

Li Diffusion and Electrochromism in Amorphous and Crystalline Vanadium Oxide Thin Film Electrodes

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Filmes amorfos de óxido de vanádio foram depositados sobre substratos de vidro recobertos com ITO, pela técnica de deposição de filmes de óxidos metálicos por filamento aquecido. Os espectros de difração de raios-X mostraram que os filmes como-depositados tratados termicamente em atmosfera de argônio em 200 e 300 °C continuaram amorfos e os tratados a 400 e 500 °C tornaram-se policristalinos, com a estrutura do V_2O_5 . Os eletrodos foram eletroquimicamente reversíveis sob intercalação de Li^+ , exibindo o efeito electrocrômico, observado por medidas da transmitância ótica em 632,8 nm. O coeficiente de difusão do Li, DC, foi medido pela técnica de titulação galvanostática intermitente (GITT) em função da carga inserida. Para os filmes cristalinos, a absorvância ótica e o DC aumentam com a quantidade de Li inserido, nas regiões de fase única de $Li_xV_2O_5$ cristalino e decrescem nas regiões de duas fases. Para essas, um DC efetivo foi considerado. Nos filmes cristalinos foi inferida a presença de outros óxidos de vanádio misturados à matriz de V_2O_5 , através das medidas de cronopotenciometria e de DC.

Amorphous vanadium oxide films were synthesized onto ITO-coated glass substrates by the hot filament metal oxide deposition technique. The as-deposited samples were heat-treated in an argon atmosphere. X-ray diffraction analysis revealed that the films treated at 200 and 300 °C were still amorphous, while those treated at 400 and 500 °C were crystalline, with a V_2O_5 structure. All electrodes were electrochemically reversible for Li^+ intercalation, exhibiting the electrochromic effect, observed from optical transmittance measurements at 632.8 nm. The Li-diffusion coefficient, DC, was measured by the galvanostatic intermittent titration technique (GITT) as function of the inserted charge. For the crystalline films it was observed that the optical absorbance and the DC increase with increasing Li insertion in the single-phase regions of crystalline $Li_xV_2O_5$ and decrease in the two-phase regions. For the latter, an effective DC was considered. The presence of other vanadium oxides mixed to the V_2O_5 matrix was inferred for the crystalline films from the chronopotentiometric and DC measurements.

Keywords: vanadium oxide film, chronopotentiometric, DC measurements

Introduction

Thin films of vanadium oxides have been extensively studied as electrodes for lithium electrochemical insertion. Owing to the usually high charge intercalation capacity of these films, they are highly promising as cathodes for secondary microbatteries¹ and electrochromic devices.² The interest in these oxides lies on their performance as high Li intercalation capacity, high potential, high energy density, good cycling performance and on the unusual

double electrochromic effect. The latter is the appearance of an anodic coloration in the near-ultraviolet region and a cathodic coloration in the near-infrared region as Li is intercalated.³

Amorphous and crystalline vanadium oxide thin film electrodes have been prepared using chemical⁴ or physical⁵ vapor techniques as well as wet chemical^{6,7} and electrochemical⁸ depositions methods. Electrochemical studies have shown that the performance of vanadium oxide films is directly related to their morphology, crystallinity, degree of disorder, stoichiometry and other parameters related to the deposition methods and conditions. In particular, significant differences

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were reported on the potential and on the optical transmittance of amorphous and crystalline vanadium oxide thin film electrodes, under lithium electrochemical intercalation.⁹ In polycrystalline V_2O_5 electrodes, Li intercalation induces the formation of $Li_xV_2O_5$ phases, whose structures are, at present, well known.¹⁰

Recently we developed a thin film deposition process, the hot filament metal oxide deposition (HFMOD),¹¹ with which tungsten and molybdenum oxide film electrodes were produced, and their electrochromic properties for Li intercalation were studied.^{12,13}

In this paper, we investigate the optoelectrochemical properties of vanadium oxide films synthesized onto ITO-coated glass substrates by the HFMOD technique. The investigations were carried out in the amorphous as-deposited films and in those thermally-treated at 200, 300, 400 and 500 °C. The electrochemical characterization was made by cyclic voltammetry and chronopotentiometry. We also measured the chemical diffusion coefficient, DC, an important parameter to characterize the kinetic in Li-insertion electrodes. The galvanostatic intermittent titration technique (GITT) was used for these measurements. The electrochromic effect was observed by measuring the optical transmittance at 632.8 nm during the electrochemical experiments.

