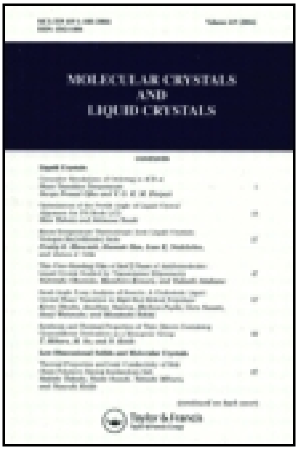

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Lithium insertion in $Bi_4V_2O_{11}$: study of the $Li_xBi_4V_2O_{11}$ (0<x<12) phases

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A large amount of 16 lithium ions reacts with the phase $Bi_4V_2O_{11}$ between 3 and 1 Volts. From the structural characterisation of inserted compounds $Li_xBi_4V_2O_{11}$ (0<x<12) we can infer that the insertion mechanism does not involve the reduction of $(VO_{3.5})^{2-}$ layers, and that lithium ions locate around the Bi^{+3} lone pair. Electrostatics interactions Bi^{+3} $6s^2$ -Li^+ may originate the observed irreversibility of the insertion reaction.

Keywords: intercalation; electrode material; electrochemistry

INTRODUCTION

The compound $Bi_4V_2O_{11}$ crystallizes with a layered structure where $(Bi_2O_2)^{2+}$ and oxygen deficient perovskite $(VO_{3.5}\square_{0.5})^{2-}$ sheets alternate[1]. In a recent study, we have tested $Bi_4V_2O_{11}$ and related compounds as positive electrode for lithium rechargeable batteries[2]. Further investigation concerning the mechanism of the insertion reaction, through the structure of the chemically lithiated phases $Li_xBi_4V_2O_{11}$ (0<x<12), is presented in the current work.

EXPERIMENTAL

The pristine material $Bi_4V_2O_{11}$ was synthesised from a stoichiometric mixture of the starting oxides[2]. Details of the electrochemical experiments are given in reference 2. The synthesis in sizeable amounts of the $Li_xBi_4V_2O_{11}$ phases was carried out by direct reaction of powder $Bi_4V_2O_{11}$ with an appropriate amount of 1.6 M n-butyl lithium solution in n-hexane. The mixture was stirred for 15 days and then, after extracting the solvent, the final product was washed three times with 5 ml of n-hexane. All the operations were done under an argon atmosphere. Lithium contents and vanadium-bismuth ratio were determined from an acid solution by inductively coupled plasma (ICP) analysis using a Jobin-Yvon JY-70 plus equipment.

X-ray diffraction patterns of the pristine and lithiated phases were collected in a Siemens D-5000 diffractometer using monochromated Cu K_α radiation. To avoid contact with moisture, the samples were disposed under argon into a hermetic closed aluminium sample holder having a foil of beryllium as window for X-ray.

X-ray absorption measurements were performed in the neighbourhood of the vanadium K-absorption edge (5465 eV) in the transmission mode for V_2O_5, $Bi_4V_2O_{11}$ and $Li_xBi_4V_2O_{11}$. A vanadium foil was used as reference. All spectra were collected at the E4 line in DESY (Hamburg) using the light emitting by DORIS storage ring operating at about 4.5 GeV and 70 mA, monochromated with a Si(111) double crystal.

RESULTS

Figure 1a shows the electrochemical behaviour of $Bi_4V_2O_{11}$ in a 1-3.3 voltage window. During the first discharge, 8 lithium ions per vanadium atom can be inserted in the active material, reaching the composition $Li_{16}Bi_4V_2O_{11}$. When charging the cell the inserted lithium ions can not be totally removed from $Li_{16}Bi_4V_2O_{11}$. We have also cycled a cell of the same configuration, but only up to the compositions $Li_{9.5}Bi_4V_2O_{11}$ and $Li_4Bi_4V_2O_{11}$. Both results are respectively plotted in figure 1b and 1c. It is noteworthy that in all the cases the irreversible loss of capacity corresponds to the same number of lithium ions.

