XAS STUDY OF THE REVERSIBLE REACTIVITY MECHANISM OF MICRO- AND NANOSTRUCTURED ELECTRODEPOSITED Cu_2O THIN FILMS TOWARDS LITHIUM

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ABSTRACT

Highly uniform electrodeposited Cu_2O electrodes for Li-ion batteries, with variable particle size, morphology and thickness, have been studied in the charged and discharged steps as a function of the number of cycling processes, by means of X-ray absorption spectroscopy (XAS) at the Cu K edge. Both, fingerprint analysis of the X-ray Absorption Near Edge Structure spectra (XANES) and the radial atomic distribution obtained by the analysis of the Extended X-ray Absorption Fine Structure (EXAFS) spectra, have allowed us to quantify the bimodal distribution (Cu and Cu_2O) of the electrodes. These results correlate qualitatively well with their different electrochemical response, establishing a deep insight into the reversible reactivity mechanism of these films towards lithium in Li batteries. Our results demonstrate that the reversibility of the reduction process upon the number of cycles depends on the thickness, as it was suggested in previous works but also on the morphology of the electrodes. Higher reversibility corresponds to smaller thickness electrodes. For similar thickness, the reversibility is higher for porous and nanometric particles electrodes than for compact and micrometric particles electrodes. The thinnest film exhibited an increase of capacity after several recycling steps, which agrees with the increase of the Cu_2O content.

1. INTRODUCTION

Nowadays the investigation of metal oxide anodes as electrodes in Li batteries has received considerable attention.¹ Many transition metal oxides such as FeO, Fe₃O₄, NiO, CoO, Co₃O₄, CuO, ZnO and SnO have been investigated as promising anode materials for lithium ion batteries.²⁻⁹ These metal oxides exhibit different electrochemical performances and reaction mechanisms with Li ion. For example, we recently reported the reversible reactivity of Cu₂O towards lithium, which showed that the cycling process differs from the classical Li-alloying mechanism.^{10,11} More specifically, it would consist of the Li-driven decomposition of the Cu₂O into a composite made of metallic Cu nanograins dispersed into a Li₂O matrix with, upon subsequent oxidation, a reoxidation of Cu into Cu₂O concomitant with a decomposition of Li₂O according to the following reaction mechanism proposed by the group of Tarascon:^{2,12}

In those preliminary reports, Cu₂O thin films of variable particle size, morphology and thickness were electrodeposited over titanium substrates. Electrodeposition is a very versatile preparation technique which allows a control of the characteristics of the deposited material through the deposition parameters.¹³ Some of those films were subsequently tested as electrodes in lithium batteries. Their electrochemical response suggested the key role played by the coating thickness, which seems to be more important than that played by particle size and crystallinity. To have a more accurate understanding of the electrochemical reaction that these deposits experience towards lithium, *ex-situ* XAS measurements were performed. XAS is a powerful technique that has the capability to observe the changes in the local atomic structure and oxidation states around a specific atom at different states of charge and/or discharge of the electrodes during the cycling process. Information about the valence state and coordination geometry of the investigated element can be obtained from the XANES region, whereas the EXAFS region can probe the local structural environment of the absorbing atom, that is, interatomic distances, coordination number and static and dynamic disorder¹⁴.

In this work, *ex-situ* XAS measurements were carried out at the Cu K-edge in Cu₂O films whose electrochemical response as cathodic electrodes in lithium-ion batteries has been studied previously.^{10,11} In fact we have selected for this analysis, Cu₂O electrodes that have different surface morphologies, thicknesses and particle sizes in order to determine the influence of these parameters in their electrochemical response. The volume analysis of the phase composition (Cu/Cu₂O ratio) of these electrodes as a function of number of cycles also allows us to confirm the irreversible loss of electrical capacity in the first cycle of these electrodes.

