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Structural, chemical and electrochemical analyses of $Cu_xV_2O_5$ bronzes thin films

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Abstract

Vanadium pentoxide is one of the most attractive cathodic materials for use in microbatteries. However, the continuous insertion and extraction of lithium ions generate gradative losses in its intercalation capacity during the charge and discharge cycles. The insertion of metallic ions in the oxide matrix, forming bronzes of general formula $Me_xV_2O_5$ is an alternative to increase the electrochemical performance of V_2O_5 . In this work, vanadium oxides and bronzes, in thin film form, were deposited by means of co-sputtering. Structural, chemical and electrochemical characterizations were realized in order to identify the cristallinity, composition, density and oxidation states of the elements in the film. The electrochemical techniques were used for analysis of the reversibility, charge capacity and determination of the diffusion coefficient for lithium ions. The main conclusion is that the addition of copper increased the specific volumetric capacity of the thin films and a better performance was attained during the charge/discharge cycles.

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1. Introduction

Vanadium pentoxide is studied as a cathode material for rechargeable batteries since the end of the seventies [1], due to characteristics like high energy density, high discharge capacity $(3.0 \text{ Li}^+ \text{ per V}_2\text{O}_5)$, low self-discharge and interstitial sites that allows an easy diffusivity of lithium ions [2-4]. For the same reasons, allied to the fact that it is rather easy to obtain the compound in thin film form, V₂O₅ is also one of the most investigated materials for use as cathode in microbatteries. In spite of the above mentioned characteristics, the compound presents a continuous loss in charge capacity during cycling, due to trapping of lithium ions in the oxide structure [5,6]. In thin film form, the crystalline material presents a higher capacity loss in comparison to the amorphous compound, due to the higher structure deformations induced by the intercalation process [6]. Also, in amorphous materials, the trapping of lithium ions has been pointed out as the main reason for the

capacity loss and the consequent decrease in the ionic diffusivity and electronic conductivity of the films [3].

Vanadium bronzes are an alternative to improve lithium diffusivity and the coulombic efficiency in the charge/discharge cycles [7,8]. The vanadium bronzes have the general formula Me_xVO_n ; the Me atoms are ionized in the structure, and the electrons are localized near the V atoms, reducing its oxidation state [9].Vanadium bronzes in thin film form grown by the aerogel technique have been studied in a series of papers [8,10,11]. Concerning bronze films deposited by the sputtering technique, only one work has been reported, but the authors were not able to produce homogeneous films [12]. In this paper, thin films of $Cu_xV_2O_5$ were deposited by reactive co-sputtering and their structure, oxidation state and electrochemical behavior were analyzed.

2. Experimental

The bronzes thin films were deposited by d.c. and r. f. sputtering techniques from copper and vanadium targets, respectively, in an reactive O_2 +Ar atmosphere. The flow of the gases was controlled by two mass flowmeters, and was fixed at

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45.0 sccm (Ar) and 2.5 sccm (O₂). The pressure under deposition was 7.0×10^{-3} mbar. The r.f. sputtering deposition (vanadium target) was done with a power value of 250 W. The d.c. sputtering deposition (copper target) was done with either 2 or 3 W, in order to obtain films with two different compositions. Vanadium pentoxide films were also deposited. Conductive ITO glass, glass or silicon was used as substrates. Thicknesses of the films were in the range 130–160 nm, as measured with an Alpha-Step profilometer.

The presence of crystalline phases was investigated by X-ray diffraction under grazing incidence geometry with Cu K α radiation in the X Pert MRD Philips equipment. Cu and O contents were obtained by Rutherford Scattering Spectroscopy (RBS) using a 2.2 MeV He⁺ beam. The chemical state of the metals was analyzed by X-Ray Absorption Near-Edge structure (XANES). The experiments were performed at the XAS beamline (LNLS, Laboratório Nacional de Luz Síncrotron, Campinas, SP). The photon energy was in the range 8900–9100 eV (copper absorption K-edge) or 5380–5600 eV (vanadium absorption K-edge). The thin film samples were analyzed in the fluorescence mode, and the control samples (CuO, Cu₂O and V₂O₅ pellets) were measured in transmission mode. The chemical state of the elements was also analyzed by X-Ray Photoelectron Spectroscopy (XPS).

Electrochemical cells with the copper-oxide films as the working electrode and two Li metal foils as the negative and counter electrode were used for electrochemical measurements. The electrolyte was 1 M LiClO₄ in propylene carbonate. Chronopotentiometric experiments were performed from rest potential to 1.5 V vs Li, using a current density of 2.0 μ A/cm⁻², by means of a multipotentiostat (VMP system, Biologic) operating in the galvanostatic mode. During the experiments, the cell was maintained inside an Ar dry-box. The Galvanostatic Intermittent Titulation Technique (GITT) [13] was used in order to evaluate the diffusion coefficient. In these experiments, a current pulse of 100 μ A/cm² with duration of 5 s was followed by an open circuit relaxation interval for a maximum time period of 7200 s, or till the potential presented a change less than 100 μ V/h.

