LITHIUM INTERCALATION IN $Ta_xNb_{1-x}VO_5$ MIXED OXIDES

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ABSTRACT:

$Ta_xNb_{1-x}VO_5$ compounds act as host lattices for lithium intercalation following redox reactions carried out by treatments with LiI in acetonitrile. The intercalated phases constitute a new family of Li-bronzes, which have been characterized by X-ray diffraction, conventional chemical analysis, XPS as well as complex impedance spectroscopy in order to correlate the electrical properties with the composition of the host lattice and the lithium intercalation degree.

INTRODUCTION

In previous works [1,2], we have shown the potential application of the sol-gel methods to the synthesis of new crystalline phases in the M–V–O (M = Nb, Ta) system, characterized as $Ta_xNb_{1-x}VO_5$ ($0 \leq x \leq 1$). These mixed oxides belong to the family of monophosphate tungsten bronzes $[(PO_2)_4(WO_3)_{2m}]$ with a value of m=2 [3,4]. These compounds are built up by corner sharing tetrahedra ($[VO_4]$) and octahedra ($[(Ta,Nb)O_6]$), the most salient structural feature being the presence of channels with pentagonal and rhomboidal sections along the [010] direction (Fig. 1).

This work is focused towards the synthesis of lithium insertion compounds of $Ta_xNb_{1-x}VO_5$ mixed oxides, in view of their potential applications as cathode materials in solid state batteries. We will apply impedance spectroscopic measurements for characterizing the electrical behaviour of the lithium insertion compounds.

EXPERIMENTAL

Lithium intercalation reactions.

Synthesis of the mixed oxides is based on a sol-gel procedure described elsewhere [1]. Lithium intercalation was carried out by treatment with LiI/CH_3CN solutions at 373K in autogenic PTFE reactor, according with I or II procedures. All manipulations were done in a dry box under controlled atmosphere (N_2), to avoid unsuitable secondary reactions.

Procedure I

25 ml of a saturated solution of LiI (Fluka, 98%) in acetonitrile was added to 0.5 g. of the mixed oxide. The resulting mixture was kept into an autogenic PTFE reactor, which was maintained at 373 K. After specified periods, aliquots were removed from the autoclave, filtered, and washed with acetonitrile until complete elimination of the characteristic iodine colour.
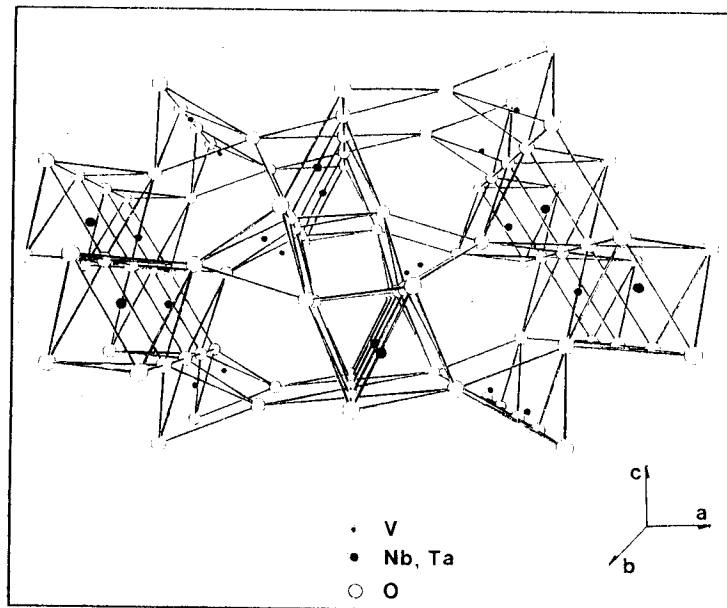
Fig.1.-Schematic representation of the $Nb_xTa_{1-x}VO_5$ structure

Procedure II

Similar to procedure I but, after each extraction of aliquot, a proportional amount of the initial solution was added to the system, in order to minimize the reversibility of the intercalation process (see eq.1). This one procedure was mainly adopted to synthesize Li_yTaVO_5 bronzes.

The evolution of the intercalation reaction with the treatment was followed by spectrophotometric measurements of the lithium content in the solid samples.

Characterization

$Li_yTa_xNb_{1-x}VO_5$ bronzes were characterized by X-ray powder diffractometry (Philips PW1710 instrument), IR spectroscopy (Perkin Elmer 580B spectrophotometer; KBr pellets), SEM-EDX analyses (Zeiss model DSM-950, EDX Tracor-Northem model Z-II instrument) and XPS spectroscopy (Vacuum Generator ESCA LAB MKII spectrometer; radiation: Mg K_α (E = 1253.6 eV) or Al K_α (E = 1486.6 eV)); the signal of V_{2p}, Nb_{3d}, Ta_{4f} have been used in order to characterize the oxidation state of these elements both, in the starting and in the intercalated samples.