2. EXPERIMENTAL DETAILS

Single-phase Cu₂O thin films have been electrodeposited potentiostatically onto titanium substrates by the cathodic reduction of copper ions in an aqueous solution of cupric lactate at pH 9 and bath temperature of 30 °C, according to an experimental procedure described in a previous work.¹³

Concretely, we have synthesized films at two values of applied potential, -400 and -575 mV vs. a saturated calomel electrode (SCE), in order to obtain pure Cu_2O samples with different surface morphologies. In this work, for each applied potential, electrodes with two different thicknesses have been prepared by controlling the transferred charge during the electrodeposition. So, four different types of electrodes have been prepared: electrodes A and B at -575 mV, and electrodes C and D at -400 mV. The amount of oxide attached to the substrate was determined by weighing the electrode before and after electrodeposition on a Sartorius microbalance sensitive to within $\pm 1 \mu\text{g}$.

The structure and phase composition of the electrochemically deposited films were identified by X-ray diffraction (XRD) on a Siemens D5000 diffractometer using $\text{Cu K}\alpha$ radiation. The surface morphology of the films was examined in a JEOL JSM-5410 Scanning Electron Microscope (SEM) with accelerating voltage of 35 KV.

Electrochemical measurements were carried out in two electrodes cells, using lithium as counter-electrode. The electrolyte used was Merck battery electrolyte LP 40 (ED:DEC = 1:1 (w/w) 1 M LiPF_6). Rectangular 8 x 9 mm pieces of titanium coated with the active material were used as working electrodes. Cells were galvanostatically discharged and charged on a voltage range from 0.0 to 3.0 V at a C/12 cycling rate, C being defined as 1 Li^+ exchanged in 1 h. All electrochemical measurements were controlled via a MacPile potentiostat-galvanostat. Five duplicates of each electrode A, B, C and D were prepared. So, after the electrochemical cycling of the electrodes, 20 different samples were obtained. We labeled them as A0, B0, C0 and D0 that correspond to the electrodes before cycling; A1D, B1D, C1D and D1D that correspond to the electrodes after the 1st discharge process; A1C, B1C, C1C and D1C are the electrodes after the 1st charge process; A10C, B10C, C10C and D10C that correspond to the electrodes after the 10th charge process, and finally, A30C, B30C, C30C and D30C that correspond to electrodes after the 30th charge process.

The local atomic structure at the copper site in the different electrodes has been studied by means of XAS at the Cu K-edge. XAS experiments were carried out at the beamline BM29 at the European Synchrotron Radiation Facility (ESRF; Grenoble, France) using a fixed-exit Si (111) double crystal monochromator with an energy resolution $\Delta E/E$ around 8×10^{-5} at the Cu K-edge (8979 eV)). The XAS measurements were performed at room temperature in fluorescence mode using a Ge solid-state (13 elements) detector. Energy calibration was performed in each measurement using the Cu foil as reference. Harmonic rejection better than 10^{-5} was achieved by using the Si mirror coating of the double flat mirror installed after the monochromator.

A qualitative fingerprint analysis of the XANES spectra was carried out¹⁴. Experimental XANES spectra of the electrodes were fit with linear combinations of those of Cu_2O and metallic Cu reference compounds to determine the proportion of each reference compound in the electrodes. Spectra averaging, background subtraction and amplitude normalization required to obtain the EXAFS signals $\chi(k)$, were performed using the Athena (version 0.0.058) program.¹⁵ The Fourier transform (FT) of the k-weighted EXAFS spectra was calculated between 2 and $12 \text{ \AA}^{-1}$ using a sine window. The best fit to the

data was performed by means of the Artemis (version 0.0.013) program,^{15,16} using as starting model a mixed phase of metallic Cu and Cu₂O in a ratio according to the derived one from the XANES analysis.

3. RESULTS

3.1 Structural and morphological characteristics of the electrodes before cycling

Table 1 shows preparation conditions and some properties of the deposited films. In this table, the density mass was obtained from the weigh of the electrode before and after the electrodeposition. It was always in good agreement with the value estimated from transferred charge using Faraday's law and assuming the electrodeposition reaction:

Theoretical film thickness included in table 1 was calculated from the measured density mass and the compound density (taken as 6 g·cm⁻³).

