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Electrochemical characteristics of lithium insertion in several 3D metal tungstates (MWO_4, M = Mn, Co, Ni and Cu) prepared by aqueous reactions

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Abstract

In this work we present a study of the synthesis and electrochemical characteristics of lithium insertion into several tungstates of general formula MWO_4 (M = Mn, Co, Ni and Cu), prepared by aqueous salt metathesis reaction. From those tried, only $MnWO_4$ was obtained from solution as a partially crystalline compound while the remaining tungstates were obtained as amorphous hydrated materials which crystallized between 400 and 500 °C. The electrochemical study showed that none of these materials are good hosts for insertion reactions because of the irreversibility of the process although they could be used as electrodes in primary cells.

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1. Introduction

A great deal of effort is currently dedicated to improve the performance of secondary lithium batteries. Since the materials used today as electrodes in the systems commercially available are not completely free from problems (e.g. possibility of reversible cycling only in a limited range of compositions as in $LiCoO_2$ or $LiNiO_2$ or capacity fading at elevated temperatures and during overcharge as in $LiMn_2O_4$), the search for new compounds which could be used for this purpose or the improvement of the properties of those already known are being pursued by a large number of researchers. The list of inorganic compounds which have been proposed as possible electrodes is large and include mixed oxides such as vanadates [1] or more complex materials such as NASICON-related compounds as $Li_3Fe_2(PO_4)_3$ [2] or $Fe_2(MO_4)_3$ (M = Mo, W, S) [3] where open 3D frameworks containing $(MO_4)^{n-}$ polyanions instead of the smaller O^{2-} ions allow fast Li^+ ion conduction. These latter compounds, $Fe_2(MO_4)_3$ (M = Mo and W), have been also shown to be able to reversibly intercalate up to 2 sodium ions per formula unit [4]. Many of these compounds, perform better in electrochemical cells when obtained as poorly crystalline materials by a soft chemistry route than when prepared by traditional solid state reactions. Soft chemistry routes allow a better control of morphology and particle size and therefore can be used to improve the electrochemical performance of a given compound.

Metal tungstates MWO_4 (where M is a 3D divalent transition metal ion with an ionic radius <1 Å) crystallize with the wolframite type of structure which can be described as made up of hexagonal close-packed oxygen atoms with certain octahedral sites filled by M^{2+} and W^{6+} cations in an ordered way. Compounds belonging to this family have been studied as gas sensors [5], catalysts [6] or electrochromic systems [7]. However, we found no available data in literature of previous electrochemical studies in these metal tungstates but for $CuWO_4$ which was studied by Scrosati and coworkers some years ago and proposed for use in high energy primary Li power sources [8]. Arora et al. also carried out an analysis of the electrochemical characteristics of

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copper tungstate single crystals in order to use them for fabricating photoelectrochemical solar cells [9] finding out that this compound is an n-type semiconductor and that the efficiency and fill factor of such cells decrease with increasing input intensity. In this work, we present a study the electrochemical characteristics of lithium insertion in a series of 3D metal tungstates obtained by aqueous salt metathesis reactions. The materials were also prepared by solid state reaction in order to use them as a reference for those prepared by the soft chemistry method.

2. Experimental

The synthesis of the compounds studied in this work, was carried out by (i) solid state and (ii) aqueous salt metathesis reactions. For the first one, tungsten (VI) trioxide (WO_3, 99.995%) and the corresponding metal oxides (MO, M = Mn, Co, Ni and Cu) were used as starting chemicals. They were weighed in the appropriate stoichiometric ratio (1:1) and intimately mixed in an agate mortar under acetone. The reaction mixtures were placed in high alumina crucibles (Adolph Coors Co.) and fired (in air) in an electrical furnace at temperatures between 600 °C ($CoWO_4$) and 800–850 °C (MWO_4, M = Mn, Ni and Cu) with periodic grindings to favour reaction. After firing, samples were reground and reheated to ensure homogeneity.

In solution, tungstates were prepared by mixing equal volumes of two 0.4 M aqueous solutions of the corresponding hydrated metal nitrates (99% +) and $Na_2WO_42H_2O$ (99%). Precipitates obtained were filtered, washed with distilled water and oven dried at 100 °C for 15 h. After this initial treatment, samples were fired (15 h) at each one of the following temperatures: 200, 400, 600 and 800 °C.