Experimental

Vanadium oxide films were obtained by the HFMOD technique heating a metallic vanadium wire in a rarified oxygen atmosphere. Details of the deposition apparatus can be found elsewhere.^{11,12} The deposition chamber was kept at a pressure of 0.24 Pa of oxygen, introduced *via* a high precision mass flowmeter. During deposition, the chamber was continuously pumped. The temperature of the vanadium wire during the depositions was 1370 ± 10 °C, as measured with an optical pyrometer. The films were deposited onto indium tin oxide (ITO)-coated glass slabs.

Controlling the deposition time, a set of vanadium oxide films with different thicknesses was obtained. Subsequently, the films were thermally treated under argon flow in a quartz tube furnace, at temperatures of 200, 300, 400 and 500 °C for 1.5 h each. The film thickness was measured using a high resolution profilometer.

The optoelectrochemical measurements were carried out in a hermetic three-electrode cell with lithium wires as reference and counter electrodes. The electrolyte was a 1 mol L⁻¹ LiClO₄-PC (propylene carbonate) solution. The electrolyte and the cell were handled inside a glove box filled with Ar and at a water vapor concentration lower than 10 ppm. A potentiostat (Radiometer, VoltaLab 10)

was used to perform the Li insertion and extraction of the vanadium oxide electrodes. Electrochemical Li insertions into the polycrystalline films were made above 2.0 V *versus* Li/Li⁺ or with x in the range $0 < x < 1$ in $Li_xV_2O_5$, in which the electrochemical reactions are reversible.¹⁴

The redox reaction of the V_2O_5 electrodes were observed by cyclic voltammeteries performed at scan rates of 10.0 mV s⁻¹ (samples A, B, C and D) and 1.0 mV s⁻¹ (sample E). Galvanostatic charge-discharges (chronopotentiometry) were applied to record the EMF curves of the electrodes and to observe their electrochromic effect. The applied current was ± 15 μ A in an electrode geometric area of 1.0 ± 0.1 cm².

To characterize the Li diffusion mass transport trough the vanadium oxide film the GITT technique was employed by applying current pulses of -100 μ A during 10 s, each one followed by 40 min with the cell in open circuit. The diffusion coefficient was calculated using the expression

$$DC(Q) = \frac{4I^2L^2}{\pi} \left[\frac{dV^e/dQ}{dV/d\sqrt{t}} \right]^2 \quad (1)$$

where I is the pulse current intensity, L the film thickness, V^e is the potential at the end of the open circuit, V is the transient electrode potential during the current application and Q is the charge inside the vanadium oxide electrode. DC is calculated from the titration curve dV^e/dQ and from the slope of the potential transient curve $dV/d\sqrt{t}$. Description and experimental details of this method can be found, particularly, in reference 15. This equation is valid just for single-phase regions, but current pulses were applied in both single and two-phase regions generated during the Li intercalation in these vanadium oxide electrodes. The lithium DC measured in these two-phase regions can be considered only as an effective one. Measurements of DC in two-phase intercalation systems are frequently found in the literature.^{16,17}

The electrochromic effect was observed *in situ* from optical transmittance measurements of a laser beam at 632.8 nm during galvanostatic charge-discharge experiments. A light intensity photodetector was used to measure the transmitted beam throughout the film electrode. The transmittance and the potential curves were recorded simultaneously.