Figure 1 shows XRD patterns of the as-deposited films A0, B0, C0 and D0. They only exhibited sets of reflections assigned to Ti substrate and Cu₂O compound. The Cu₂O reflections for the film D were very weak, consistent with the small amount deposited. The intensity of reflections of films A and B, prepared at -575 mV vs. SCE, were consistent with those reported for bulk Cu₂O, being (111) reflection stronger than (200) reflection. However, the intensity of both reflections tended to equalize for film C, prepared at -400 mV vs. SCE, thus indicating a certain tendency of particle to growth along [h00] direction.¹³ In all films the reflections were very broad, indicative of a low crystallite size.

Figure 2 shows top-view and cross-section SEM images of two of the films prepared, which are representative of those obtained at the two distinct applied potentials. They revealed that the superficial texture and morphology strongly depend on the applied potential used during the deposition.¹³ The films deposited at the more cathodic potential (films A and B), exhibited identical granular surface morphology and the grains agglomerate with a cauliflower-like appearance, irrespective of their different thickness. The estimated grain size is smaller than 1 µm (ca. 150-300 nm) but these grains are formed by smaller crystals which size has been estimated on the order of tens of nanometers (see Table 1). The SEM images of the film A also show a highly porous texture. The texture of film C (prepared at -400 mV vs. SCE) was quite different and estimating the size of the particles forming the agglomerates was beyond the resolution of the microscope. The cross-section image revealed a more compact and less porous deposits than films A and B. To circumvent that particle size estimation inconvenience, we have used AFM, the resolution of which is better than SEM.¹¹ The AFM images of the films C and D (not shown) confirmed the compactness of these films and allowed the estimation of particle size. It can be observed in table 1 that the particle size decreased as the deposition time decreased, from around 150-450 nm for film C, to 60-240 nm for film D.

Cross-section images allowed estimation of film thickness included in table 1. As can be seen, all films, except A, showed a fair correlation between the thickness estimated from SEM and the

theoretical one. The SEM thickness of film A was higher than that calculated from its density mass, in accordance with its high porosity. As expected, for films deposited at the same applied potential, the average thickness estimated from SEM images decreases as the density mass decreases.

In table 1, particle size values corresponding to films synthesized at -575 mV vs. SCE were estimated by approaching to the crystallite size. Thus, the FWHM of the principal diffraction peak observed in XRD patterns, i.e. from (111) peak, was used in the Scherrer formula.¹⁷ As indicated, for the case of films deposited at -400 mV vs. SCE, particle size values were taken from AFM images due to the low intensity of the diffraction peaks of deposited material (see Figure 1).

3.2 Electrochemical behaviour

The use of films A to D as electrodes in lithium batteries was studied. The first and thirtieth galvanostatic discharge-charge curves for Li/Cu₂O cells are shown in Figure 3. The voltage profiles are similar to those already described for Cu₂O electrodes and consistent with the proposed reaction (1).¹⁸ The most significant features are related with the extension of the first discharge curve, the reversibility of the subsequent charge process and the electrical performance on cycling. During the first discharge, the Faradaic yield of the electrodes exceeds the stoichiometric value for two electrons, which was ascribed to the formation of a solid electrolyte interphase (SEI) layer.⁷ Conversely, no more than 1.8 Li⁺ ions were extracted from any film during charge process, which is attributed to the incomplete decomposition of Li₂O and SEI. On cycling tests, the consumption of Li⁺ ions is reduced respect to the theoretically expected values as maximum. The above commented findings differ among electrodes, and are influenced by their thickness and morphology. Thus, for each class of electrode – prepared at -400 and -575 mV vs. SCE –, the extension of the first discharge curve, the reversibility of reaction and the electrochemical performance increase as the film thickness decreases. Nevertheless, this assertion is not true when comparing electrodes of different class, indicating that thickness is not the only key factor that influences the electrochemical properties of electrode. Moreover, from the observation of the evolution of the specific capacity values delivered by the Li/Cu₂O cells on cycling (Figure 4), it results even more difficult to correlate the morphology characteristic of films with the electrochemical behaviour. In that sense, the electrode D delivers the higher values but only after an initial period of successive discharge-charge processes. This increase on capacity values on cycling is only found in a subtle manner for electrode B. The thickest electrode for each class of films delivers low but sustainable capacity values on cycling (electrodes A and C).

