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“ CARACTERIZACION ELECTROQUIMICA DE LA
INSERCIÓN DE LITIO EN $MnNb_2O_6$ (M=,Co,Ni,Cu, Zn, Cd)
Y EN $Li_2X_2NbO_6$ (X = Mn, Co, Ni) “

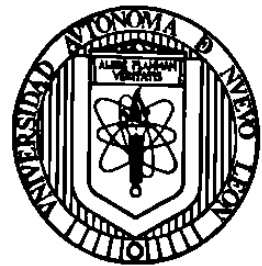
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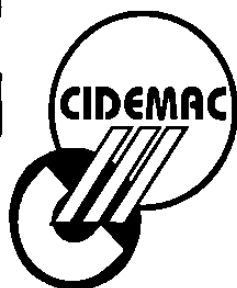
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P R E S E N T E .-

Por medio de la presente me permito solicitarle la inscripción del trabajo titulado "Caracterización Electroquímica de la Inserción de Litio en $MnNb_2O_6$ ($M=Co, Ni, Cu, Zn, Cd$) y en $Li_8X_2NbO_6$ ($X = Mn, Co, Ni$)" al concurso para premiar a la mejor tesis de Maestría de la U.A.N.L. en el área de Ciencias Exactas.

Adjunto remito copia de Acta de Examen así como de una Publicación Internacional derivada del mismo. Sinceramente suyo.

A T E N T A M E N T E
"ALERE FLAMMAM VERITATIS"
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DR. ANTONIO FERNANDEZ FUENTES
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Electrochemical lithium insertion in some niobates MNb_2O_6 ($M = Mn, Co, Ni, Cu, Zn$ and Cd)

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Abstract

Several oxides with the general formula MNb_2O_6 ($M = Mn, Co, Ni, Cu, Zn$ and Cd) have been tested as cathodes for lithium batteries. When discharging electrochemical cells using these niobates as active materials down 0.5 V, the maximum observed lithium content (x) in $Li_xMnNb_2O_6$ was $x = 0.9, 0.9, 1.15, 1.5, 2.3$ and 3.0 for $M = Mn, Co, Zn, Cd, Ni$ and Cu , respectively. In situ X-ray diffraction experiments revealed in all cases a certain loss of crystallinity as the insertion reaction proceeds. Only the copper niobate showed an almost complete amorphization after the initial discharge. The kinetics of lithium insertion in these compounds was studied by electrochemical spectroscopy in a stepping potential mode. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Electrochemical lithium insertion; Niobates; Lithium batteries

1. Introduction

The search for new materials to replace metallic lithium or graphites normally used as anodes in 'lithium-ion' or 'rocking-chair' batteries has recently become a subject of particular interest. In this context, several crystalline and amorphous vanadates have been described in the literature as showing large capacities and good cycling behaviour [1,2]. In this paper, a study of the electrochemical lithium insertion in six isostructural niobates with the general formula MNb_2O_6 ($M = Mn, Co, Ni, Cu, Zn$ and Cd) is presented. These compounds crystallize with the columbite structure, forming alternate layers of distorted oxygen coordinated niobium and transition metal octahedra linked by corner or edge sharing [3].

Step potential electrochemical spectroscopy has here been used to study such processes in the present system of materials. Structural rearrangements associated with guest-host matrix interactions can be studied by in situ X-ray diffraction, which is the case for the oxides studied here.

2. Experimental

The synthesis of the parent oxides, MNb_2O_6 ($M = Mn, Co, Ni, Cu, Zn$ and Cd), were carried out by solid state reaction as described in a previous work [3]. A mixture of MO_2 and Nb_2O_5 (Alfa, 99.5%) were heated, after mixing in the appropriate stoichiometric ratios (see Table 1).

Structural characterisation of the parent oxides, including the in situ X-ray diffraction experiments, were carried out using a Siemens D-5000 diffractometer with $Cu K_\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation.

Electrochemical insertions were performed with a MacPile multichannel galvanostat/potentiostat system [4] using Swagelok type cells [5] and lithium as negative and reference electrode. A 1 mol dm^{-3} solution of $LiClO_4$ in a 50:50 mixture of ethylene carbonate (EC) and diethoxy ethane (DEE) was used as electrolyte [6]. The positive electrode was a 7 mm diameter pellet obtained by pressing 15–20 mg of a mixture containing the oxide to be tested, carbon black and ethylene-propylene-diene terpolymer (EPDT) in a 88:10:2 ratio. The cell assembly was carried out in an argon filled glovebox.