The crystallinity of the as-deposited and of the thermally treated vanadium oxide films were observed from grazing incidence angle X-ray diffraction measurements, using the monochromatized Cu-K α radiation of 0.154518 nm.

Results and Discussion

Table 1 shows the thicknesses, the heat treatment temperatures and the visual appearances of the as-deposited

and heat-treated vanadium oxide films. The as-deposited film was black. Under annealing at 200 and 300 °C the films became transparent, with a bluish green color, and, when annealed at 400 and 500 °C, with a yellow color. The latter is characteristic of vanadium pentoxide films. Although these colors may be due to light interference, it should be noted that the bulk oxides are also colored, with V_2O_5 being yellow, V_6O_{13} being green, VO_2 being deep blue, V_2O_3 being black and VO being metallic grey.¹⁸ These observations strongly suggest that the as-deposited films are formed by V_2O_3 or VO, which, when thermally-treated to 200 and 300 °C, change to higher oxides or a mixture of these, and when treated at 400 and 500 °C change to V_2O_5 or even to a mixture of V_2O_5 and an other lower oxides.

Table 1. Vanadium oxides samples, their thicknesses, annealing temperatures and the corresponding visual film appearances

Sample	Thickness/(Å)	Treatment temperature/(°C)	Visual appearance
A	2000	-	black
B	740	200	bluish green
C	1200	300	bluish green
D	900	400	yellow
E	660	500	yellow

The X-ray diffraction patterns for the as-deposited and the heat-treated films are shown in Figure 1, as well as for the ITO-coated glass substrate. As it can be seen, only ITO peaks are exhibited in the as-deposited sample and in those treated at 200 and 300 °C. An amorphous structure is thus ascribed to them. However, when heat-treated at 400 and 500 °C (samples D and E, see inset) the films present a crystalline structure, since other peaks, aside from those of ITO, are observed. These peaks were assigned to the (001), (101), (110) and (400) planes of the orthorhombic V_2O_5 polycrystalline lattice, in accordance with our preliminary observations regarding the film yellow color.

Figure 2 presents the differential intercalation and deintercalation capacity, C_{diff} , as function of the electrode potential for the as-deposited and thermally-treated films. $C_{diff} = dQ/dE = I v^{-1}$ was calculated from the corresponding cyclic voltammograms (I vs. E) and provides an adequate form to compare cyclic voltammograms performed at different v scan rates. In the Figure 2, C_{diff} is presented normalized to the film thickness.

The shapes of the voltammograms (presented in Figure 2 on their differential form) of the as-deposited film and of those annealed at 200 and 300 °C, confirm their amorphous structure. The almost proportional dependence observed between the applied potential and the resulting differential capacity indicates a bad intercalation electrode

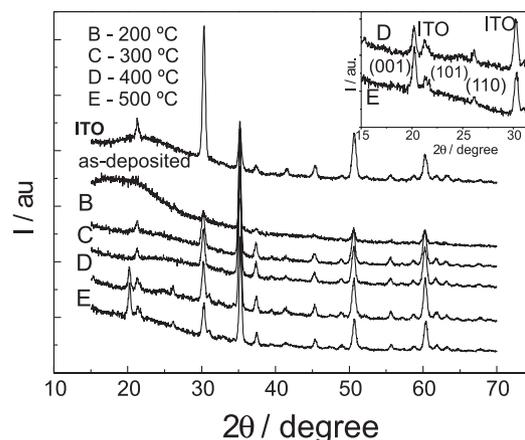


Figure 1. X-ray diffractograms for as-deposited and annealed vanadium oxide films. The inset shows the diffractograms for samples D and E. The diffractogram of the ITO-coated glass substrate is also shown.