Several questions remains unresolved from the study of the electrochemical behavior of these electrodes, namely: i) the charge recovery accounted on the first discharge-charge cycle does uncertain about the completion of the conversion reaction (1); ii) the role of the morphology characteristics on the electrochemical response; iii) the anomalous evolution of capacity values showed by electrode D.

3.3 XANES and EXAFS analysis

3.3.1 Electrodes before cycling

Figure 5 shows the Cu K-edge XANES spectra for the electrodes before any cycling process (electrodes A0, B0, C0 and D0) compared to those of metallic copper and binary (Cu_2O and CuO) oxides, which correspond to the Cu^0 , Cu^+ and Cu^{2+} oxidation states, respectively. The main difference among the XANES spectra of these reference compounds is related to the energy position of the absorption edge that shifts to higher energies with increasing oxidation state of Cu. The energy of the absorption edge is defined as the first inflection point in the derivative spectra (not shown) and the values obtained are 8978.9, 8980.4 and 8983.6 eV for metallic Cu, Cu_2O and CuO , respectively. This fact will be used in the following to identify and quantify the different phases that may appear in our electrodes at different stages of the cycling. Irrespective of the morphology and film thickness, the XANES spectra for the four electrodes before cycling are identical to each other and overlie that of the Cu_2O reference compound. This indicates that the as-deposited electrodes consist on single phase polycrystalline Cu_2O with Cu atoms in a +1 oxidation state. This result is well consistent with the XRD data presented in former works.^{10,11} Moreover, EXAFS data confirm the Cu_2O cuprite phase for the as-deposited films. Figure 6(a) compares the modulus of the FT for the four electrodes before cycling. Electrodes with cauliflower-like morphology, A0 and B0, show a decrease in the intensity of the peaks in the FT with respect to the more compact electrodes, C0 and D0. The aforementioned difference could be related to the different crystal size, as deduced from FWHM of XRD peaks and AFM data, showed by films electrodeposited at different potentials (see table 1). The samples with cauliflower-like morphology have a crystal size around 25 nm, while C0 and D0 samples show a bigger crystal size, more than 100 nm. The FT features can be easily interpreted in terms of scattering paths, once the shortening of distances due to the phase shift effect is taken into account. The first peak between 1 and 2 Å is only due to the first coordination shell (two oxygen atoms at a distance $R = 1.85$ Å). The second peak between 2 and 3.5 Å contains single scattering contributions from the second (12 Cu at 3.02 Å) and the third (6 O at 3.54 Å) coordination shells, together with multiple scattering contributions. All the fits have been done up to 3.5 Å using the cubic cuprite (space group, Pn-3m) crystallographic structure as the input model. In Figure 6(b), we show the best fit simulation for the electrode C0. Similar results were found for the other electrodes. The coordination numbers were fixed to their crystallographic values and the amplitude reduction factor s_0^2 and the threshold energy E_0 were fixed to 0.79 and 5.7 eV, respectively for all samples. The derived structural parameters are the typical distances in Cu_2O bulk compounds.¹⁸