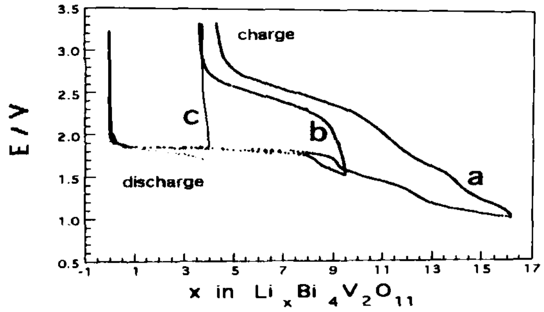

FIGURE 1 Cycling behaviour of cells Li/ 1 mol dm LiClO4+DEE+EC (50:50)/ $Bi_4V_2O_{11}$ (a) between 3.3 and 1Volts; limiting the degree of intercalation to(b) 9.5 lithium ions and (c) 4 lithium ions per formula weight.

The insertion of 16 lithium cations to form the compound $Li_{16}Bi_4V_2O_{11}$ should be accompanied by donation to the host of 16 electrons. Having in mind that the Bi metal is itself able to react with lithium to form alloys with maximum content of 3Li/Bi atoms, *i.e.* $BiLi_3$, we may think about a possible mechanism in which vanadium has no relevancy. In this way 16 lithium ions would alloy with segregated bismuth atoms forming the thermodynamic stable phases BiLi and $BiLi_3$, as happens in another material host[3]. However, in the present case, this is rather unlikely since as it is well known, lithium intercalation in Bi metal takes place below 1 Volt[4]. Therefore the potential of the lithium insertion reaction in $Bi_4V_2O_{11}$, is not low enough to consider neither lithium deposition (or clustering inside the host), nor lithium-bismuth alloying.

Figure 2 shows the X-ray diffraction patterns, under argon atmosphere, from the chemically lithiated compounds, $Li_xBi_4V_2O_{11}$ with x=2.8, 5.4, 8.3, 10, and the highest obtained composition 11.8. All these $Li_xBi_4V_2O_{11}$phases present the same main reflexions, that can be indexed using an orthorhombic cell with parameters a=5.4874(6) Å, b= 5.7620(5) Å and c=15.02(9) Å. The contraction of the initial $Bi_4V_2O_{11}$ structure along the c axis may obey a strong electrostatic interaction between lithium ions and the bismuth inert pair . Such a position for lithium ions would allow also an interaction with apical oxygen of the vanadium polyhedron, with the corresponding decreasing in the c cell parameter. The insertion of lithium in the structure of $Bi_4V_2O_{11}$ also gives rise to a distortion on the basal plane of the cell, as can be clearly seen from the shift of the 200 and 020 reflexions. Besides the cell volume, as expected, increases because of the large number of inserted ions in the unit cell. A loss of cristallinity of the starting compound $Bi_4V_2O_{11}$ is observed in correlation with the amount of inserted lithium.

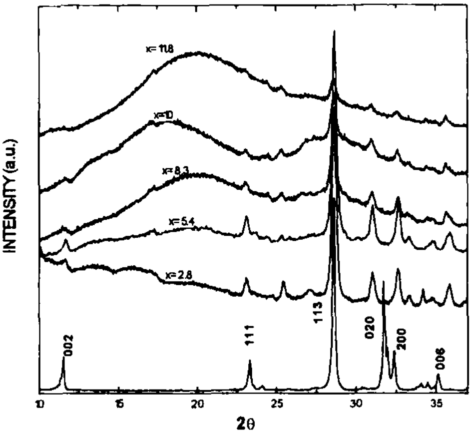

FIGURE 2 Powder X-ray diffraction patterns of $Li_xBi_4V_2O_{11}$ under argon.