The structural changes in the lattice of MNb_2O_6 produced by the insertion of lithium were studied by in situ X-ray diffraction. The main advantage of this technique is

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Table 1
Experimental condition for the synthesis of MNb_2O_6 by solid state reaction

Phase	Temperature (°C)	Time (h)
MNb_2O_6	1220	24
CoNb_2O_6	1200	18
NiNb_2O_6	1200	6
CuNb_2O_6	1100	16
ZnNb_2O_6	1400	6
CdNb_2O_6	1000	12

that it increases the accuracy with which this process can be studied, since changes in intensity are only due to structural and not morphological effects. In this paper, we have used a laboratory made electrochemical cell [7] to collect X-ray diffraction data during the discharge of several cells.

3. Results and discussion

3.1. Lithium insertion in MNb_2O_6 ($M = \text{Mn}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$ and Cd)

When lithium is inserted into the different parent oxides using an electrochemical cell with configuration $\text{Li}/\text{electrolyte}/\text{MNb}_2\text{O}_6$, different behaviour is observed in the corresponding $E-x$ plots. Fig. 1 shows the evolution of the voltage during an experiment carried out between 3.0 and 0.5 V vs. Li^+/Li^0 for the six phases studied here.

When the cells are discharged at a constant current rate (typically 1 Li/35 h), the oxides showed different abilities to incorporate lithium atoms: 0.9 for Mn and Co, 1.15 for Zn, 1.5 for Cd, 2.3 for Ni, and 3.0 for Cu per formula unit. In all cases when lithium is being deintercalated, the corresponding curve is different compared to the discharge case. This clearly indicates that lithium insertion is not reversible, so that only part of the lithium can be extracted from the structure. The origin of this irreversibility can be associated with irreversible structural transformations. Nevertheless, successive cycles of charge–discharge showed a narrow region of reversible lithium incorporation. Of all these niobates, copper niobate reacts reversibly with a larger number of lithium ions (about 0.5 Li^+ per formula unit) during the first cycle. For the second and subsequent 18 cycles, the cells exhibit a gradual loss of capacity (see Fig. 2).

To discover more about this irreversibility, in situ X-ray diffraction experiments were made. The diffraction patterns revealed in all cases, a certain loss of crystallinity as cell discharge proceeded. The copper niobate, which accepts the largest number of lithium, showed an almost complete amorphization after the initial discharge (see Fig. 3). In fact, for composition $\text{Li}_x\text{CuNb}_2\text{O}_6$ ($x \geq 1.2$), i.e.,

during the plateau labelled as *I* in Fig. 1, the main reflections also have disappeared. On the other hand, X-ray diffraction patterns for $\text{Li}_x\text{MNb}_2\text{O}_6$ (for Mn, Co, Ni, Zn and Cd; $x = x_{\text{max}}$) still show the main reflections of the corresponding parent oxides, indicating only partial amorphization. These observations are in agreement with previous reports of higher capacity in amorphous than crystalline materials [8].

Some cells with configuration Li/LiClO_4 1 mol dm^{-3} in EC + DMC (50:50)/ MNb_2O_6 , were also discharged down to just above 0.02 V. In all cases, a major irreversibility was observed during the cycling of each cell. The in situ X-ray experiments revealed that, although their intensities decrease, reflection remain down to 0.02 V.