3.3.2 Electrodes after the 1st discharge process

They correspond to the samples named as A1D, B1D, C1D and D1D. After the first discharge of electrodes up to 0.0 V, there is a reduction of Cu_2O by lithium, leading to the formation of both Li_2O and metallic Cu. X-ray diffractograms were taken at this step but due to the amorphous character of the material in the films after the discharge process, definitive conclusions about this fact could not be

deduced¹¹. In that sense, X-ray absorption has been a crucial tool to confirm the composition of the electrodes and the reaction mechanism mentioned in the introduction.^{2,12} Figure 7 shows the Cu K-edge XANES spectra owing to A1D, B1D, C1D and D1D electrodes. The edge features resemble with Cu foil pattern used as reference (shown in figure), indicating that these electrodes can be ascribed to metallic Cu. Figure 8(a) shows the modulus of the FT of the EXAFS signals for the electrodes after the 1st discharge process. A least squared refinement to the observed FT signals up to 5 Å is shown in Figure 8b for the D1D electrode as a matter of illustration. All the peaks observed are fitted according to the radial distance of surrounding Cu atoms in the face-centred cubic structure of the Cu foil, as indicated in the figure. In the refinements, the S_0^2 factor was fixed to 0.8, the value obtained from the fit of a Cu foil used as reference. From this XAS analysis, we could confirm the complete reduction of Cu₂O into metallic Cu during the first discharge.

3.3.3 Electrodes after the charge processes

All electrodes show an irreversible capacity between the first discharge and charge processes, as it is shown in Figure 3. This implies that not all of the metallic Cu formed during discharge reoxidised. XANES and EXAFS analysis of the electrodes after any of the charge processes investigated confirms a mixture of both phases, metallic Cu and Cu₂O. In order to quantify the ratio between them, we have simulated the experimental XANES spectra as the weighted sum of those of Cu₂O and metallic Cu in its adequate proportion. The good agreement between the different experimental spectra and the signals constructed starting from the reference compounds after applying the appropriate proportion is shown in Figure 9 and the resulting Cu₂O/metallic Cu ratios are given in Table 2. EXAFS analysis has been done on the basis of these XANES results. Figures 10 to 12 compare the FT of the $k \chi(k)$ signals for the electrodes at the first, tenth and 30th charge processes, respectively. Red lines are the best fits of the experimental spectra (points) using the fraction of Cu⁰ and oxidised Cu₂O phases found in the XANES analysis.

XANES spectra of the electrode A, corresponding to the thickest one (thickness = 3.5 µm), after the 1st, 10th and 30th charge processes are identical to each other and they can be fitted in every case with a mixture of 20% Cu₂O / 80% metallic Cu. Moreover, the FTs of the EXAFS signals (Figs. 10, 11 & 12) are quite similar to that of metallic Cu, showing the most intense peak at about 2 Å, which corresponds to the Cu-Cu first shell distance of 2.56 Å. This means that only a little quantity of the electrode mass is able to follow the cycling process when an electrochemical cycle towards lithium is undergone. The conclusion that can be deduced is that after the 1st discharge process, most of the electrode material remains inactive as a metallic Cu phase and it continues as an inert part of the electrode during all the subsequent cycles.

After the 1st charge process, when talking about the thinnest electrode with cauliflower-like morphology, sample B1C, 80% of its total mass has followed the complete cycle, coming back to the original composition Cu₂O. The FT clearly reflects this fact, as shown in Fig. 10, where only the two

main peaks typical of the Cu_2O reference are observed. This result could indicate that a small particle size, associated with a high porosity of the deposited material, is a favourable aspect concerning the cycling process, since this is the best behaviour among all the tested electrodes after the first cycle. However, after the 10th charge process, the ratio between Cu_2O and metallic Cu, changes to 50% / 50%, which represents a deterioration of the electrode behaviour. Finally the sample B30C, maintains equal quantities of both metallic Cu and Cu_2O phases. This trend is followed by the FT curves (Figs. 10, 11 & 12) and it represents an improvement of the electrochemical yielding regarding to the electrode A.