Phase identification was carried out by X-ray powder diffraction in a Siemens D-5000 diffractometer (Ni-filtered CuK_α radiation, $\lambda = 1.5418$ Å). A typical identification experiment was run between 10 and 70° (2θ) using a step size of 0.04°/s. Thermal analyses were carried out in a Thermal Analyst 2100 (TA Instruments) using a heating rate of 5 °C/min and a constant air flow of 100 ml/min (typical sample weight of 15 mg). The presence of water molecules was followed by using infrared spectroscopy in a FTIR Perkin Elmer Paragon 1000 PC working between 4000 and 500 cm^{-1}. Samples were also characterized by SEM (Scanning Electron Microscopy) in a Jeol JSM-6300 fitted with a NORAN Instruments, Inc. 660D-1SSS energy-dispersive X-ray detector (EDX).

Electrochemical experiments were carried out in a Multichannel potentiostatic-galvanostatic system MacPile II [Bio-Logic Corp., Claix (France)] using Swagelok (TM) type test cells. Positive electrodes were prepared by mixing and pressing, a mixture of the phases being tested, carbon black and a binder (0.5% ethylene-propylene-diene terpolymer, EPDT, in cyclohexane) in a 89:10:1 molar ratio. Metal lithium acted simultaneously as negative and reference electrode while a 1 M solution of $LiPF_6$ in a 2:1 mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) was used as electrolyte. Several experiments were run for each tungstate, either in a current-controlled or in a potential-controlled mode at 25 °C.

3. Results

3.1. Synthesis

The solid state reaction of WO_3 and the corresponding metal oxides MO, yielded in every case a compound with a powder pattern similar to that reported in literature for the different tungstates, MWO_4 (M = Mn, Co, Ni and Cu). However, results obtained using the aqueous method presented different characteristics depending on the metal nitrate used. For reason of clarity, the synthesis of these tungstates will be discussed in two groups: MWO_4 (M = Co, Ni and Cu), and $MnWO_4$.

3.1.1. MWO_4 (M = Co, Ni and Cu)

In these three cases, an instantaneous precipitate evolved from solution as soon as the two starting solutions were mixed. While the final pH of the nickel and cobalt solutions were similar (7.1 and 7.4 respectively), copper nitrate produced an acid solution (pH = 4.6). The precipitates were aged overnight, filtered and washed and finally oven dried at 100 °C for 15 h. The resulting powders were then fired at different temperatures as specified above. The evolution of the powder patterns of such precipitates with temperature is shown in Fig. 1. As it can be seen, the three precipitates when dried at 100 or heated at 200 °C, produced featureless powder patterns typical of amorphous materials. However, when heated at 400 °C for 15 h, the three begin to show the characteristic reflections of the corresponding tungstates, MWO_4 (M = Co, Ni and Cu; JCPDS 15-0867, 15-0755 and 21-0307, respectively). Firing the samples at 600 °C produced an increase of tungstates crystallinity as evidenced by better defined powder patterns with sharper and more intense peaks while further firing at 800 °C produced no changes in the powder patterns.

Thermal analysis of these three precipitates showed basically the same features: a total weight loss of around 8% taking place during several thermal events. Half of the weight loss is taking place below 200 °C and could be assigned to the volatilisation of loosely bound water molecules. This process corresponds in the DTA curve, with an endothermic event, as expected. The remaining

weight loss is taking place between 200 and 400 to 500 °C and finishes with an important exothermic peak observed in the DTA curves. This weight loss is thought to be due to the release of more strongly bound water molecules (structural water). The complete removal of water molecules in the samples fired at 400 °C was confirmed by FTIR spectroscopy. Combining thermal analysis and X-ray powder diffraction, one could ascribe