A.C. impedance measurements were carried out at temperatures ranging from 423 to 723 K, with a frequency response analyzer (FRA) (Solartron 1174) coupled to an electrochemical interface (Solartron 1286). The applied signal amplitude was 50 mV in the 1MHz-10mHz frequency range. Samples previously sintered at 573 K, were placed in a Pyrex cell provided with a platinum grid as current collector. By silver sputtering on the two opposite flat surfaces of the sample, two identical electrodes were formed on the solids.

RESULTS AND DISCUSSION

Lithium intercalation

Chemical intercalation of Li^+ ions into $Ta_xNb_{1-x}VO_5$ $(0 \leq x \leq 1)$ was carried out according to equation 1.:

$$Ta_xNb_{1-x}VO_5 + y\ LiI \longleftrightarrow Li_yTa_xNb_{1-x}VO_5 + y/2\ I_2 \qquad (eq.\ 1)$$
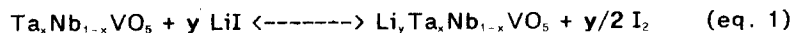
This is a redox reaction in which the iodide ions act as reducing agent of the transition metal ions of the host-lattice; thus, lithium ions are intercalated in the solid, balancing the net charge of the system.

TABLE I

Amount of intercalated Li (y) in the $Ta_xNb_{1-x}VO_5$ mixed oxides

x (in $Ta_xNb_{1-x}VO_5$)	1	0.79	0.53	0.26	0	(1)*
y (in $Li_yTa_xNb_{1-x}VO_5$)	0.03	0.06	0.08	0.18	0.18	(0.22)*

(*) With regeneration of the initial solution (Procedure II)

As the Li-intercalation progresses the colour of the sample changes from yellow to dark-grey. Any change is observed in the X-ray diffraction patterns of the starting materials after the intercalation reactions, showing the topochemical character of the process. The amount of Li intercalated depends both on the nature of the constituting elements on the oxide and on the adopted experimental conditions. Thus, in experiments performed following the procedure I, the Li content increases as the x value in the $Ta_xNb_{1-x}VO_5$ compounds decreases, reaching a lithium intercalation degree of about 0.2 lithium/formulae. To enhance this value we have applied in some experiments the procedure II, i.e., by reiterated regenerations of the initial LiI reagent, obtaining in this form lithium richest bronzes (for instance $Li_{0.22}TaVO_5$, Table I). The use of more active reducing agents, as n-butyl lithium, has provoked drastic structural changes of the starting $Ta_xNb_{1-x}VO_5$ oxides, giving amorphous materials.

It is difficult to decide what is the main cause of the decreasing of the Li intercalation degree maximum value in the oxides richest in tantalum, compared to those oxides richest in niobium, at the same experimental conditions (Procedure I). At the present we have not an interpretation to ascertain this behaviour, in spite of, at least, the two following factors: i) the structural similarities between the $Ta_xNb_{1-x}VO_5$ oxides, and ii) the XPS measurements on the intercalates, which indicate that only the V atoms are able to participate in the redox process (eq. 1) whereas both, niobium or tantalum, preserves its oxidation state after the LiI treatments.

Electrical properties

From the complex impedance spectra of the intercalates we have determined the specific conductivity and the activation energy (E_a) associated to the electrical

transport process. The host material, $TaVO_5$ and $NbVO_5$ lacks electrical conductivity in the measured temperature range, which produces a dispersion of points in the Nyquist diagram. Table II shows the values calculated for the geometric capacitance, C_g, and specific conductivity, σ_i, obtained from the corresponding Nyquist diagrams [5,6] of the most representative selected bronzes.

TABLE II

Calculated values, from the Nyquist diagrams, for the geometric capacitance, C_g, and specific conductivity, σ_i, of the $Li_y Ta_x Nb_{1-x} VO_5$ ($0 \leq x \leq 1$) bronzes (T=573 K).

Sample	C_g (F)	σ_i $(\Omega cm)^{-1}$
$Li_{0.18}NbVO_5$	4.6E-11	3.5E-6
$Li_{0.08}Ta_{0.53}Nb_{0.47}VO_5$	1.6E-11	7.8E-6
$Li_{0.03}TaVO_5$	8.3E-12	0.8E-7
$Li_{0.22}TaVO_5$	1.2E-11	7.8E-7

In all cases, the values of the C_g fall within the 10^{-11}-10^{-12} F range, which can be associated with a capacitance whose dielectric properties are mainly due to a phenomena controlled by the bulk material, rather than other effects as grain boundary, sample/electrode interface, etc.[7]. The low values obtained from the capacitance suggest that the contribution related to electronic transport must be negiglible [8].