The thickest electrode with compact morphology after the first complete cycle, C1C, fits well with a 20% Cu_2O / 80% metallic Cu mixture. After the 30th charge, the ratio between both phases deduced from the fit shows a little evolution to 22% Cu_2O / 78% metallic Cu. Sample corresponding to electrode C after the 10th charge process has not been included in this analysis since it was not possible to fit either XANES or EXAFS data with a mixture of metallic Cu/ Cu_2O . Probably this sample was damaged during any of the manipulation steps. When comparing the electrochemical performance of the electrode C30C with the one observed for the B30C electrode, we can conclude that particle size is another key parameter that rules out the cycling processes on these electrodes. We should remember that electrode B was originally thicker than electrode C (see table 1). In spite of that, the electrode B has better electrochemical performance than the electrode C (Figures 3 & 4) and the X-ray absorption data shows a bigger proportion of electrode mass involved in the cycling process for the electrode B than for the electrode C. The lower crystallite size in the electrodes with cauliflower-like morphology should be the reason that explains a better electrochemical behaviour.

Conversely, the electrode D presents a surprising behaviour showing a positive evolution when the number of cycles is bigger than 20. The composition of the electrodes has been evaluated after the first, the tenth and the 30th charge. In every one of these steps, the sample is composed by a mixture of Cu_2O -like and metallic Cu-like local structures, but with different ratios. XANES spectra (Fig. 9) and the FT curves (Figs. 10, 11 & 12) indicate that the proportion of the Cu_2O -like phase increases with the number of cycles. The peak at about 1.5 Å corresponding to the Cu-O distance in Cu_2O , becomes more intense whereas the peak at about 2 Å correspondent to the Cu-Cu distance in metallic Cu is reduced, almost disappearing after the 30th cycle. After the first complete cycle, sample D1C contains 45% Cu_2O vs. 55% metallic Cu. As the number of cycles increases to 10, this ratio evolves slightly to a mixture of 55% Cu_2O / 45% metallic Cu, but after the 30th charge process, the Cu_2O phase represents 85% of the total electrode mass. It means that, from this moment, most of the electrode mass is involved in the charge-discharge cycles in a reversible way. Thus, although this electrode does not show a good result after the 1st cycle, its low thickness favours the oxidation/reduction of copper atoms and it allows a positive evolution of the electrode behaviour as it was already presented in a former work.¹¹ In that way, X-ray absorption results confirm the hypothesis pointed out in that work, that electrode thickness is the crucial parameter that rules out their performance in a Li-ion battery.

4. DISCUSSION

The results obtained from XAS analysis must be interpreted combined with those inferred from the electrochemical test in order to know about the electrochemical mechanism accounted in the electrodes. In this sense, Table 3 shows, on the one hand, the capacity values delivered by the electrodes after the 30th charge process (obtained from Figure 4) and, on the other hand, the evaluation in the progression of the conversion reaction $\text{Cu}_2\text{O} + 2\text{Li}^+ + 2\text{e}^- \leftrightarrow 2\text{Cu} + \text{Li}_2\text{O}$ in percentage. From the electrochemical tests, the progression in % was calculated referred to the theoretical capacity value corresponding to the reaction (1), 375 Ahkg^{-1} . In the case of XAS analysis, the $\text{Cu}_2\text{O}/\text{Cu}$ ratios before mentioned in table 2 were included in the last column.