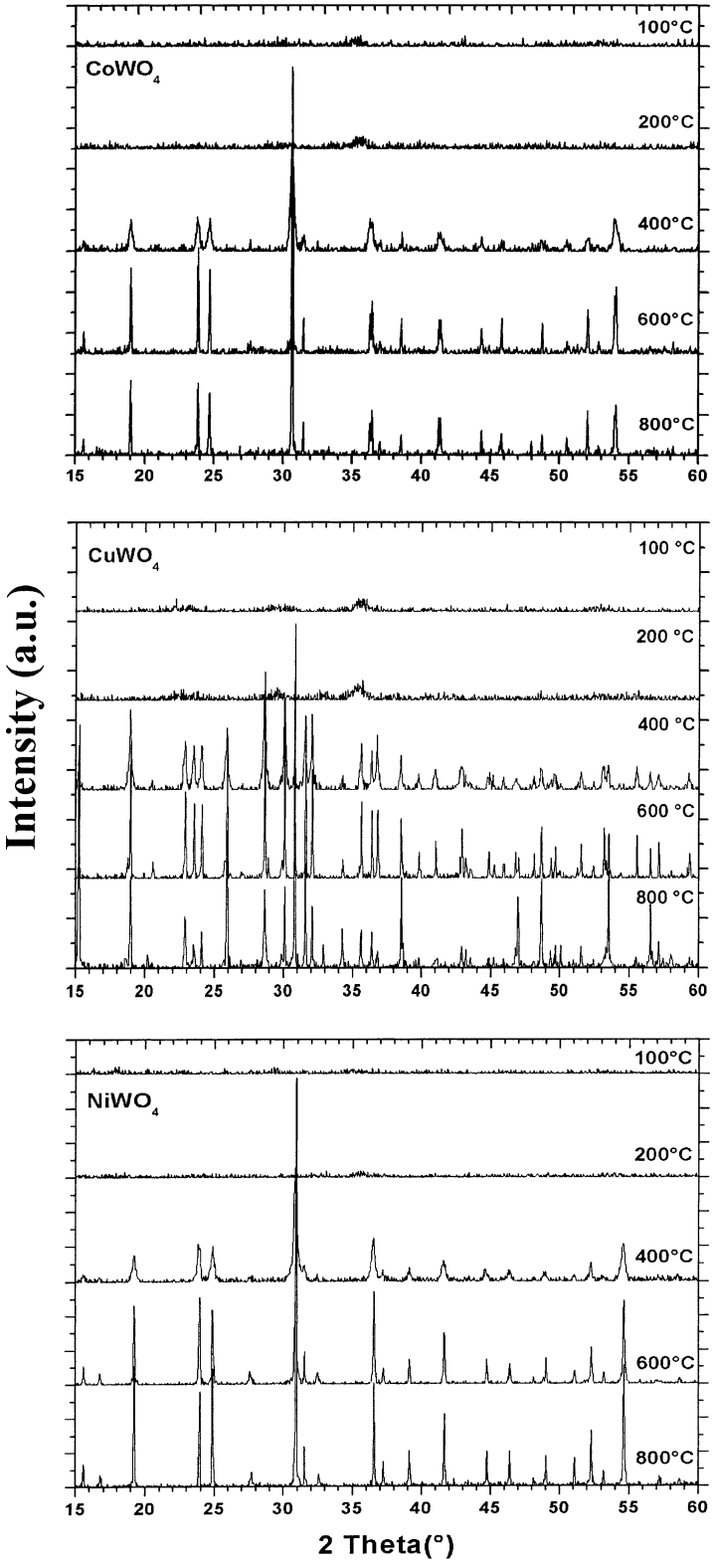

Fig. 1. Evolution of the precipitates with temperature obtained from solution for cobalt (top), copper (middle) and nickel tungstates (bottom).

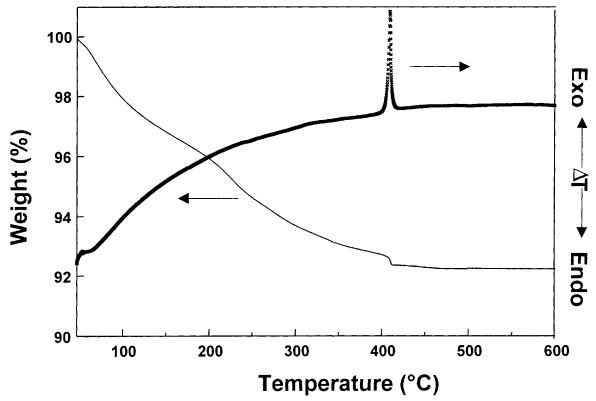

Fig. 2. TGA and DTA curves for $CuWO_4$ precipitated from solution and dried at 100 °C/15h prior to the analysis.

the exothermic event observed in the DTA curves with the crystallization of the amorphous phase precipitated from solution. As an example, Fig. 2 shows the TGA and DTA curves obtained for the precipitate filtered from the copper nitrate/sodium tungstate solution. Table 1 summarises these findings.