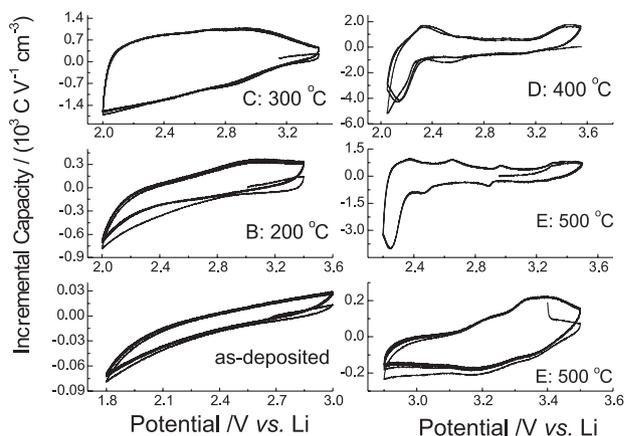


Figure 2. Differential capacity for the deposited and for the annealed vanadium oxide thin film electrodes. Annealing was performed at 200, 300, 400 and 500 °C in argon atmosphere. Electrolyte: 1 mol L⁻¹ LiClO₄. Scan rate 10.0 mV s⁻¹ and 1.0 mV s⁻¹ for sample E, when scanned between 2.2 and 3.5 V.

for the as-deposited film, but reversible electrodes with higher capacities were obtained for the oxide films treated at 300, 400 and 500 °C. The differential capacity curves of the films annealed at 400 and 500 °C indicate that a polycrystalline vanadium oxide was formed, as also observed from the X-ray diffractograms (Figure 1). However, it is observed from the two voltammograms of the films treated at 500 °C that besides the well known reduction potential at 2.25, 3.2 and 3.4 V, attributed to the Li insertion into the oxide V_2O_5 ,¹⁹ reduction peaks are also observed at 2.55 and 2.9 V, which can be attributed to ionic insertion into another vanadium oxide, mixed to the V_2O_5 oxide. These and the X-ray diffraction results suggest that the films annealed at 400 and 500 °C could be a V_2O_5 composite oxide although only diffraction peaks for vanadium pentoxide were observed in the spectra of Figure 1.

The galvanostatic charge-discharge curves as function of the electrode charge capacity (in mA h cm⁻³) for the

thermally-treated films are displayed in Figure 3. Figure 3a shows that the B and C samples present no step during the charging process, a typical behavior of amorphous electrodes. The deep ohmic drop observed in sample B is due to its low conductivity. Charge-discharge curves for D and E samples present steps and plateaus corresponding to phase regions of the crystalline $\text{Li}_x\text{V}_2\text{O}_5$ compound. Lithium intercalations were performed down to 1.8 V for the amorphous B and C samples and down to 2.0 V for the crystalline D and E samples. The latter voltage is the limit of the safe region for the reversibility of crystalline vanadium oxide electrodes, since deeper Li intercalation promotes an amorphization in the oxide structure, as shown in the curve deep D (Figure 3a), obtained after sample D was charged down to 1.8 V. The highest capacity was observed for the amorphized D sample (deep D) and the lowest one for the amorphous B sample. The charge capacities for the electrodes annealed at 300 and 400 °C are almost similar but when treated at 500 °C the electrode capacity decreases (sample E). Very similar results were found for vanadium pentoxide electrode films prepared by the sol-gel technique.^{6,20}

Figure 3b shows the first galvanostatic charge-discharge curves as a function of the charge capacity for the amorphous

