Elucidation of the electrochromic mechanism of nanostructured iron oxides films

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ABSTRACT

Nanostructured hematite thin films were electrochemically cycled in an aqueous solution of LiOH. Through optical, structural, morphological, and magnetic measurements, the coloration mechanism of electrochromic iron oxide thin films was elucidated. The conditions for double or single electrochromic behavior are given in this work. During the electrochemical cycling, it was found that topotactic transformations of hexagonal crystal structures are favored; i.e. \( \gamma - Fe_2O_3 \) to \( Fe(OH)_2 \) and subsequently to \( \delta - FeOOH \). These topotactic redox reactions are responsible for color changes of iron oxide films.

1. Introduction

Electrochromic (EC) materials reversibly change their optical properties when an electric potential is applied. One topical use of EC materials is in smart windows, which helps to minimize the energy consumption for climate control in buildings [1–3]. Currently, tungsten and nickel oxides are the most popular EC materials, although there are many transition metal oxides and some polymers that exhibit electrochromism [4,5]. The iron oxides have been studied for a great variety of applications [6,7]; however, their EC properties have not been fully explored, and their coloration mechanism is not completely understood [4]. There are two outstanding published books regarding electrochromism; they were published—over the last two decades [4,5]. It is important to note that these books dedicated a short discussion to the EC behavior of iron oxides. Based in some seminal works, both books describe that iron oxides exhibit a bleached state at cathodic potentials or an anodic-like coloration [8–11]. These works employed iron electrodes oxidized electrochemically in an aqueous solution of \( OH^- \) ions; subsequently, the thick oxide layers were cycled displaying EC activity. However, the prepared EC films on iron rods were not able to develop practical applications [8–11].

Some papers published some years later also reported bleached states at cathodic potentials in iron oxide films prepared by sol–gel techniques [12,13]. As a conclusion, it was reported that only the \( \gamma - Fe_2O_3 \) phase displays electrochromism, while the \( \alpha - Fe_2O_3 \) phase is chromogenically inert [12]. Furthermore, other works reported that iron oxide films immersed in organic solvents get dark at cathodic potentials with a little optical modulation when \( Li^+ \) ions are inserted [14]; also, higher optical modulation has been reported for amorphous and \( \beta - Fe_2O_3 \) films [15,16]. Additionally, in iron oxide films prepared with sulfate residues, a double EC behavior was described later [17]. All these discrepancies can be caused by the presence of different phases of the iron oxide films and to the electrolytes/solvents used in the electrochromic cycles.

In order to explain the EC mechanism of iron oxides, the reported papers can be divided into two groups, those that use basic aqueous solutions and those that use organic solvents with a Li electrolyte. For the latter, the coloration mechanism can be considered similar to that described in WO 3 electrochromic films [4], where the \( Li^+ \) ions are intercalated/deintercalated in the iron oxide structure: i.e., \( Fe_2O_3 + xLi^+ + xe^- = Li_xFe_2O_3 \) [15,16]. This reaction describes a cathodic darkening by the \( Li^+ /e^- \) intercalation in the iron oxide structure. Although it has not been completely understood, similarly to tungsten oxide, the darkening can be due to the formation of small polarons. Otherwise, when aqueous solutions of \( NaOH, LiOH \) or \( KOH \) are used, the coloration mechanism is absolutely different, and only some assumptions have been made in some papers. By visual inspections and reflectance...
spectroscopy, it was assumed that the EC effect may be due to the cyclic transformation of Fe(OH)$_2$ to FeOOH [8,11]. It was supposed because the Fe(OH)$_2$ is white in color, while FeOOH phases present the absorption edge at wavelengths between 380 and 420 nm [10,11].

In order to fill the gap on the EC properties of iron oxides, this paper reports a systematic study of changes that take place in the structure, morphology, optical and magnetic properties of nanostructured iron oxide films. All the information generated in this study helps us to elucidate an EC mechanism of nanostructured iron oxide films immersed in basic aqueous solutions and increase the understanding of the properties of iron oxides at the nanoscale level.