3.1.2. $MnWO_4$

A dark-yellow precipitate evolved from solution after mixing the starting reagents. The pH of the final solution, 7.5, was similar to that observed for the Ni and Co solutions. The X-ray powder pattern of this precipitate (Fig. 3a) revealed already the main characteristic reflections of $MnWO_4$ (JCPDS 13-0434). Therefore, $MnWO_4$ obtained from solution was already partially crystalline (powder pattern with broad and not very intense peaks). This fact was also corroborated by thermal analysis (Fig. 3b). The DTA curve did not show any thermal event that could be associated with a crystallisation process as observed in the other tungstates. Further firing up to 400 °C did not produce noticeable changes in the powder diffraction pattern of this sample although crystallinity improved when the sample was fired above that temperature. The TGA curve revealed a smaller weight loss in this case (3%) than that detected for the other compounds studied corresponding to a proposed formula of $MnWO_4 0.5H_2O$ for the solution precipitate.

Table 1
Characterisation of the precipitates obtained by aqueous salt metathesis reaction for cobalt, nickel and copper

M in MWO_4	Weight loss (%)	Crystallisation temp. (°C)	Proposed precipitate formula
Co	≈8.0	410	$CoWO_4.1.5H_2O$
Ni	≈8.0	495	$NiWO_4.1.5H_2O$
Cu	≈8.0	410	$CuWO_4.1.5H_2O$

3.1.3. Characterization of the precipitates by SEM

Samples obtained from solution and fired at 100, 400 and 800 °C were also analyzed by SEM. Independently of the metal nitrate used, a common feature of the precipitates fired at lower temperatures was the presence of a large number of agglomerates which in some cases could be observed in large quantities even in the samples fired at 800 °C. Chemical analyses were also carried out to detect the presence of basically, sodium ions co-precipitated with the tungstates finding out that only the cobalt and nickel samples contained traces of this element. No other impurities were found by this technique. Fig. 4 shows particles of three tungstates obtained from solution and fired at 800 °C. Particle morphology was observed to depend on the second metal present in the tungstates. Thus, $MnWO_4$ formed agglomerates of round-shaped particles which, with increasing temperature, evolved into needle-shaped particles of different sizes, from a few μm to ≈60 μm length, (Fig. 4a). Isolated agglomerates were still present at this temperature. Cobalt tungstate was obtained also as agglomerates of small round-shaped particles which conserved this form at 800 °C, (Fig. 4b). Copper (Fig. 4c) and nickel tungstates obtained by this method showed to be formed