film treated at 300 °C (sample C) and for the crystalline film treated at 400 °C (sample D), both charged from the equilibrium potential down to 1.8 V. For the crystalline film the step and plateau regions in the charge-discharge curve closely match those of powders¹⁰ and crystalline $\text{Li}_x\text{V}_2\text{O}_5$ films.^{20,21} The potential step observed in the beginning of the Li insertion is attributed to the formation of the $\alpha\text{-Li}_x\text{V}_2\text{O}_5$ phase ($0 < x < 0.1$). The next smooth step is caused by the settlement of $\epsilon\text{-Li}_x\text{V}_2\text{O}_5$ phase ($0.3 < x < 0.55$) and, between them, the mixed $\alpha+\epsilon$ phase. The deep step starting at 3.1 V and ending at 2.3 V would be the single $\delta\text{-Li}_x\text{V}_2\text{O}_5$ phase ($0.9 < x < 1.0$) for a pure vanadium pentoxide, but between them small shoulders are observed at 2.8 and 2.6 V. Upon further lithium insertion a $\delta+\gamma$ two-phase region is formed before the single $\gamma\text{-Li}_x\text{V}_2\text{O}_5$ phase, when the electrode potential drops to 2.0 V. At this region lithium insertion make the oxide structure irreversible.²² Under deeper Li insertion a weakly crystalline $\omega\text{-Li}_x\text{V}_2\text{O}_5$ single phase occurs, starting at 1.8 V.¹⁰

The dependence of the Li^+ diffusion coefficient, DC, and of the electrode open circuit voltage, V^e , as function of the electrode charge capacity for the Li insertion are shown in Figure 4 for the annealed films. All data were obtained from the GITT procedure applied to the diffusion measurements. It should be stressed that the DC values calculated in the two-phase regions of $\text{Li}_x\text{V}_2\text{O}_5$, as previously outlined, are just effective diffusion coefficients. It can be seen that the shapes of V^e and DC curves are markedly dependent of the film annealing temperatures. From the V^e potential curves, Figure 4, or even from the dynamic chronopotentiometric curves, Figure 3, we can see that during the charge insertion process, the electrode potential decreases monotonically with the inserted charge for the films annealed at 200 and 300 °C but, presents plateaus and steps for the films annealed at 400 and 500 °C, indicating, respectively, the amorphous and the crystalline nature of the vanadium oxides.

Figure 4 shows that the diffusion coefficient decreases with the inserted charge in a scattered way for the film annealed at 200 °C, while a broad peak and shoulder are seen on the DC curve of the film annealed at 300 °C. These are true DC measurements of an amorphous single-phase film. On the other side, peaks and shoulders are observed at the diffusion coefficient curves of the films thermally-treated at 400 and 500 °C. The magnitude of DC is also dependent of the film annealing temperature, with the lowest and the highest values observed, respectively, for the amorphous films treated at 200 °C and for the crystalline film treated at 500 °C, while intermediate DC values are observed for the films treated at 300 and 400 °C. The maximum DC was measured in the crystalline film E and is one order of magnitude higher than the maximum DC

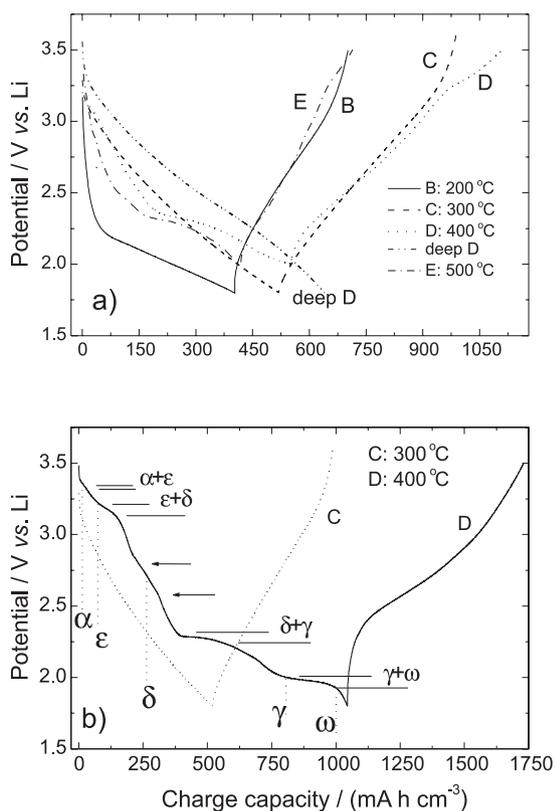


Figure 3. a) Galvanostatic charge-discharge curves performed at $\pm 15 \mu\text{A}$ for amorphous or nanocrystalline B and C films, for crystalline D and E films and for amorphized E film. b) Charge-discharge curves till 1.8 V, for the amorphous C and crystalline D films, with the crystallographic phases indicated for the crystalline D film.