The ability of each electrode to perform reaction (1) was identified in similar way by both techniques, being the higher performance obtained for the electrode D, followed by electrode B and finally by A-C electrodes. Nevertheless, the quantitative results were so different. Considering the powerful of XAS technique in the determination of oxidation state of atoms, it is necessary to accept the existence of secondary electrochemical reactions, to that of conversion reaction (1), to explain the measured capacity values. Thus, in the case of electrodes A and B, the amount of Cu_2O formed at the 30th charge, determined by the XAS analysis, is 20 and 50 %, respectively. This would mean capacity values of 75 and 187 Ahkg^{-1} , respectively, in terms of electrochemistry. These values are far from the 250 and 311 Ahkg^{-1} experimentally measured. The excess of faradaic yield must be associated with the reversible formation of SEI phase on cycling, as reported in other transition metal oxides studied as electrodes in lithium batteries.^{2,20-23} That secondary electrochemical process should be more important in electrodes A and B, since their porous morphology lets that higher area of Cu_2O particles contacts with the electrolyte, facilitating the electrochemical cycling of the last one. In contrast, in the case of the compact film D, the accessibility of electrolyte to Cu_2O inside the film volume is limited, minimizing the participation of electrolyte in the electrochemical process. In this case, the progression values estimated from electrochemical and XAS analysis are enough similar indicating that the conversion mechanism (1), is the main reaction accounted. The texture of the electrode particles played also a major role on the global reactivity of other oxides like hematite.²⁴ Conversely, in the case of electrode C, and in spite of being a compact film, there is also a significant difference in the values for the progression of the conversion reaction obtained by electrochemical and XAS analysis. This could be explained by considering the change in morphology observed for the electrodes C and D after the cycling process, and reported by our group in reference 11. After the first cycle, the C electrode, constituted by a thicker film, appeared fractured with large cracks among Cu_2O islands. Even though this structural change does no affect to its electrochemical performance, a higher Cu_2O surface will be in contact with the electrolyte through the cracks and as a consequence, its role in the electrochemical process will be reinforced.

The scheme 1 shows the chemical evolution of Cu_2O films with different thickness during the discharge and charge processes according to the results obtained from XAS analysis. During the charge process, as the metallic substrate act as the electron source, the inner layers are the first to be oxidized. Subsequently, the electron conduction towards the outer layer becomes limited because Cu_2O is a poor

conductor. Thus, in the thicker films the complete formation of Cu_2O will not account, as previously demonstrated. Conversely, for the thinnest film (electrode D) in which the conversion reaction is highly conducted, the progressive expansion and shrinkage of the structure caused by the lithium insertion/extraction processes would lead to the pulverization of particles up to the nanometric domain. On this scenery, shorter path lengths will be available for the Li^+ diffusion and electron transfer, explaining the progression of the conversion reaction for this electrode. This progression was confirmed by both analysis, electrochemical and XAS, in similar way and with small differences on the values estimated, indicating that conversion reaction advanced cycle by cycle.

5. CONCLUSIONS

XAS data corresponding to thin film Cu_2O electrodes submitted to cycling towards lithium have demonstrated that the composition of these electrodes in different cycling stages is strongly dependent on thickness and morphology of the original films. The smaller the thickness in the non-cycled electrodes, the bigger is the proportion Cu_2O / metallic Cu, showing that this parameter plays a crucial role in the electrochemical yielding of these films. The particle size associated with the porosity of the films, has also influence on the capacity of these electrodes, but between those two parameters, thickness seems to have a more definitive impact on the reversibility of the electrochemical reaction that takes place during the cycling. On the other hand, the reversible formation of a SEI phase on cycling is favoured by the porosity of the electrodes, and it could affect their measured capacity values. XAS techniques have allowed us to elucidate the electrochemical yielding of these films, which demonstrates its power as materials analytical tool.

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Table captions:

Table 1: Preparation conditions and some properties of the deposited films. ^aValues estimated from FWHM of XRD peak; ^bvalues estimated from AFM images.

Table 2: Cu₂O/Cu metallic ratio in per cent of each of electrodes as a function of the number of cycles.

Table 3. Capacity values delivered by the electrodes after the 30th charge process, and progression of the $\text{Cu}_2\text{O} + 2\text{Li}^+ + 2\text{e}^- \leftrightarrow 2\text{Cu} + \text{Li}_2\text{O}$ electrochemical reaction estimated from that and the values obtained from XAS analysis.