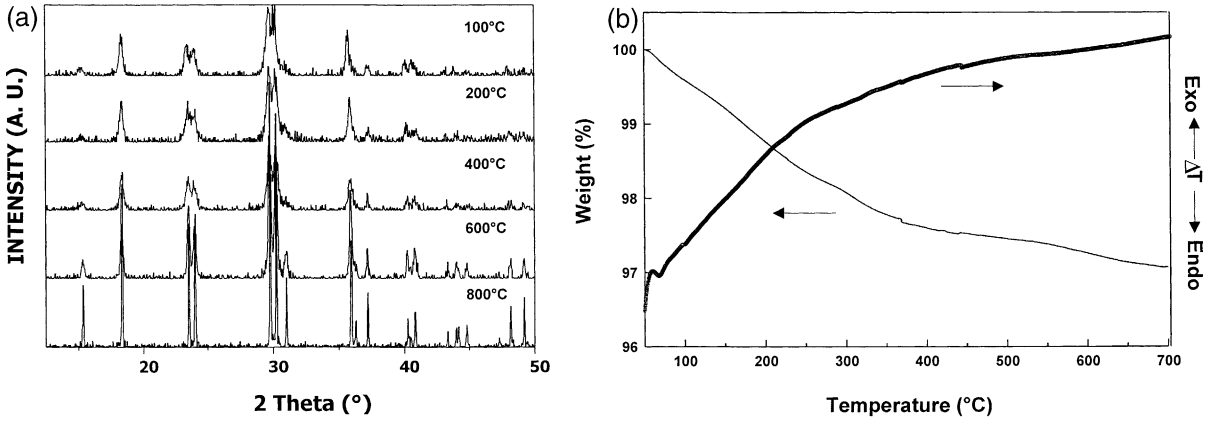

Fig. 3. (a) Evolution with temperature of $MnWO_4$ obtained from solution and (b) TGA and DTA curves for $MnWO_4$ powders obtained from solution and preheated 15 h at 100 °C prior to thermal analysis.

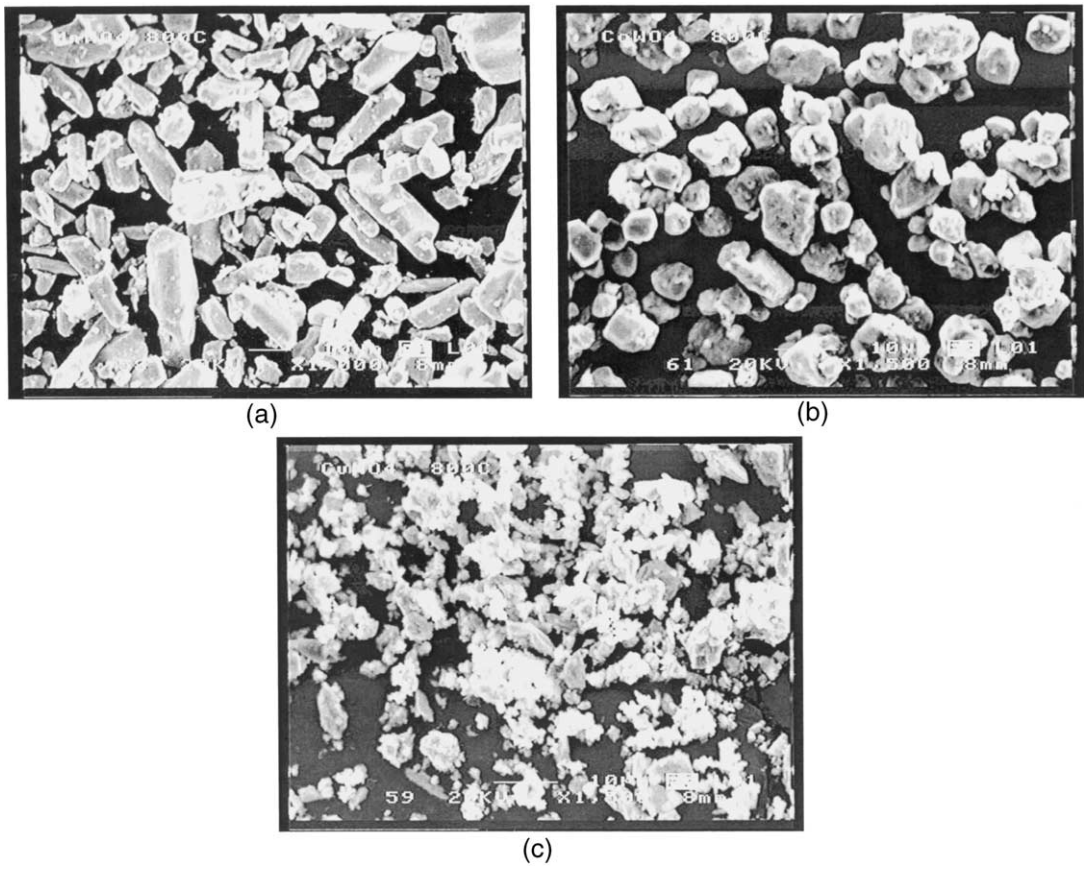

Fig. 4. Micrographs of MWO_4 obtained from solution and fired at 800 °C: (a) M = Mn, (b) M = Co and (c) M = Cu.

basically by agglomerates of irregular shaped small particles even when fired at the highest temperature used in this study.