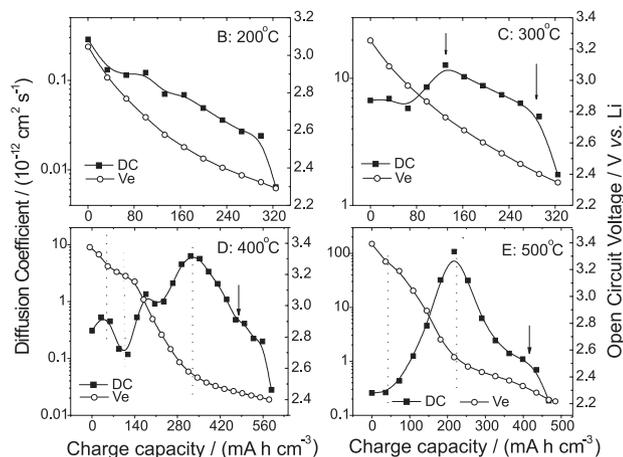


Figure 4. The dependence of the Li diffusion coefficient (DC), obtained from the galvanostatic intermittent titration technique (GITT), and the electrode open circuit voltage (V^e) with the charge capacity for the annealed vanadium oxide electrodes. The dotted vertical lines help to define the boundaries between $\text{Li}_x\text{V}_2\text{O}_5$ crystallographic phases.

observed in the amorphous film C and in the crystalline film D. However, the charge capacity for the electrode E is not the highest among those of all other electrodes.

Significant conclusions about the dependence of DC on the crystalline phases of $\text{Li}_x\text{V}_2\text{O}_5$ can be drawn from Figure 4, for the crystalline films (D and E samples). Analyzing the diffusion coefficient and its concurrent V^e curves in Figure 4, it can be seen that a correlation exists between them, with DC increasing with the inserted charge in the step regions of the V^e curves and, decreasing with the charge in the plateau regions of these curves. Therefore, a dependence of DC on the crystalline phases of the compound $\text{Li}_x\text{V}_2\text{O}_5$ can be inferred, according to the discussion regarding Figure 3 for the crystalline film. From these results it can be concluded then, that DC increases with Li content in the single-phase regions of $\text{Li}_x\text{V}_2\text{O}_5$ and decreases in the two-phase regions. In fact, is easily observable from Figure 4, that in the δ -single phase region (the deep step in the V^e curve of the D and E crystalline films), DC increases from 0.1×10^{-12} to $10 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ for the D sample and from 0.2×10^{-12} to $100 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ for the sample E. After that, the effective DC decreases in the neighbor ($\delta+\gamma$) two-phase region for both crystalline films. The dotted vertical lines in Figure 4 help to visualize the phase boundaries. The increase of the DC in the single-phase regions of crystalline $\text{Li}_x\text{V}_2\text{O}_5$ was already observed for a thin film electrode obtained by pulsed laser deposition.¹⁶

On this hypothesis, the small peak at the beginning of the DC curve of sample D can be explained as due to an increase in DC with the charge inserted during ϵ -single phase region of the compound $\text{Li}_x\text{V}_2\text{O}_5$, followed by a decrease in the effective DC with the charge, at the neighbor $\epsilon+\delta$ two-phase region.

