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Electrochemical lithium insertion in the hexagonal cesium vanadium bronze $Cs_{0.35}V_2O_5$

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Abstract

The vanadium bronze $Cs_{0.35}V_2O_5$ has been synthesized by a sol–gel process. It exhibits a hexagonal symmetry with lattice parameters $a = 13.341(1)$ Å, $c = 3.610(1)$ Å. These are very close to those given for $Cs_{0.3}V_2O_5$ obtained by high temperature solid state reaction. Preliminary results on the electrochemical lithium insertion in the tunnel structure of the bronze $Cs_{0.35}V_2O_5$ show two main insertion steps in the potential range 3.5–1.8 V with a maximum Li uptake of 1.65. The irreversible trapping of some Li ions limits the cycling capacity to 145 A h kg^{-1} in the voltage range 4.2–1.8 V at a $C/10$ rate. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The interest in using the sol–gel process to prepare cathodic materials for secondary Li batteries has been previously demonstrated [1]. The V_2O_5 group constitutes a wide variety of compounds: gels, xerogels, oxides and bronzes. Oxides and bronzes are obtained from the V_2O_5 xerogel (VXG). When monovalent cations such as sodium, potassium or silver are exchanged in VXG, a subsequent heat-treatment in air leads to the formation of the corresponding monoclinic $M_xV_2O_5$ bronzes: β-$Na_{0.33}V_2O_5$, β-$K_{0.25}V_2O_5$ and β-$Ag_{0.3}V_2O_5$ [2,3]. The present paper reports preliminary results on the synthesis of a cesium vanadium bronze prepared via the sol–gel process and its electrochemical properties as Li insertion compound.

2. Experimental

2.1. Synthesis procedure

The vanadium bronze $Cs_{0.35}V_2O_5$ with a hexagonal structure was synthesized by a sol–gel process. Vanadium pentoxide sols were prepared via the acidification of a sodium metavanadate solution $NaVO_3$ through a column loaded with a proton exchange resin [4]. A yellow solution of decavanadic acid is first obtained. It polymerizes slowly into a dark red gel. The gel is spread into a thin layer on a glass plate. After drying at room temperature, a xerogel corresponding to the composition V_2O_5, 1.6 H_2O is obtained. It is constituted of negatively charged ribbons, with about 0.3–0.4 charge per V_2O_5. This charge is compensated by 0.3–0.4 H_3O^+ ions leading to ionic exchange properties between the H_3O^+ cations and other charged species such as for example M^{m+} cations [5].

Intercalation of Cs^+ ions is realized by direct immersion of a VXG sample in a 0.1 M solution of $CsNO_3$. This reaction is achieved within 20 min. The intercalation of Cs^+ between the xerogel ribbons preserves the 1 D order associated with the stacking of ribbons upon on each another. Nevertheless, the d-spacing between the xerogel ribbons is equal to 11.10(5) Å for Cs^+ and greater in xerogel case (11.60(5) Å). This difference can be explained by the electrostriction phenomenon due to the Cs^+ ion [6].

The last step in the preparation of vanadium bronze $Cs_{0.35}V_2O_5$ consists of a thermal treatment of the exchanged xerogel $Cs_{0.35}V_2O_5$, 1.1 H_2O. It was heated at 520°C during 2 h under an argon/hydrogen (90/10) atmosphere. This reducing atmosphere was used to prevent the formation of the $Cs_2V_6O_{16}$ phase. The cesium content was

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determined by atomic emission spectroscopy (Induced Coupled Plasma). The oxidation state of vanadium was deduced from chemical redox titration. The results lead to the formula $Cs_{0.35}V_2O_5$.

2.2. Electrochemical measurements

High purity propylene carbonate (PC) was obtained from Fluka and used as received. Anhydrous lithium perchlorate was dried under vacuum at 200°C for 12 h. We used conventional three electrode cells filled up with a 1 M $LiClO_4$ solution in PC as electrolyte and maintained under a purified argon atmosphere. Lithium was used as reference and counter electrodes in separate compartments containing the electrolyte. The working electrodes consist of a stainless steel grid with a geometric area of 1 cm^2 on which a mixture of bronze (80% by weight) with a binder agent (Teflon, 5%), graphite (7.5%) and acetylene black (7.5%) as electronic conductors is pressed under 5×10^3 kg/cm^2.