3.2. Electrochemistry

3.2.1. Li//$CuWO_4$

Fig. 5 shows the main features of the electrochemical lithium insertion into crystalline $CuWO_4$ obtained by the aqueous method and fired at 800 °C. The first two curves of Fig. 5A and B, show results obtained during SPECS experiments [10] run using ±10 mV/h potential steps. As it can be seen, lithium insertion proceeds through at least three very well defined reduction steps which can be noticed as regions of approximately constant E values in Fig. 5A (E vs. Lithium content in Li_x-$CuWO_4$ plot) and as peaks in 5B (I vs. E plot). These three reduction steps, labeled as I, II and III, take place at 2.7, 1.7 and 0.5 Volts vs. Li^+/Li, respectively. The number of lithium atoms inserted in $CuWO_4$ when the cell was discharged down to 0.01 V vs. Li^+/Li, was high, 5.90 (2.95 Li/metal atom) leading to a capacity of about 500 Ah/kg although in an irreversible reaction since most of them can not be extracted during charge. According to time dependence of the current when crossing each reduction step, it could be determined that the three are first order transitions [11]. As an example, Fig. 5C shows time dependence of the current in the first reduction step (using −10 mV/h potential steps) with a profile obviously not governed by a simple diffusion process which would have given a monotonic tendency towards I = 0. With the idea of studying the reversibility of each of these three processes, several experiments were run between different voltage limits observing that the region labeled as I, is responsible for the irreversibility of lithium insertion (Fig. 5D). During this first plateau, crystalline $CuWO_4$ suffers irreversible structural changes and produces a material showing reversibility versus electrochemical lithium insertion. It was not possible to follow structural changes by in situ XRD since the powder pattern of $CuWO_4$, transformed into that characteristic of an amorphous material during this initial step. The presence of a similar plateau at approximately the same voltage, 2.6 V vs. Li^+/Li, was observed by Sato and Hama when studying lithium insertion into another copper containing mixed oxide (e.g. $CuNb_2O_6$, a columbite type of structure [12]) and has been associated with the irreversible $Cu^{2+} \rightarrow Cu^+$ reduction. The second step which corresponds to the insertion of 1 lithium atom per formula unit should then, be associated with the $W^{6+} \rightarrow W^{5+}$ reduction and is shown to be a reversible process. A deeper lithium