Some other particular features are seen in the DC curve of the crystalline film D, such as the small peak around 2.85 V in the respective V^e , between the δ -single phase region and a shoulder in the effective DC curve, in the range 2.4–2.5 V. These potentials are in good correspondence to those observed for the reduction peaks of the voltammogram of sample E (Figure 2). A correlation seems to exist between the peaks and shoulders in the DC curve, as well as in the effective DC curve, with the peaks at the voltammograms for the crystalline vanadium electrodes. In fact, extensive studies about the correlation between the DC and the redox potential in intercalation electrodes have been carried out by Levi and co-workers.²³

Figure 4 shows that the dependence of DC on the crystalline phases for sample E is very similar to that obtained for sample D, for which the DC increases with the inserted charge in the δ single-phase region and with the effective DC decreasing in the $\delta+\gamma$ two-phase region. The absence of the two peaks in the DC curve of sample E, one at the region comprising the ϵ single-phase and $\epsilon+\delta$ two-phase, and the other at the middle of the δ phase, can be assigned to the low resolution in the experimental data of this sample, as it can be seen by the scarceness of points on its DC and potential curves, when compared to the experimental data points of sample D.

On this supposition, we inquire also if the peak and the shoulder observed in the DC curve of the film treated at 300 °C (sample C), around 2.7 and 2.4 V in the corresponding V^e curve, would not be due to the presence of micro or nanocrystallites phases in the film composition.

In the literature,^{16,17,24–26} measurements of DC as a function of the Li-inserted charge in crystalline $\text{Li}_x\text{V}_2\text{O}_5$ electrode films confirm our results of a dependence between the Li-diffusion coefficient and the crystalline phases of this compound.

Figure 5 shows the electrochromic effect measured by the optical transmittance at 632.8 nm as a function of the charge, for one galvanostatic charge-discharge cycle and the concurrent electrode potential curves. An overall low variation in the optical transmittance with the inserted charge is seen for all electrodes. Furthermore, it is observed for all films, that the optical transmittance decreases with increasing inserted charge until the electrode potential decays to a minimum value between 2.2 and 2.4 V, depending on the film treatment temperature. After that, the transmittance increases with the charge and turn to decreases till the end of the charge insertion. In the deintercalation processes the transmittance increases with the extracted charge, but a synergetic effect is observed on it at the end of the intercalation and at the beginning of the deintercalation processes. For the polycrystalline

D and E films, the transmittance presents better defined minimum and maximum. It should be noted that the ending intercalation potential are not the same for all electrodes. These unusual electrochromic effect in vanadium oxide electrodes, scarcely reported in the literature,^{20,27} was never completely understood.

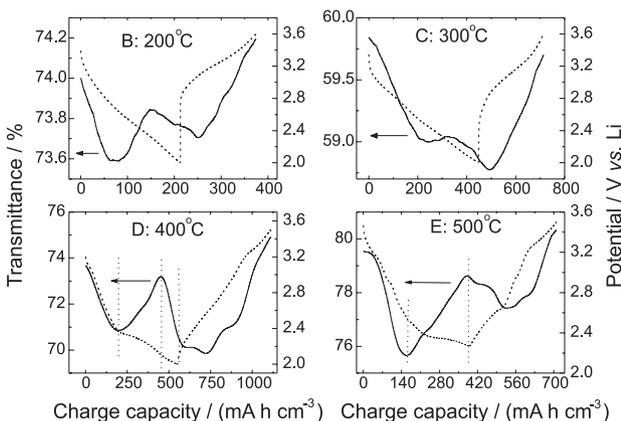


Figure 5. Changes in the optical transmittance at 632.8 nm (electrochromic effect) and in the concurrent electrode potential, obtained by the application of a $\pm 15 \mu\text{A}$ current a galvanostatic charge-discharge cycle, as function of the charge capacity for the annealed vanadium oxide electrodes. The dotted vertical lines help to define the boundaries between $\text{Li}_x\text{V}_2\text{O}_5$ crystallographic phases.