3. Results and discussion

The oxygen, vanadium and copper content for each sample were determined by RBS. From these data, the composition and density were calculated. The obtained values are shown in Table 1. For clarity, the composition of the copper-containing samples are presented in a way that allows an easier comparison to the vanadium pentoxide. The thickness of the samples,

Table 1			
Composition,	density	and	thickness

Sample	r.f./d.c. power	Composition	Density (g/cm ³)	Thickness (nm)
VC0	250/0	V _{2.0} O _{5.0}	2.27 ^a	164
VC2	250/2	Cu _{0.1} V _{2.0} O _{4.6}	3.58	138
VC3	250/3	$Cu_{0.3}V_{2.0}O_{5.0}$	3.21	130

^a $d_{bulk} = 3.35 \text{ g/cm}^3$.



Fig. 1. XRD diffractograms.

obtained by profilometry, is also shown in Table 1. XRD analysis (Fig. 1) showed that all films are amorphous.

Sample VCO is a stoichiometric vanadium pentoxide thin film, but with a density lower than the measured value for bulk materials. As expected, the increase in d.c. power increased the copper content (samples VC2 and VC3). Also, the composition of sample VC2 presented an oxygen deficiency, in comparison with the expected bronze composition ($Cu_xV_2O_5$) as has already been observed in other works [4,14,15].

The XPS measurements were performed in order to identify the oxidation state of copper and vanadium. Fig. 2 presents the XPS spectra for the V2p and O1s lines (samples VC2 and VC3). The analysis was done by adjusting and deconvoluting the spectra with Gaussian functions. The peak position and the FWHM (Full-Width at Half-Maximum) of the main peaks are shown in Table 2. In both spectra, the peak related to the broad V2p_{3/2} signal could be deconvoluted in two peaks. The peak at higher energy, for both films, was located at 517.1 eV; this value of binding energy and the value of the FWHM are consistent with V⁺⁵ [16,17]. The peak with lower energy was located at 516.2 and 516.3 eV, for the films VC2 and VC3 respectively.



Fig. 2. XPS V2p and O1s spectral lines.

Table 2 Peak position and FWHM for the O1s, Cu $2p_{3/2}$ and $V2p_{3/2}$ lines, for samples VC2 and VC3

Lines	$V2p_{3/2} (V^{5+}) (eV)$		$V2p_{3/2} (V^{4+}) (eV)$		Cu 2p (eV)		O1s(1) (eV)	O1s(2) (eV)
Samples	FWHM	Center	FWHM	Center	FWHM	Center	Center	Center
VC2	1.9	517.1	1.3	516.2	1.9	931.7	530.0	532.0
VC3	2.0	517.1	2.2	516.3	7.3	933.6	530.1	532.5

This peak is associated to the V^{+4} [18,19]. The presence of vanadium in two oxidation states (V^{+5} and V^{+4}) is due to the insertion of copper ions that partially reduces the oxidation state of vanadium ions. This result is typical for the XPS spectra of vanadium bronzes, as can be seen, e.g., in the works of Q.-H. Wu et al. [20,21].

In what concerns the O1s line, the fitting procedure indicated the presence of two peaks, one at 530.0-530.2 eV (herein called O1s(1)) and the other at 532.0-532.6 eV (herein called O1s(2)). The energy presented by the first peak (O1s(1)) can be associated both to the energy of the O1s line in copper oxide and in or vanadium pentoxide [16,18,19,22]. The second peak (O1s(2)) appears as a shoulder on the main peak, O1s(1), at higher energy. Peaks with these characteristics were observed in other papers concerning vanadium bronzes [20,21]. Then the O1s(2) peaks can be related to oxygen bonding with the incorporated metal, being a signature of the vanadium bronzes. Also, since XPS is a surface technique, the results indicate that copper did not migrate to the film/substrate interface, as observed by other authors [12].

Fig. 3 presents the results concerning XPS measurements for the Cu2p orbital. The copper oxidation state for sample VC3 (Cu_{0.3}V₂O₅), due to the absence of the shake-up satellite, was identified as +1 [16,22]. The analysis of the spectrum for VC2 could not be done due to the low photoemission intensity. The identification of the copper oxidation state for this sample was done by XANES.