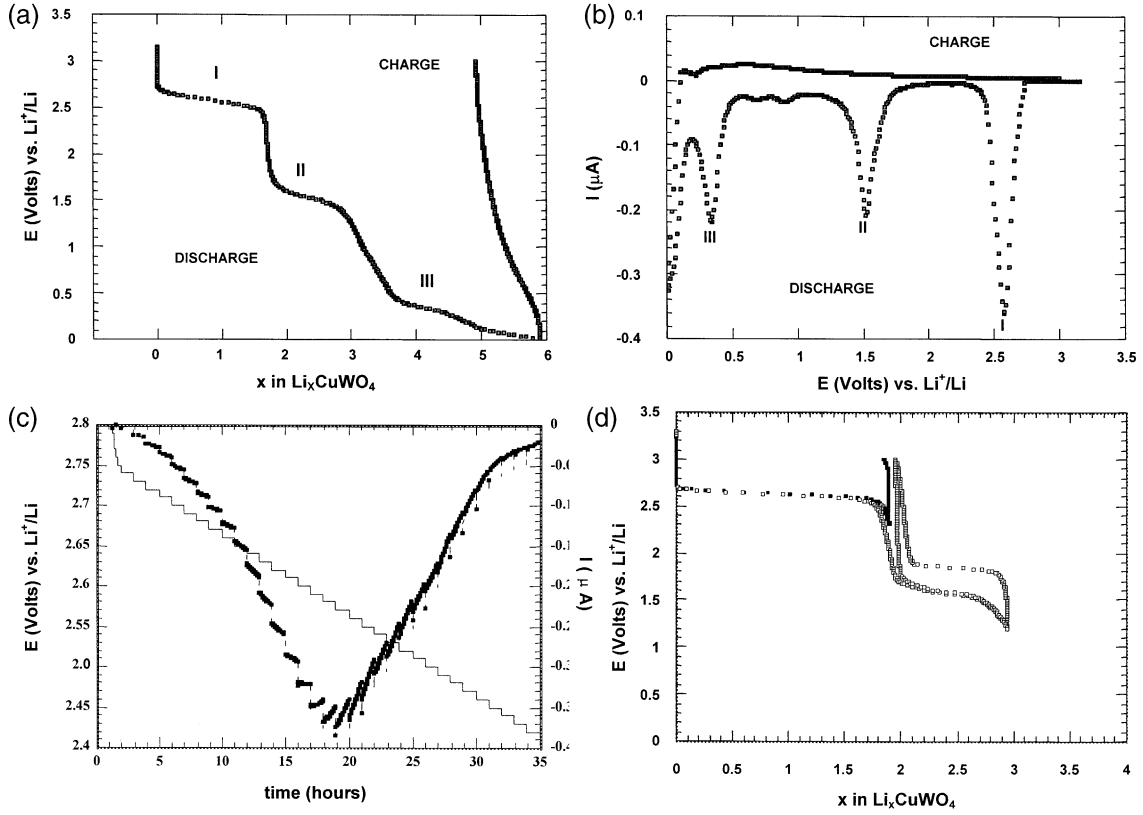

Fig. 5. Electrochemistry of lithium insertion in $CuWO_4$: (A) evolution of the voltage-composition curve for crystalline $CuWO_4$; (B) intensity vs. voltage curve showing the irreversibility if lithium insertion into $CuWO_4$ and confirming the existence of at least three reduction steps; (C) evolution of cell current and voltage with time during SPECS experiment run using −10 mV/h potential steps; (D) evolution of cell voltage with composition between different limits.

insertion induced reduction of this tungstate (possibly further reduction of tungsten ions) produces irreversible structural changes on the original framework. The curves obtained for $Li//CuWO_4$ using the tungstate prepared by the aqueous method and fired below 800 °C or prepared by solid state reaction, were analogous to the ones shown in Fig. 5.

3.2.2. $Li//MWO_4$ ($M = Co$ and Ni)

The electrochemical lithium insertion reaction in these two isostructural tungstates presents similar characteristcs. In both cases, the number of lithium atoms inserted when discharging cells using the tungstates fired at 800 °C or prepared by solid state reaction, as active materials of the positive electrode down to 0.01 V vs. Li^+/Li, is similar (approx. 8). Important differences were observed on the electrochemical behaviour of the samples prepared by the aqueous method and heated at different temperatures. In particular, precipitates fired at 400 °C showed a dramatic increase in the number of lithium atoms inserted when compared with the same samples fired at 800 °C or that obtained by solid state reaction. In the nickel case for example, the tungstate heated at 400 °C inserted 12.5 lithium atoms leading to a capacity of 1100 Ah/kg although in an irreversible reaction. Even the shape of the electrochemical curves, are different (Fig. 6). Although they present a plateau of approximately constant E values for x in Li_xNiWO_4 between 0 and 2, on the precipitate fired at 400 °C, this plateau appears at 1.5 V (vs. Li^+/Li), much higher than the 0.9 V of the same precipitate fired at 800 °C. The tungstate prepared by solid state reaction presents a behaviour which might be seen as a mixture of both described above with two plateaus: one at 1.4 V ($0 \leqslant x \leqslant 1$) and a second one at 0.9 V ($1 \leqslant x \leqslant 4$). Results presented as an I (μA) vs. E (V vs. Li^+/Li) plot show that the electrochemical reduction of MWO_4 ($M = Ni$ and Co) due to lithium insertion in the compound obtained by the solution-precipitation method and fired at 400 °C presents a very sharp peak approximately at 1.5 V vs. Li^+/Li, which corresponds to a first order transition and is hardly seen on the materials prepared by solid state reaction or by the solution-precipitation method and fired at 800 °C. At this point, we can not determine the cause of these differences although the degree of crystallinity could be at least partially responsible. TGA analysis run in the sample fired at 400 °C/15 h did not show any presence of water molecules which also could