From the transmittance and the concurrent potential curves for the crystalline films (samples D and E, Figure 5), it can be seen that there is a correlation between the crystalline phases of $\text{Li}_x\text{V}_2\text{O}_5$ and the variation in the optical transmittance: the transmittance decreases with the inserted charge in the single-phase regions and increases with the charge in the two-phases regions. (In Figure 5, the vertical dotted lines in D and E curves help to define the phase boundaries). Figure 5 shows that for sample D, the optical transmittance decreases in the δ -single phase region, increases in the $(\delta+\gamma)$ -two phase region and turns to decrease at the γ -single phase region. The same behavior between the optical transmittance and phases is seen for sample E, although the γ -phase was not attained for this sample and a synergetic effect on the transmittance is observed at the end of charge insertion and at the beginning of the charge extraction, generating a minimum in the transmittance during the deintercalation process.

The transmittance decreases till 2.3 V for the crystalline films because this is the end of the δ - $\text{Li}_x\text{V}_2\text{O}_5$ single phase region in the crystalline Li-vanadium pentoxide. Since a minimum in the transmittance was also observed for the amorphous B and C samples during the charge insertion, it can be supposed that these films have in fact, a micro or nanocrystalline structure, as was already inferred from the Li-diffusion coefficient curve for sample C (Figure 4).

The dependence between the electrochromic effect and the $\text{Li}_x\text{V}_2\text{O}_5$ crystalline phases is cited in the literature⁹ but, as far as we know, never relating the changes in the optical transmittance with the single and two-phase regions.

From Figure 4, a correlation is proposed between the Li-diffusion coefficient and the crystallographic phases of $\text{Li}_x\text{V}_2\text{O}_5$ electrodes. On other hand, a correlation was also found between the optical transmittance and these crystallographic phases, as observed from Figure 5. Thus, a correlation between DC and the optical absorbance (or transmittance) due to the electrochromic effect is supposed to exist: The diffusion coefficient and the optical absorbance at 632.8 nm increase in the single-phase regions of $\text{Li}_x\text{V}_2\text{O}_5$ and decrease in the two-phase regions. The electrochromic effect is then a Li-diffusion controlled process.

Conclusions

We have made Li electrochemical intercalation experiments in electrodes of vanadium oxide films, measured the electrochromic effect at 632.8 nm and the Li diffusion coefficient as function of the inserted charge. The films were obtained by heating a vanadium wire in a rarified oxygen atmosphere (HFMOD technique). Some of the films were thermally treated in an argon atmosphere at 200, 300, 400 and 500 °C. It was observed that, depending on the temperature, the film composition and structure changed with thermal treatment. As indicated by the X-ray diffraction spectra, the films treated at 200 and 300 °C were still amorphous, as the as-deposited films. A V_2O_3 or VO composition was supposed for the as-deposited films due to their black color. For the films annealed at 200 and 300 °C other compositions are supposedly formed due the different film colors. The yellow color and the X-ray diffractograms of the films treated at 400 and 500 °C assure to them a polycrystalline V_2O_5 structure. However, the curve of the electrode potential as a function of the inserted charge strongly indicated, for these films, the presence of another oxide mixed in the V_2O_5 matrix. The change in the optical absorbance (due to the electrochromic effect) and the diffusion coefficient were seen to depend on the Li inserted charge and on the film structure. For the crystalline films, the electrochromic effect and the diffusion coefficient are directly related to the crystalline phases of $\text{Li}_x\text{V}_2\text{O}_5$. It was observed that for these films the optical absorption and the diffusion coefficient increase in the single phase $\text{Li}_x\text{V}_2\text{O}_5$ regions and decrease in the two-phase regions (in fact, a effective diffusion coefficient is measured in the two-phase region). A small peak observed in the diffusion coefficient curve, between the δ - $\text{Li}_x\text{V}_2\text{O}_5$ single-phase of crystalline sample D and a shoulder observed at the $\delta+\gamma$ two-phase of

D and E samples were supposed to belong to crystalline phases other than $\text{Li}_x\text{V}_2\text{O}_5$ phases.

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