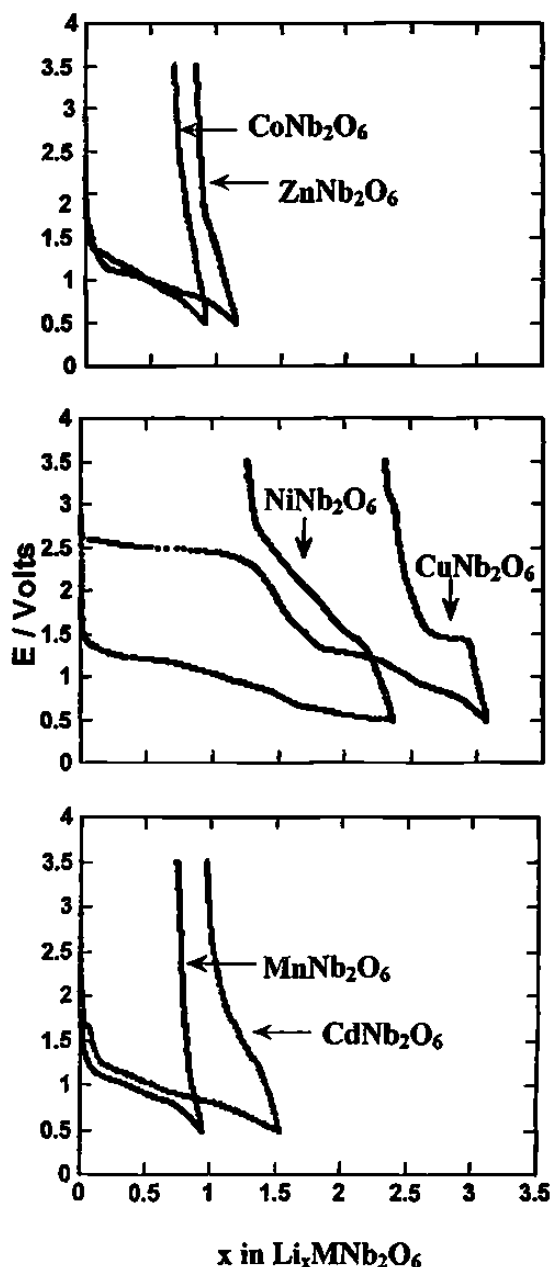


Fig. 1. Voltage vs. composition curves for the niobates MNb_2O_6 ($M = \text{Mn}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$ and Cd). A rate of 1 Li in 35 h was used between 3.0 and 0.5 V.

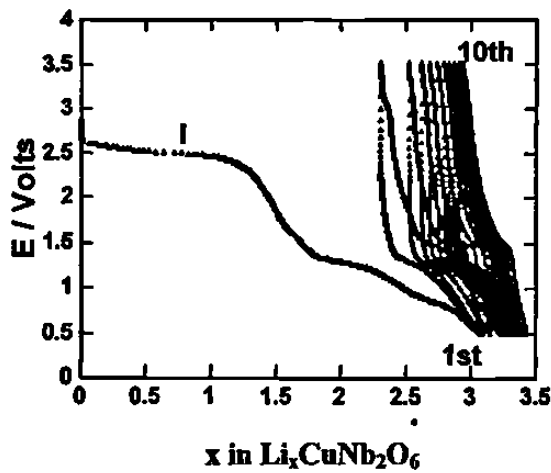


Fig. 2. Voltage vs. composition for successive charge–discharge cycles of a cell using CuNb_2O_6 as active material.

Potentiostatic experiments have also been performed. The information obtained from these experiments (through $I-t$ relaxation curves) gives detailed information about the nature of the different reduction processes that occurs in the electrodes [9]. Fig. 4a shows some features observed during the discharge of the cell $\text{Li}/\text{CuNb}_2\text{O}_6$. Between 3.0 and 2.6 V, only small currents are detected and the cell exhibits a low capacity. At lower potential values, (< 2.6 V), the current increases, reaching a maximum value at 2.5 V. In this region (the peak labelled *I*), the behaviour of current vs. time is far from a $t^{-1/2}$ law.

Lithium ion diffusion does not, therefore, control the insertion reaction process [10]. Note that this region corresponds to the large plateau observed in the $E-x$ plot

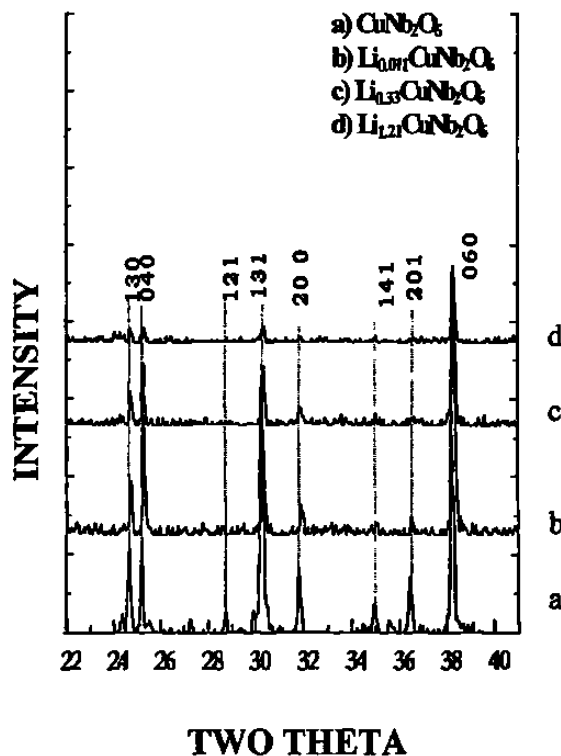


Fig. 3. X-ray diffraction patterns obtained from an in situ experiment using CuNb_2O_6 as the active material.