As it is known, there is a direct relationship between the number of charge carriers and the ionic conductivity of the materials. Thus, we can explain the differences found in the insertion compounds of $TaVO_5$, observing that conductivity increases as the lithium content increases. This fact supports the idea that the lithium ions are the responsible for the electrical transport process.

Figure 2 shows the Arrhenius plot's for the samples $Li_y Ta_x Nb_{1-x} VO_5$ in which x adopts the values= 0, 0.53, and 1 respectively. It is shown a lineal relationship between (1/T) and $\log(\sigma_i T)$. Table III shows the values of the activation energies for the ionic conductivity process in the studied bronzes. In general, the obtained values are all of the same order of magnitude of the values described in the bibliography for good lithium-ion conductors[9]. It is notheworty the relatively low value shown by the compound in which x=0, i.e. $Li_{0.18}NbVO_5$, suggesting that the transport process of the lithium ions in this compound are favoured with respect to those compounds with Ta in their composition.

TABLE III

Activation energies calculated from the Arrhenius plot's

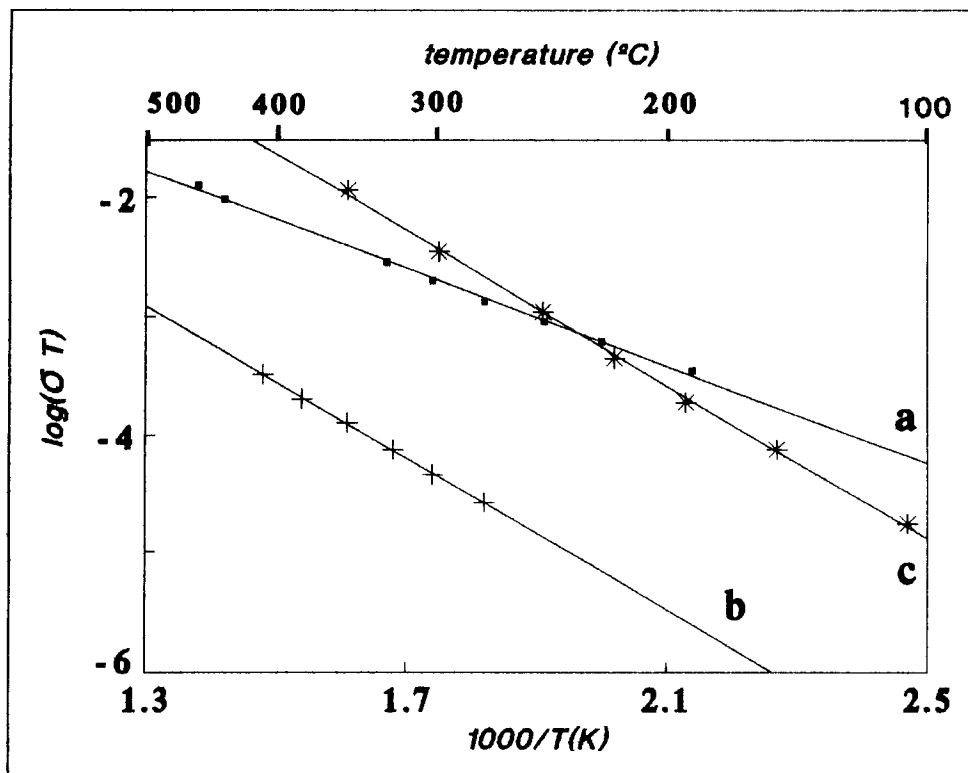| Sample	E_a (eV)
$Li_{0.18}NbVO_5$	0.39
$Li_{0.08}Ta_{0.53}Nb_{0.47}VO_5$	0.65
$Li_{0.03}TaVO_5$	0.65

Fig.2.- Arrhenius plot's for ionic conductivity in the following Li-bronzes:
a: $Li_{0.18}NbVO_5$, b: $Li_{0.03}TaVO_5$ and c: $Li_{0.08}Ta_{0.53}Nb_{0.47}VO_5$

CONCLUSIONS

A novel family of Li-bronzes can be achieved by redox processes involving chemical reactions between the MVO_5 (M=Ta, Nb) oxides and LiI dissolved in acetonitrile. Lithium insertion appears as a topotactic and reversible process. This interesting property opens a way to potential future applications in the field of electronic devices (cathode batteries, electrochromic materials, etc.). Electrical conductivity of the Li-bronzes studied by impedance spectroscopy reveals suitable values for the activation energy, although the number of charge carriers (Li^+) is relatively low.

ACKNOWLEDGMENTS

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Intercalation Compounds

Lithium Intercalation in Ta$_x$Nb$_{1-x}$VO$_5$ Mixed Oxides