3. Results and discussion

3.1. Structure

X-ray powder diffraction (XRD) data were collected at room temperature with a Siemens D5000 diffractometer using $CoK\alpha$ radiation and a back graphite monochromator.

The XRD experiment in reflection geometry, directly performed on the thin bronze layer, is shown in Fig. 1a. Only h00 peaks are present, indicating a preferred orientation along the a-direction which strongly contrasts with the 001 preferred orientation observed for the sol–gel orthorhombic $M_xV_2O_{5+y}$ mixed oxides (M = Al^{3+}, Cr^{3+}, Ni^{2+} ...) and the β-monoclinic $M_xV_2O_5$ bronzes (M = Na, K, Ag). The interpretation of this diagram was made by

Fig. 2. Perspective view of $Cs_{0.35}V_2O_5$ structure. Cs^+ ions are located in two types of tunnels: (i) within the hexagonal tubes; (ii) between the tubes.

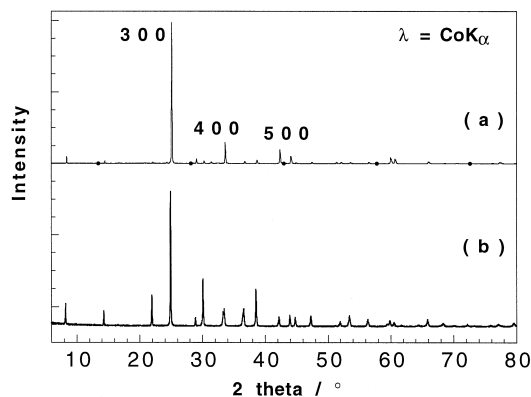Fig. 1. X-ray diffraction patterns (Co–Kα) in reflexion geometry of hexagonal cesium vanadium bronze $Cs_{0.35}V_2O_5$ as thin layer (a) and previously ground (b).
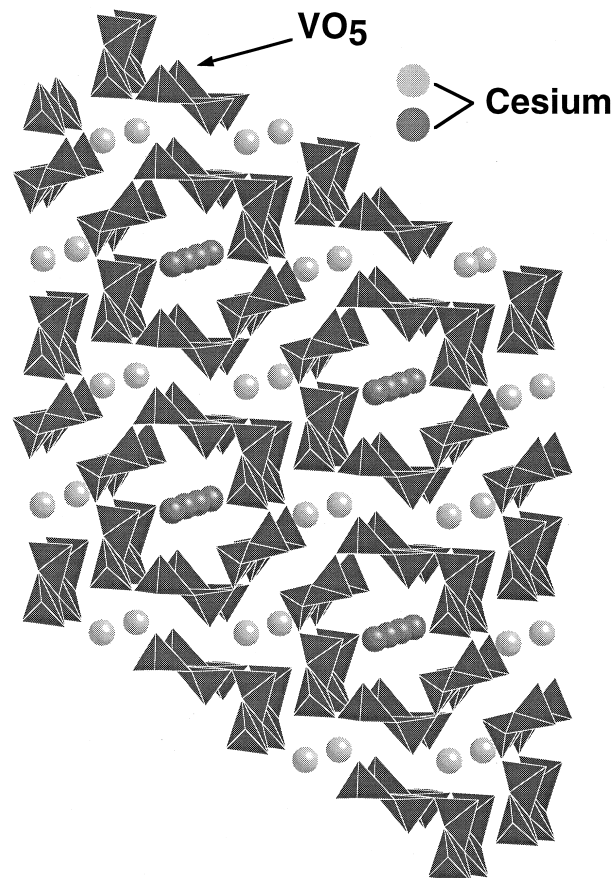
comparison with that of the sample previously ground in a mortar (Fig. 1b).