2. Experimental details

2.1. Deposition of Fe$_2$O$_3$ thin films

Iron oxide films were formed on SnO$_2$:F (FTO) substrates (5 Ω/□) by the spray pyrolysis technique. For the spraying process, two different starting solutions of FeCl$_3$ were prepared, a 1 M aqueous solution and a 0.25 M ethanolic solution. The solutions were atomized through a pneumatic nebulizer operated at 2 bar of compressed dried air. The depositions were carried out inside of a gas extraction chamber at different temperatures ranging from 200 to 400 °C. The substrate temperature was regulated with a temperature controller (Omron E5CN) and kept constant during the deposition time by pausing the spraying process for intervals of 10 s. In order to decrease the residual stress of the film/substrate system, the coated substrates were slowly cooled until reaching ambient temperature.

2.2. Characterization

In-situ optical changes of iron oxide films during the electrochemical cycles were registered in an Ocean Optics USB4000-VIS-NIR spectrometer at wavelengths from 350 to 930 nm. Electrochemical measurements of cyclic voltammetry and chronoaamperometry were realized in a Pine Wavenow potentiostat, the electrolyte used was LiOH dissolved in water, though NaOH or KOH yields similar results. The structure of as-prepared, bleached and colored films was determined using X-ray diffraction (XRD) in a Philips X’Pert diffractometer, Micro-Raman spectroscopy in a Horiba LABRAM-HR (laser of λ=532 nm), a Witec CRC200 (laser λ=514.5 nm), and transmission electron microscopy (TEM) in a FEI-Titan 80–300 kV microscope. In order to minimize the structural changes promoted by the laser, a light intensity as low as 0.7 mW was used for the Raman characterization [18,19]. The morphology of the as-prepared and cycled films was determined by atomic force microscopy (AFM) in a Witec Mercury 100 microscope. The thickness of the iron oxide films was measured using a Vecco Dektak-8 Stylus profiler. The magnetic properties were measured at room temperature in an alternating gradient magnetometer (AGM Micromag 2900) manufactured by Princeton Measurements Corporation.

3. Results and discussion

3.1. As-deposited films

Fig. 1(a) shows the XRD patterns of iron oxide films prepared at different temperatures using starting ethanolic solutions. It is important to note that XRD patterns for films prepared with aqueous solutions exhibit a similar behavior. The more intense reflections located at 2θ = 26.6°, 33.9°, and 38° correspond to the cassiterite structure of the FTO substrates, which is preferably oriented in the (2 0 0) plane. Additionally, some weak reflections located at 2θ = 33.18° and 35.64° can be observed (see arrows in Fig. 1(a)), corresponding to the γ-Fe$_2$O$_3$ phase and are observable at temperatures as low as 200 °C. With the reflection located at 2θ = 35.6°, the presence of γ-Fe$_2$O$_3$ can be inferred; the weak signals of the XRD patterns, however, are not adequate to make a realistic conclusion about the occurrence of this phase in the films. Fig. 1(b) shows a typical AFM image of the topography of the surface of an iron oxide film deposited at 200 °C. It shows that the films are composed of round shaped particles with two particle size distributions, the smallest of around 150 nm, while the bigger conglomerates are around 500 nm.

Fig. 2 shows the Raman spectra of as-deposited iron oxide films prepared at different temperatures. All the spectra show a band lying near 1100 cm$^{-1}$, it coming from the FTO/glass substrate. Additionally, the other bands lying at 225, 245, 291, 411, 500, 611, and 1320 cm$^{-1}$ match very well to the Raman modes of the α-Fe$_2$O$_3$ phase [18–20]. The films prepared from ethanolic solutions exhibited a band located at ~655 cm$^{-1}$; this band has also been assigned to hematite and is related to disorder [18]. For the films prepared from ethanolic solutions, it is observed that higher deposition temperatures promote stronger bands; it indicates an improvement of crystallinity with deposition temperature. Additionally, the spectrum observed in the upper side of Fig. 2 exhibits weaker bands than those observed in the other spectra. It indicates

![Fig. 1](image-url) (a) XRD patterns of as-deposited iron oxide thin films prepared on FTO substrates at different temperatures. (b) AFM image of an as-deposited γ-Fe$_2$O$_3$ film prepared at 200 °C.
that the use of aqueous solutions promotes the growth of less crystallized hematite films even at high temperatures. All the Raman spectra shown in Fig. 2 corroborate the presence of $\alpha$-Fe$_2$O$_3$ as a unique phase; similar results have been reported using spray pyrolysis [21]. The pyrolytic reaction that forms hematite films can be written as follows:

$$\text{FeCl}_3 + \text{H}_2\text{O} \rightarrow 2\alpha\text{-Fe}_2\text{O}_3 + \text{HCl}$$  \hspace{1cm} (1)