Fig. 4 presents the copper K-edge XANES spectra for the CuO and Cu₂O samples used as standards, as well as the data for the thin film samples. For CuO, the spectrum presents an intense band centered at 8996 eV, and a shoulder at \sim 8986 eV typical of Cu^{+2} species in CuO [23,24]. The spectrum for the Cu₂O standard sample presents a pre-peak located at 8981 eV, and the main peak at energy 8994 eV. The spectrum is characteristic of Cu^+ species [23,24]. The comparison of the copper K-edge XANES spectra for the VC2 and VC3 (Fig. 4) revealed the differences between the oxidation state of copper in these two samples. The absorption edge for the VC2 thin film sample is in agreement with the one presented for the CuO standard sample. The shoulder, however is not present, as has been observed in other vanadium/copper bronze samples [10], in which the copper oxidation state is +2. Also, the VC3 thin film sample spectrum is very similar to the one presented by the Cu₂O standard sample.

XANES measurements were also performed at the vanadium absorption K-edge. Fig. 5 presents the spectrum for the thin film samples and for the standard vanadium pentoxide sample. All spectra present a pre-peak, located at 5469.9 eV, attributed to 1s–3d forbidden transitions. The intensity of the pre-peak generally increases with the increase of the vanadium oxidation state in vanadium oxides and is also related to the consequent decrease in the oxygen symmetry (distortion of the VO_6 group) [25]. It can be also noted that there is a shift of the absorption edge to lower energy values when copper is added to the vanadium pentoxide structure in order to form the bronze compound (Fig. 5). This result implies that the vanadium oxidation state decreases in the order V₂O₅-VC3-VC2. This is compatible with the fact that, due to the oxygen deficiency presented by sample VC2, the V⁺⁴ amount present in this sample is greater than in the VC3 sample. The XANES spectra observed in the vanadium K-edge are similar to the ones for copper vanadium bronzes in xerogel film samples [10]. The electrochemical behavior for the films (lithium insertion and extraction) was analyzed. The potential composition curves for the films VC0, VC2 and VC3 are presented in Fig. 6. The profiles are typical of amorphous materials.

The vanadium pentoxide film (VC0 sample) was able to intercalate ~3.25 Li ions per V₂O₅ unit; the charge capacity was then ~109 μ Ah/cm²- μ m in the first cycle. Intercalation levels greater than 3 lithium ions have been measured for aero-gel films [26]. The film VC2 was able to intercalate ~3.0 lithium ions per compound molecule. Even if the amount of intercalated ions for this sample is lower than the corresponding number for film VC0, its volumetric capacity was greater, 158 μ Ah/cm²- μ m, due to its higher density. The film VC3 was able to intercalate 3.8 lithium ions per compound molecule, and the charge capacity was then ~191 μ Ah/cm²- μ m. The significant increase in the specific charge capacities of the bronze samples can be attributed to the copper ions reduction during the discharge process [10].



Fig. 3. XPS Cu 2p spectral line.



Fig. 4. Copper K-edge XANES spectra for the CuO and Cu₂O standard samples and for the thin film samples.

The discharge capacity as a function of cycling is shown in Fig. 7. The measurements show that the copper insertion in vanadium pentoxide improved significantly the electrochemical performance, making the intercalation/de-intercalation processes more reversible. After 110 cycles, samples VC2 and VC3 presented ~ 75 and $\sim 64\%$ of the initial capacity, respectively, while for VC0 sample (vanadium pentoxide) the value represented 53% of the initial capacity. The charge capacity values and the cycling stability presented by the bronze samples are better than the behaviour reported for similar sputtered thin film samples [12]. Also, the loss of stability with the increase of copper content is in agreement with the behaviour of bronze samples obtained by the aerogel technique [8].

The diffusion coefficient (*D*), estimated from the GITT data, is presented in Fig. 8, for all films. The films containing copper (bronze films) presents the greatest values for *D*; the film VC3 presented a value ~ 2 magnitude orders above the value presented by sample VC0, indicating an improvement of the ionic diffusion with the copper content. The increase in the diffusion coefficient is linked to the expected increase in the electronic conductivity with copper addition. [13,27]. However, for samples VC2 and VC3, *D* is severely affected when lithium is progressively intercalated in the structure. The results for the



4. Conclusions

In this work, copper ions were inserted in vanadium pentoxide thin films, in order to obtain bronze samples, by means of reactive co-sputtering from vanadium and copper targets As expected for bronze samples, vanadium is present in the +5 and +4 oxidation state. Copper insertion increases the charge capacity and decreased the capacity loss on cycling, contributing to a better efficiency of the insertion and extraction of lithium ions. The analysis concerning the diffusion coefficient showed that the copper inclusion also contributed to a better lithium displacement inside the matrix V₂O₅.

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Fig. 5. Vanadium K-edge XANES spectra for the V_2O_5 standard sample and for the thin film samples.





Fig. 7. Discharge capacity as a function of cycling.



Fig. 8. Diffusion coefficient vs intercalation level.

XPS and XRD experiments. The XANES experiments were performed at the Laboratório Nacional de Luz Síncrotron (LNLS, Campinas, Brazil).

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