It corresponds to an hexagonal structure very close to that of the bronze obtained by solid state reaction [7]. The space group is $P6_3/m$ ($Z = 6$), with lattice parameters ($a = 14.341(1)$ Å, $c = 3.610(1)$ Å, $V = 642.98$ Å^3) which are nearly the same than those given by Waltersson and Forslund [7] ($a = 14.360(5)$ Å, $c = 3.611(1)$ Å, $V = 644.86$ Å^3). The structure of the sol–gel compound has been refined by the Rietveld method [8]. It exhibits two kinds of tunnels containing Cs atoms (Fig. 2). They correspond to two independent crystallographic sites for cesium ions. The structure is built up from square pyramid VO_5 which are linked by edges to form zigzag strings in the c-direction. Hexagonal tubes are made by six zigzag strings linked together sharing corners. The two kinds of tunnels are localized within the tubes for the first one, and between them for the second one (Fig. 2). According to the Rietveld refinement, 63% of the total Cs content is distributed between the hexagonal tubes; corresponding to a partial occupation of the crystallographic position 2c. The remaining Cs atoms are distributed within the tubes in the crystallographic site 4e which are partially occupied.
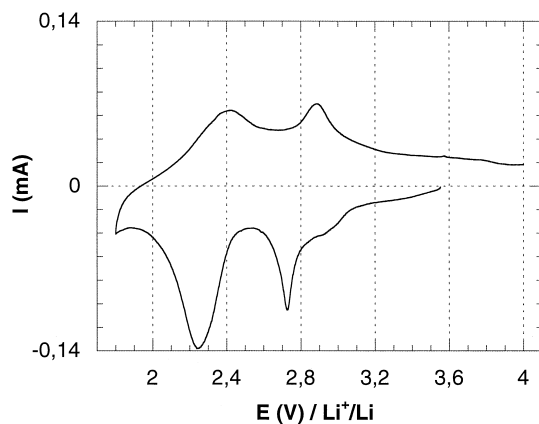
Fig. 3. Cyclic voltammetric curve of a $Cs_{0.35}V_2O_5$ electrode in 1 M $LiClO_4$/PC at a sweeping rate of 20 μV/s.

Fig. 5. Discharge–charge curves of $Cs_{0.35}V_2O_5$ electrodes at a current density of 100 μA/cm^2 in various potential windows.

Hence, 0.65 sites are unoccupied by cesium ions and are possibly available for Li accommodation.

3.2. Electrochemical behaviour

The electrochemical insertion of lithium in the vanadium bronze $Cs_{0.35}V_2O_5$ is illustrated in Fig. 3 by the cyclic voltammogram recorded at a sweeping rate of 20 × 10^{-6} V/s. The reduction process is characterized by two main steps located around 2.7 and 2.2 V, involving the insertion of respectively 0.65 and 0.95 lithium ions per $Cs_{0.35}V_2O_5$. This electrochemical behaviour differs from that known for the β-monoclinic bronzes like $Na_{0.33}V_2O_5$ or $K_{0.25}V_2O_5$ which are characterized by three main steps located around 3.3, 2.9 and 2.5 V involving respectively the insertion of about 0.33, 0.33 and 1 lithium ions. The 0.65 Li$^+$ inserted during the first reduction step could ensure the filling of the sites unoccupied by Cs$^+$. Afterwards 0.95 lithium are inserted up to 1.8 V in order to achieve the total reduction of vanadium V to vanadium IV. The deinsertion process occurs in two corresponding steps located near 2.4 and 2.9 V, but about 0.2 lithium ions
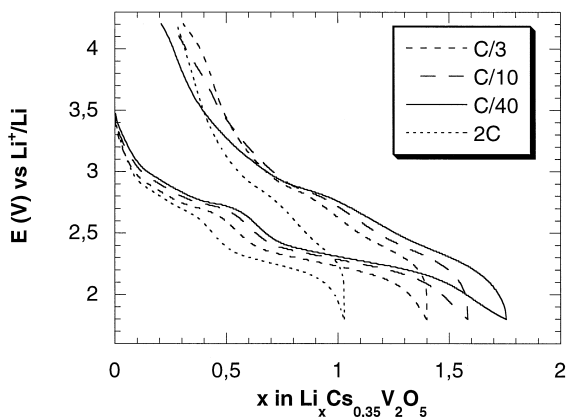
cannot be extracted even at a 4 V cut off voltage. Therefore, the efficiency of the redox process does not exceed 87%.