3.2. Electrochemical behavior of electrochromic iron oxide films

It is worthy to mention that iron oxide films with a thickness of around 120 nm exhibit the bleached state at cathodic potentials ($-1.1$ V vs. Ag/AgCl) and turn colored at anodic potentials ($0.2$ V vs. Ag/AgCl). This behavior is known as anodic electrochromism and does not depend on the solvent used in the spraying process. Otherwise, if thicker films are evaluated (about twice as much in thickness), the bleached state is also reached at $-1.1$ V (vs. Ag/AgCl), but very long times are needed. This is because the coloration change is limited by the diffusion rate of ions into the films. Nevertheless, if the potential is increased up to $-1.5$ V, the films become black; this performance can be described as cathodic electrochromism; however, although the color change is very noticeable, its reversibility is much lower. In this work, a major highlighting is directed to the thinner films, because their optical modulations are quicker and exhibit their electrochromic properties in the potential window of water.

Fig. 3 shows the electrochemical behavior of iron oxide films prepared at different temperatures with a typical thickness of $\sim120$ nm. In Fig. 3(a), the voltammograms of the 10th cycle obtained at different sweep rates is shown, while Fig. 3(b) shows the evolution of current density with cycling in a current density vs. time graphic. One can observe that the deposition temperature has not a great effect on the extent of current density; also, as is expected, a higher sweep rate yields an increment of the current density. It is important to note that the current density increases with the number of intercalation/deintercalation (IC/DIC) cycles and reaches almost stable values at longer times. On the other hand, the cyclic voltammograms for thicker films are similar to those obtained for thinner films. However, if a cathodic potential of $-1.5$ V is applied, the presence of water hydrolysis is the main drawback of using the cathodic electrochromism.

3.3. Optical changes regarding electrochemical potential

Fig. 4 shows the changes that occurred in the transmittance spectra at different IC/DIC cycles of an iron oxide film of $\sim120$ nm in thickness. In these graphics, the optical measurements were taken in the electrochemical cell when the peak potentials are reached, i.e. $-1.1$ and $0.2$ V (vs. Ag/AgCl) using cyclic voltammetry; a sweep rate as low as $20$ mV/s was selected, because at higher sweep rates, the color changes are not visible. For comparison, the

Fig. 2. Raman spectra of iron oxide thin films prepared at different temperatures using aqueous or ethanolic solutions.

Fig. 3. Electrochemical behavior of iron oxide films with a thickness of $\sim120$ nm prepared at 200 and 400 °C. (a) Cyclic voltammograms of the 10th cycle. (b) Current density vs. time for the IC/DIC cycles. Filled and dotted lines indicate sweep rates of 80 and 20 mV/s, respectively. The experiments were carried out in an aqueous solution of LiOH 0.1 M in range from $-1.1$ to $0.2$ V (vs. Ag/AgCl).
spectra of the FTO substrate and of the as-deposited $\alpha$-Fe$_2$O$_3$ are included in the graphics. In Fig. 4(a), it is observed that at $-1.1$ V, the film is more transparent at wavelengths ($\lambda$) shorter than ~550 nm. Simultaneously, a slight diminishing at larger $\lambda$ is observed. This phenomenon can be described as a double cathodic electrochromism, because the films exhibit simultaneously an increasing and a diminishing of their transparency at different $\lambda$. As can be observed in Fig. 4, the original hue (wavelength cut-off) of the as-deposited films cannot be restored when the anodic potential is applied. It suggests that an irreversible phase transformation occurs after the 1st cathodic cycle. Fig. 4(b) shows the optical changes at the 10th cycle; similar to the 1st cycle, an increase in the transparency is observed at short $\lambda$. However, the diminishing at larger $\lambda$ is less noticeable. It is important to note that at the 25th electrochemical cycle (Fig. 4(c)), only an increase in the transparency is observed in all the analyzed electromagnetic spectra, and the transmittance is comparable to that of the FTO substrate. Additionally, at the anodic potential, it is observed that a gradual blue-shift of the wavelength cut-off occurs when the electrochemical cycles increase. These results suggest that (1) the double EC behavior is disappearing with the number of IC/DIC cycles, (2) the cathodic bleached state is gaining importance, and (3) a gradual transformation take place in the iron oxide films.