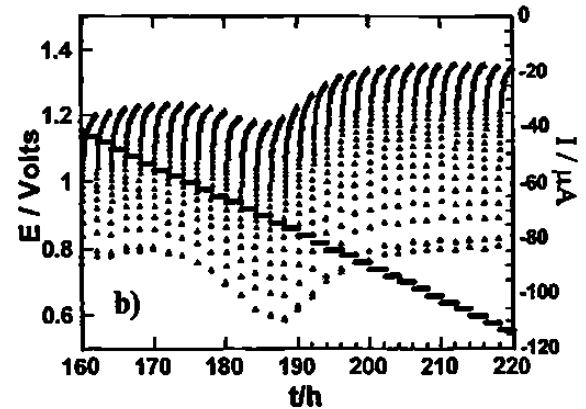
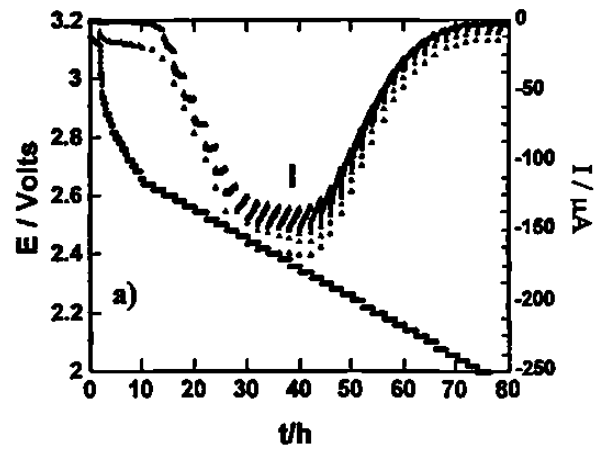


Fig. 4. A chronoamperogram showing details of the kinetics of lithium insertion into CuNb_2O_6 (a) at the first reduction process, and (b) when lithium diffusion determines the insertion reaction.

(labelled as *I* in Fig. 2). In the same way, in situ X-ray experiments show that an almost complete amorphization of this oxide occurs along this plateau, suggesting an irreversible transformation of the material.

Fig. 4b shows some typical $I-t$ relaxation curves observed at low potential values. In the region below 1.25 V, the current relaxation in each potential step follows a $t^{-1/2}$ law, indicating that lithium diffusion controls the insertion reaction. This region (between 1.25–0.5 V vs. Li^+/Li^0) corresponds to the region in which the insertion reaction is reversible in the $E-x$ plot. Similar regions were also observed for the other niobates when their $I-t$ relaxation curves were analysed in the region where lithium is incorporated through a reversible intercalation reaction.

4. Conclusions

Several oxides with the general formula MNb_2O_6 ($M = \text{Mn, Co, Ni, Cu, Zn}$ and Cd) have been tested as cathodes in lithium batteries. In all cases, a gradual amorphization is observed as lithium incorporation proceeds. Electrochemical spectroscopy and in situ X-ray experiments indicate that an irreversible structural transformation occurs in all cases. As a consequence, the cells exhibits a poor reversibility.

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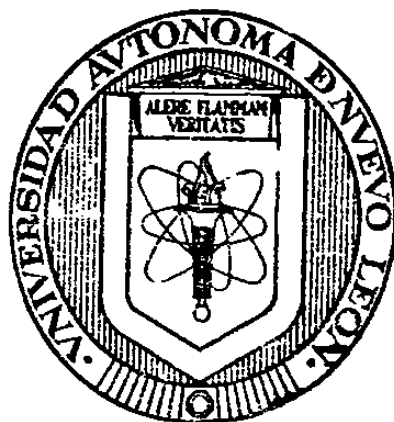
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Y EN Li_3XNbO_6 (X= Mn, Co, Ni)”

POR

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Como requisito parcial para obtener el grado de
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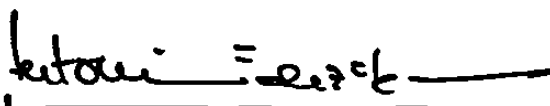
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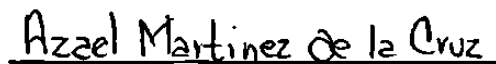
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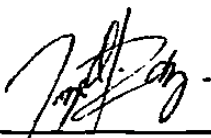
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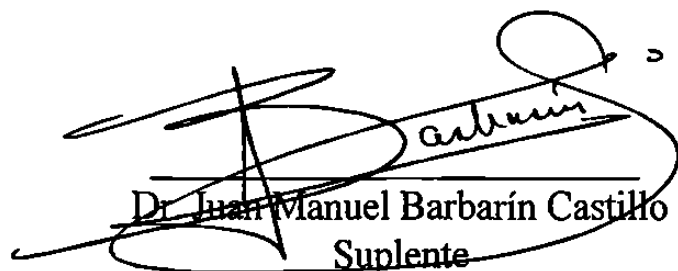
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conocimiento. El conocimiento tiene fronteras.
La imaginación es la frontera del universo.*

A. Einstein.

DEDICO ESTA TESIS A LAS DOS PERSONAS MÁS IMPORTANTES EN MI VIDA.....

MIS PADRES :

EFRAÍN LÓPEZ VILLASANA

SARA ALCARAZ DE LÓPEZ

A MIS HERMANOS :

ALFREDO

EFRAÍN

AZUCENA

A MI CUÑADA MA. GUADALUPE

Y A MIS SOBRINOS ALFREDO Y MELANI

Y DE MANERA MUY ESPECIAL A MI GRAN AMIGO Y COMPAÑERO

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