The galvanostatic discharge–charge curves recorded at different current densities are shown in Fig. 4. The oxidation cut off voltage was chosen to be 4.2 V in order to extract a maximum amount of lithium without any electrolytic degradation. At the lower rate $C/40$, a maximum of 1.75 lithium are inserted up to 1.8 V, but 0.2 lithium remain trapped in the structure. The effect of the higher current density ($2C$ rate) is to lower the discharge capacity to 1 lithium inserted while about 0.3 lithium are not deinserted. Although the overall shape of the two insertion steps is preserved whatever the current density, an important increase of the polarization is observed at the end of the oxidation process, limiting the amount of lithium extracted.

In order to understand the origin of the partial deinsertion of lithium, cycling experiments have been performed using various reduction cut off voltages at a $C/10$ rate. These results are illustrated in Fig. 5. It appears that limiting the depth of discharge to $x = 0.6$ at 2.5 V, with

Fig. 4. Galvanostatic discharge–charge curves of $Cs_{0.35}V_2O_5$ electrodes recorded at various current densities.

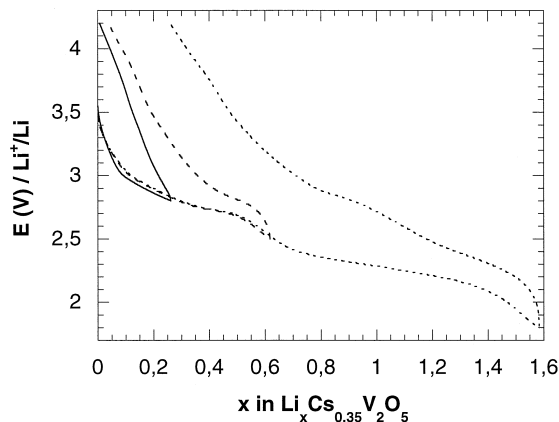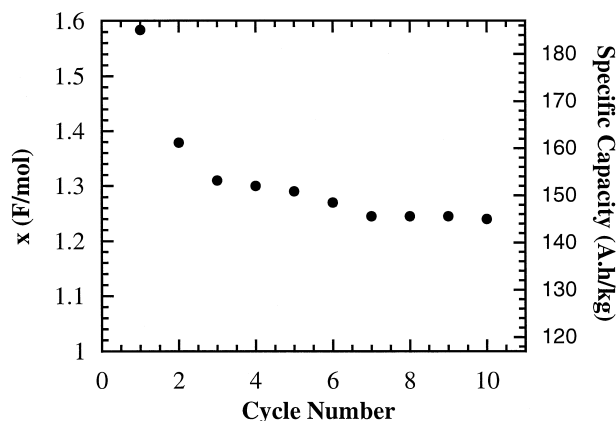Fig. 6. Cyclability of a $Cs_{0.35}V_2O_5$ electrode in the potential window 4.2–1.8 V at a $C/10$ rate.

the aim to concern only the first step, only a small amount of Li ions (0.04 Li) cannot be extracted from the host structure, in comparison with the 0.2 trapped Li^+ when the lithium uptake reaches 1.6 Li at 1.8 V. Therefore, the loss of rechargeability appears to be dependent on the depth of discharge and seems to be correlated to the amount of lithium inserted during the second process near 2.4 V.

The cyclability of the material has been investigated up to 10 cycles in the potential window 1.8–4.2 V at a $C/10$ rate. Fig. 6 shows the evolution of the discharge capacity during cycling. The capacity decreases rapidly during the first three cycles, evolving from 1.6 to 1.3 F/mol of $Cs_{0.35}V_2O_5$. Afterwards the decrease is very slow up to the seventh cycle from which the capacity seems to be stabilized at 1.25 F/mol after 10 cycles.

Structural investigation is needed to explain the reason for the irreversible trapping of about 0.35 Li and the response of this hexagonal host lattice as Li insertion proceeds. From the electrochemical viewpoint, the cycling capacity of 145 A h kg^{-1} allowed by this host lattice is much lower than that obtained for the orthorhombic oxide V_2O_5 but close to that reported for the sol–gel monoclinic β-$M_xV_2O_5$ bronzes [2]. Further improvements in the specific capacity can be expected from chemically oxidized bronzes.

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