In order to understand the kinetics of the double EC behavior, as-deposited iron oxide thin films were submitted to a constant cathodic potential of $-1.1$ V. Subsequently, the anodic potential of 0.2 V was applied; the evolution of the current and the transmittance was observed with respect to the time. Due to the optical modulation being more noticeable in the UV and the NIR part of the spectrum (see Fig. 4), the bleached state was monitored at a $\lambda=350$ nm; while for the darkish hue, a $\lambda$ of 850 nm was considered for the measurements. Fig. 5 shows the results of these experiments for a new and an aged film submitted for 100 IC/DIC cycles. For a new film submitted at -1.1 V, it is observed that the transmittance at $\lambda=350$ nm increases gradually and reaches a maximum at ~700 s. While the transmittance at $\lambda=850$ nm experiences a decrement first and reaches a minimum at ~65 s, then, it experiences a gradual increase; again, at ~700 s the maximum is reached. For the aged film, a similar behavior is observed; however, the process seems to be faster, reaching the maximum transmittance at ~35 s, while the minimum at $\lambda=850$ nm is observed at ~7 s, see Fig. 5(b).

It is worth mentioning that the duration of the darkish hue is about 10 times shorter in aged films. This explains why in the 25th IC/DIC cycle of Fig. 4(c), the darkish hue is not observed in the
spectra. Otherwise, when the anodic potential is applied to the films (see insets of Fig. 5), a rapid decrement of the transmittance at $\lambda = 350$ nm takes place, while at $\lambda = 850$ nm, the curve shows a slight decrease in the transmittance at $\sim 2$ s. It is notable that the cycle number has a modest effect on the coloration rate at anodic potentials, and in comparison with the cathodic process, the anodic one is quicker. The kinetics study realized in this work corroborates the three premises formulated above and reveals that the double EC performance is an essential step in the coloration mechanism of the iron oxide films.

During the development of this work, we found some aspects that have to be considered for the study of the EC properties of iron oxide films; these are as follows. First, if it is intended to measure the optical spectrum of the bleached state outside of the electrochemical cell, the spectra will be very similar to that obtained if the film is subjected to the anodic potential period. It speaks of the instability of the bleached state in air. Additionally, if the cathodic potential is released, the colored state is recovered in about 10 min. On the other hand, the color and the same absorption edge of the as-deposited films can be recovered, if cycled films are annealed at temperatures above 200 $^\circ$C. It suggests that the phase obtained at anodic potentials can be easily transformed to hematite with annealing.

3.4. Structural and morphological changes regarding electrochemical potential

In order to understand the changes that occur in iron oxide thin films during electrochromic cycling, a structural and morphological study was realized. First, as was shown above, the as-deposited films exhibited a single hematite phase; subsequently, using Raman spectroscopy, AFM and high resolution (HR)-TEM, its transformation with the IC/DIC cycles was studied.

It is important to mention here that similarly to the transmittance measurements, the bleached state outside of the electrochemical cell yields the same Raman spectrum as that of the films extracted in the anodic cycle. Fig. 6(a) shows Raman spectra of iron oxide films of $\sim 120$ nm submitted at two different IC/DIC cycles using a sweep rate of 20 mV/s. It is observed that at the first cathodic cycle, weak hematite bands are yet observable. On the other hand, after 25 IC/DIC cycles, new bands are clearly observed at 297, 392, and 666 cm$^{-1}$ (see Fig. 6(a) lower spectrum). These bands match very well with the $\delta$-FeOOH structure, which exhibits the strongest and the next strongest bands at 392 and 666 cm$^{-1}$ [18,20,22]. Raman spectroscopy shows clearly that the hematite phase transforms gradually to the $\delta$-FeOOH phase during the IC/DIC cycles.