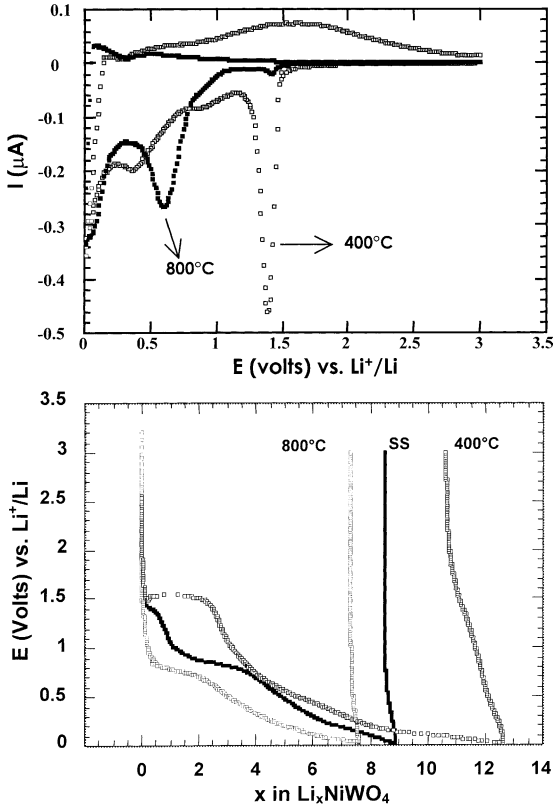

Fig. 6. Electrochemistry of lithium insertion in $NiWO_4$: intensity vs. voltage curve for $NiWO_4$ prepared by aqueous reaction and fired at 400 (void squares) and 800 °C (filled squares) (A); evolution of cell voltage with composition for $NiWO_4$ prepared by solid state (SS) and aqueous reactions with different firing temperatures (400 and 800 °C) (B).

have been responsible for this different behaviour. In any case, lithium insertion induced reduction of these two tungstates is not a reversible process.

The electrochemical lithium insertion in $MnWO_4$ showed that this compound incorporated only 1 lithium atom when discharged to 0.3 V vs. Li^+/Li and that this reaction is irreversible.

All the compounds studied having similar structure, results show that the divalent cation present in these metal tungstates plays an active role during the synthesis and electrochemical insertion. Each divalent ion determines the morphology and particle size of the compounds obtained from solution as well as the electrochemical characteristics of lithium insertion. The number of lithium atoms inserted is, in some cases, well above that theoretically needed for the complete reduction of all cations present in the tungstates. Leroux et al. [13], when studying lithium insertion in $MnV_2O_6.4H_2O$ showed that neither of the two cations were in their metallic state even in the totally reduced sample indicating that the classical insertion process mechanism does not hold for this type of reaction. A model of phase separation of the host into a finely divided electrochemically active phase and an electrochemically inert matrix and the formation of "Li-O" bonds have also been suggested by some authors to explain the large lithium uptake in some materials and the reversibility of such a process [1,14–15]. It is also generally accepted that oxygen ions play an active role as possible recipients of a significant electron transfer during lithium insertion. In our case this "phase separation" process did not produce any electrochemically active phase and lithium insertion remained mostly irreversible.

4. Conclusions

An aqueous salt metathesis reaction using $Na_2WO_4.2H_2O$ and hydrated metal (II) nitrates as starting chemical reagents, have been applied to the synthesis at room temperature, of several 3d metal tungstates. They were obtained from solution amorphous as MWO_4 (M = Co, Ni and Cu) or "partially" crystalline as $MnWO_4$. Thermal analysis showed the crystallization temperature of MWO_4 (M = Co, Ni and Cu) to be between 400 and 500 °C. The electrochemical study has shown that these compounds are not good hosts for insertion reactions because although they can incorporate a relatively large amount of lithium atoms (capacities above 1000 Ah/kg were obtained in some cases), the reaction is irreversible. However, $CuWO_4$ could reversibly incorporate 1 lithium atom although only after an initial irreversible step associated with Cu^{2+} to Cu^+ reduction. Differences in the electrochemical behavior were noticed in the nickel and cobalt tungstates as a function of precipitate firing temperature.

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