Figure 3 shows the XAS spectra for chemically lithiated phases $Li_xBi_4V_2O_{11}$ with x values of 2.8, 8.3 and 11.8. The first remarkable feature is the existence of a pre-edge peak (A) below the vanadium K-edge. This peak corresponds to a transition from the core level (1s) to the first partially filled energy level, i.e. molecular orbital O2p+ V3d. The relatively high intensity of the $Bi_4V_2O_{11}$ pre-edge is typical of vanadium in fourfold and fivefold coordination[5]. The A peak intensity in $Li_xBi_4V_2O_{11}$ is nearly the same whatever the lithium content. Therefore, the vanadium stereochemistry of the pristine compound is not affected by the lithium insertion in the composition range $0<x<12$[6]. On the other hand, the energy related to the above referred transition in $Bi_4V_2O_{11}$ corresponds to vanadium atom in an oxidation state in between 4 and 5, as can be seen in comparison with V_2O_5 spectrum. This means that our starting material presents a slight oxygen deficient stoichiometry $Bi_4V_2O_{11-y}$ which in any case is not affecting its electrochemical behaviour[2]. For $Li_xBi_4V_2O_{11}$ ($0<x<12$) no shift to lower energies, indicative of vanadium reduction, has been detected while increasing the lithium amount. In all the samples $Li_xBi_4V_2O_{11}$ the energy of the K-edge is identical, confirming that no reduction of vanadium is occurring along the studied compositional range of the insertion reaction[5] The peak just above the edge, B, corresponds to an electronic transition from the V 1s state to an antibonding state forming from the overlapping of V 4p and O 2p atomic orbitals. A clear displacement of this peak towards lower energy is observed as a function of the amount of inserted lithium. This shift is indicative of a lengthening in the longest V-O bonding distances[7], as proposed from XRD data. Finally, the peak in the continuum, C, exhibits a remarkable broadening as function of the intercalated lithium. This feature is due to a material amorphization.

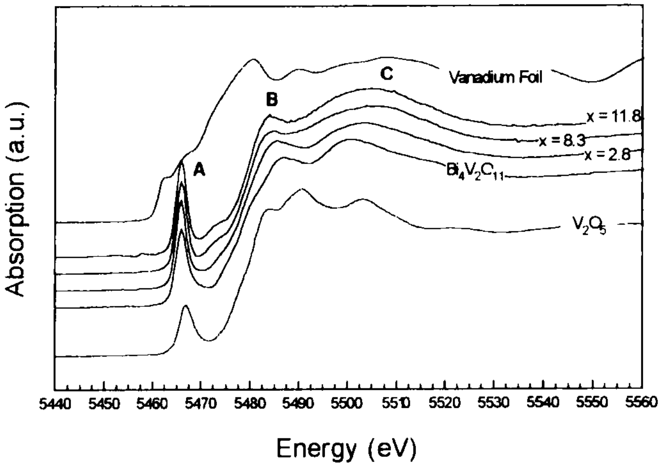

FIGURE 3 XAS spectra of $Li_xBi_4V_2O_{11}$ compounds at the vanadium K-edge.

CONCLUSIONS

From electrochemical data, we can infer that the undesired irreversibility of the lithium insertion reaction into $Bi_4V_2O_{11}$ can not be suppressed by increasing the lower cut-off of the cell. The host structure of $Bi_4V_2O_{11}$ suffers an irreversible transformation just from the beginning of the insertion reaction. From the structure, of $Bi_4V_2O_{11}$ it seems that the most likely sites for the first lithium inserted are close to the lone pair of bismuth cations. The $6s^2$ pair may interact with the lithium cations through electrostatic forces, preventing the removal of lithium. Such a location of inserted lithium would cause the lengthening in the vanadium-oxygen distance detected by XAS. This fact is consistent with the contraction of the cell parameter observed by XRD. Although Bi^0 is not detected by X-ray diffraction, electrons must be transferred to the $(Bi_2O_2)^{2+}$ layer, since XAS spectra confirms that vanadium oxidation state is not reduced during the insertion of 11.8 lithium ions. Anyway, the possibility of a reduction of vanadium cations in the region $12<x<16$ is the most probably way to complete the insertion mechanism.

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