xerogels at RH≈30%.

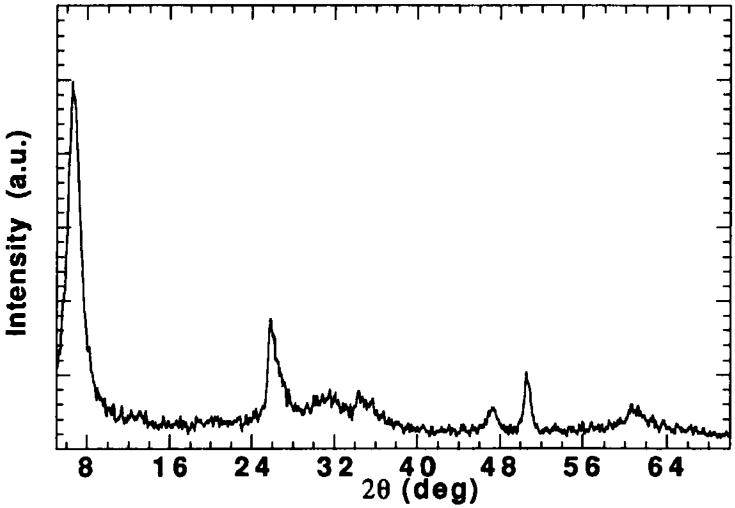

FIGURE 1 XRD pattern of e-V_2O_5 at RT.

The TGA in open air of e-V_2O_5, equilibrated at RH≈30%, shows weight loss in three steps, only identified as water losses from mass spectroscopy. Between 20 and 150°C water loss is rapid and becomes much slower from 150°C to 280°C; a third small loss is observed between 280 and 350°C. The first two dehydration steps are reversible and correspond to a large and a small endothermic phenomenon, respectively. The third one, which is exothermic, is irreversible and leads to α-V_2O_5. The formation of α-V_2O_5 implies an oxidation process in air, that was not detected by TGA. However, the weight loss at 500°C in open air (13.4%) is clearly smaller than that observed under argon (14.7%). Furthermore, the material obtained at 500°C under argon is a mixture of V_3O_7 and α-V_2O_5. Therefore, the chemical formula of e-V_2O_5, equilibrated at RH≈30%, is $H_{0.3}V_2O_5$, $1.55H_2O$.

Further experiments have shown that oxygen uptake is irreversible; it begins at T≈150°C. For T<200°C, the thermal treatments do not induce the e-V_2O_5 --> α-V_2O_5 transition. After 1 hr at 100°C under vacuum, for example, the water content is only $0.2H_2O/V_2O_5$ but the e-V_2O_5 structure is maintained as well as the original V^{4+} content. For T≥ 200°C, mixtures of α-V_2O_5 and e-V_2O_5 are observed and the proportion of α-V_2O_5 increases with time and when T increases.

When e-V_2O_5 samples are heated for 2 hrs in open air, 140≤T<200°C, and cooled down to RT, their water content remains nearly constant but their V^{4+} decreases to a few % at T≈200°C. Their interlayer distance has the dependence: d(Å)=13.5-0.01*T(°C). Consequently, after a thermal treatment of e-V_2O_5 at T≈200°C, the V^{4+} and water contents, as well as the interlayer distance are almost identical to those of V_2O_5 xerogels. It has already been shown that vanadium pentoxide gels are sensitive towards reduction, even when left in open air [10]. Their water content at a given RH increases when the V^{4+} content increases. It reaches $2.5H_2O$ per V_2O_5 when V^{4+}/V_{total} =16% and the interlayer distance increases by a step of 2.8Å up to 14.3Å, suggesting the intercalation of another water layer [10]. Therefore, it appears that with the same V^{4+} content (V^{4+}/V_{total}=16%), e-V_2O_5 exhibits a smaller interlayer distance (13.5Å) and a smaller water content ($1.7H_2O$) than a reduced V_2O_5 xerogel. In summary, the oxidation of an e-V_2O_5 compound induces a continuous decrease of the interlayer distance without any change of the water content, whereas the reduction of a V_2O_5 xerogel induces an increase of its water content and a step increase of its interlayer distance. Presently, these two behaviors are not clearly understood.