Type of surface morphology	Electrode	Electrodeposition Potential (mV vs. SCE)	Density mass (mg/cm ²)	Theoretical thickness (μm)	Thickness observed by SEM (μm)	Particle size (nm)
POROUS WITH NANOMETRIC PARTICLES	A	-575	1.18	1.97	3.5	27.7 ^a
	B	-575	0.91	1.52	1.3	19.7 ^a
COMPACT WITH SUBMICROMETRIC PARTICLES	C	-400	0.64	1.07	0.7	150-450 ^b
	D	-400	0.16	0.27	0.3	60-240 ^b

Table 1

ELECTRODE A	Cu ₂ O/Cu (%)	ELECTRODE B	Cu ₂ O/Cu (%)	ELECTRODE C	Cu ₂ O/Cu (%)	ELECTRODE D	Cu ₂ O/Cu (%)
A0	Cu ₂ O	B0	Cu ₂ O	C0	Cu ₂ O	D0	Cu ₂ O
A1D	Cu	B1D	Cu	C1D	Cu	D1D	Cu
A1C	20 / 80	B1C	80 / 20	C1C	20 / 80	D1C	50 / 50
A10C	20 / 80	B10C	50 / 50	C10C	X	D10C	55 / 45
A30C	20 / 80	B30C	50 / 50	C30C	22 / 78	D30C	85 / 15

Table 2

Electrode	Capacity value / Ahkg ⁻¹	Progress of the conversion reaction / %	
		Estimated from electrochemical tests	Estimated from XAS analysis
A	250	66	20
B	311	83	50
C	230	61	22
D	360	96	85

Table 3

Scheme 1

Figure Captions:

Figure 1: XRD patterns for Cu_2O films electrochemically deposited under different experimental conditions showed on Table 1. Ti peaks are marked with an asterisk. Dot lines are Cu_2O (111) and (200) reflections, while discontinuous line is the most intense reflection corresponding to a metallic Cu phase.

Figure 2: SEM micrographs of the top view for the films A and C (a-b) and SEM micrographs of the cross-sectional view for the films A and C (c-d).

Figure 3: Discharge/charge curves for the 1st and 30th operational cycles for electrodes A to D cycled between 3.0 and 0.0 V (vs. Li^+/Li).

Figure 4: Delivered specific charge capacity values vs. cycle number for electrodes A to D cycled between 3.0 and 0.0 V (vs. Li^+/Li).

Figure 5: Normalized Cu K-edge XANES spectra for the electrodes before any cycling process (electrodes A0, B0, C0 and D0) compared to metallic Cu (dashed line), Cu_2O (continuous line) and CuO (dot line) patterns used as references.

Figure 6a: Fourier Transforms of $k\chi(k)$ for the electrodes before any cycling.

Figure 6b: Comparison of the FT of $k\chi(k)$ (points) and the best fit (line) for the electrode C0. Inset: Fourier filtered contribution up to the second coordination shell. Points are experimental $k\chi(k)$ data and line is the best fit.

Figure 7: Normalized Cu K-edge XANES spectra for the electrodes after the 1st discharge process (electrodes A1D, B1D, C1D and D1D) compared to metallic Cu (continuous lines), Cu_2O (dashed line) and CuO (dot line) patterns used as references.

Figure 8a: Fourier Transforms of $k\chi(k)$ for the electrodes after the first discharge process.

Figure 8b: Comparison of the FT of $k\chi(k)$ (points) and the best fit (line) for the electrode D1D. Inset: Fourier filtered contribution up to the fourth coordination shell. Points are experimental $k\chi(k)$ data and line is the best fit.

Figure 9: Comparison between XANES spectrum (points) at the Cu K-edge and the weighted sums of Cu_2O and Cu metallic reference spectra (red lines) at best-fit proportions of each of electrodes as a function of number cycles.

Figure 10: Comparison of the FT of $k \chi(k)$ (points) and the best fit (line) corresponding to the electrodes after the first charge process.

Figure 11: Comparison of the FT of $k \chi(k)$ (points) and the best fit (line) corresponding to the electrodes after the 10th charge process.

Figure 12: Comparison of the FT of $k \chi(k)$ (points) and the best fit (line) corresponding to the electrodes after the 30th charge process.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6a

Figure 6b

Figure 7

Figure 8a

Figure 8b

Figure 9

Figure 10

Figure 11

Figure 12