The dx/dV vs voltage curves corresponding to the first discharge-charge cycle of e-V_2O_5 materials heated at different temperatures are displayed in fig. 2. The Li intercalation behavior of e-V_2O_5, dried at 100°C, is characterized by a broad peak located at 3.15V, a sharp one at 2.55V and a shoulder at about 2.35V (fig. 2a). This shape is maintained as long as the temperature of the thermal treatment T≤200°C. However, an increase of the specific capacity is observed when T increases; 120 mAh/g instead of 164 mAh/g for e-V_2O_5 heat treated at 100°C and 180°C, respectively. For T>200°C (fig. 2b) electrochemical phenomena characteristic of the α-V_2O_5 Li intercalation behavior are superimposed (peaks at 3.4V, 3.2V and 2.35V) [11].

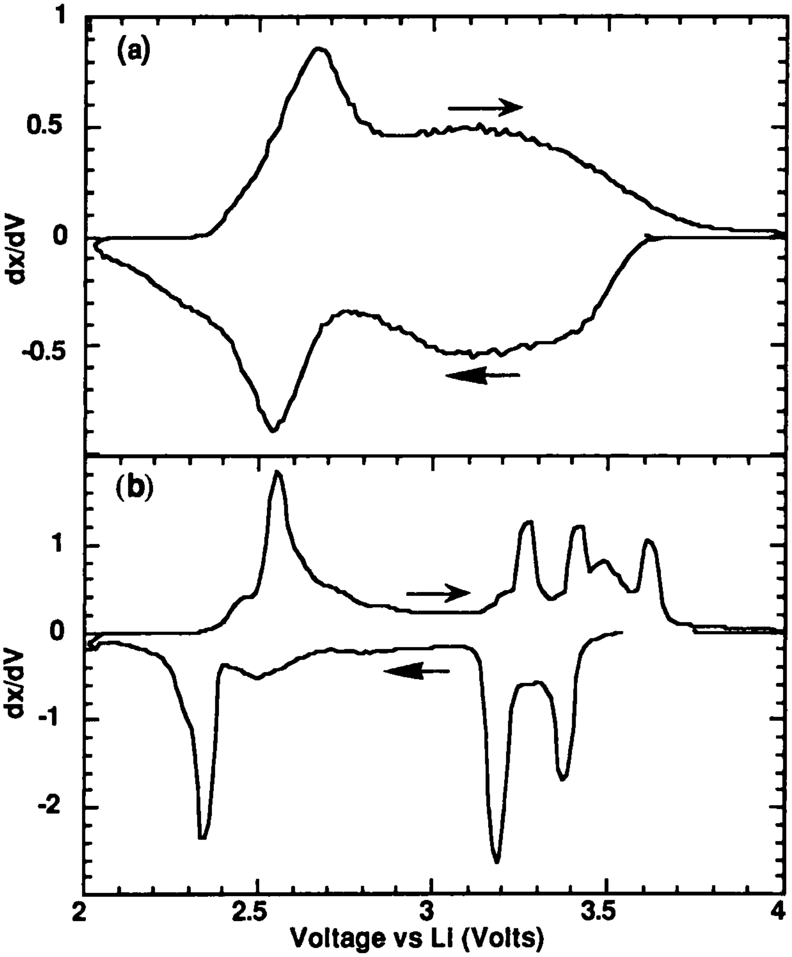

FIGURE 2 dx/dV versus voltage (C/15) during the first intercalation/deintercalation cycle of e-V_2O_5 heated at (a) 100°C and (b) 260°C.

CONCLUSION

The electrochemical oxidation of vanadyl ions in aqueous solution leads to e-V_2O_5, an hydrated 2D polyvanadic acid with an interlayer distance of 13.5Å (at RT and RH≈30%), containing about 16% of V^{4+} ($H_{0.3}V_2O_5$, $1.55H_2O$). Thermal treatments of e-V_2O_5 below 200°C induce an irreversible regular decrease of both the V^{4+} content and the interlayer distance, whereas the water content is constant. The irreversible e-V_2O_5 --> α-V_2O_5 transition occurs at 220°C. The specific capacity of heat treated e-V_2O_5 increases when the temperature of the treatment increases.

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