Otherwise, Fig. 6(b) shows the Raman spectrum of a thick iron oxide film exhibiting the cathodic darkened phase at $-1.5$ V (vs. Ag/AgCl). The bands lying at 300, 532, and 662 cm$^{-1}$ match very well with the magnetite phase [18,20]. Additionally, other bands of smaller intensity show that other structure is present in the films. Because of the presence of a high intensity band at 392 cm$^{-1}$ and a broad band at 667 cm$^{-1}$, the presence of $\delta$-FeOOH can be deduced; the smaller peak seen at 226 cm$^{-1}$ evidences the presence of hematite residues, and the presence of zero valence iron cannot be ruled out. It is important to point out that the darkened phase is very stable outside of the solution; indeed, it is stable at room conditions for more than one year.

Fig. 7 shows the topography of a cycled film obtained by AFM. It is seen that after 25 IC/DIC cycles, the round shaped hematite particles transform to $\delta$-FeOOH with a leaf-like morphology of around 600 nm in length; in the magnification seen in Fig. 7(b), the platelets thickness is estimated to be less than 15 nm. In the literature, it has been found that feroxyhyte (a low crystalized form of $\delta$-FeOOH) nanopowders grow with a platy morphology, where the platelets are of around 20–80 nm in length and a thickness of 2–8 nm [23–25]. Similarly, the cycled films of $\delta$-FeOOH present platy morphology, although the films present groupings of platelets with a bended tip and look like leaves. This morphology may be encouraged by the stress promoted by the IC/DIC of charge during the electrochromic cycles. It is worthwhile to mention that this morphology is not dependent on the preparation conditions of the as-deposited samples, thus the leaf-like morphology is promoted only by the electrochemical cycling.

Fig. 8 shows a HR-TEM image of a thin film sample prepared at 200 $^\circ$C and subsequently submitted to 25 IC/DIC cycles. Fig. 8(a) shows the image of a big single-crystal with some defective zones. According to the Fourier transforms (FT) of the image, it was taken along the [0 0 1] zone axis of the $\delta$-FeOOH structure. The structure determined by Raman spectroscopy is confirmed with the HR-TEM studies. The defective crystal shown in Fig. 8(a) shows some amorphous areas such as the one specified in the circle; it can be assumed that these defects are promoted by the IC/DIC of charge. Fig. 8(b) shows a filtered HR-TEM image where sets of moiré fringes are observed. With the FT, two lattices of similar parameters are seen. The moiré fringes observed in the figure present a periodicity of $\sim 2$ nm and a tilt angle; these are because two parallel platelets with very similar lattice parameters promote the interference. According to the moiré fringes observed by HR-TEM, a similar grouping of $\delta$-FeOOH platelets observed by AFM is inferred. Additionally, the HR-TEM images demonstrate that the platelets can be ordered in similar crystal directions.

3.5. Modification of the magnetic properties regarding electrochemical potential

Because of the fascinating magnetic properties of iron oxides, magnetic measurements are also considered in this work. Fig. 9 shows the magnetic hysteresis loops of an iron oxide thin film submitted to different numbers of IC/DIC cycles. According to Fig. 9, the saturation magnetization increases with the number of cycles, and reaches stable values after around 25 cycles. It is well known that $\alpha$-Fe$_2$O$_3$ is a canted ferromagnetic material at room temperature [20,23]; this behavior is observed in the as-deposited iron oxide films (see Fig. 9). The increase in saturation magnetization with the number of cycles is due to the transformation of hematite
to a more ferrimagnetic structure. The unique alternative is its transformation to magnetite or to $\delta$-FeOOH. As is observed in the transmittance spectra of Fig. 4, the gradual blue shift of the absorption edge with the cycle number can be associated with a transformation of hematite to an oxyhydroxide. Unlike all the other iron oxyhydroxides, the $\delta$-FeOOH phase is ferrimagnetic [23,25,26]. The transformation to $\delta$-FeOOH is also confirmed with magnetic measurements. Additionally, in the early cycles, the presence of small amounts of magnetite is not discounted because of the double electrochromic behavior observed in early IC/DIC cycles. However, it is confirmed that the major contribution to the magnetization loops comes from the $\delta$-FeOOH phase.

The hysteresis loops of darkened iron oxide thick films at $-1.5$ V exhibit saturation magnetizations up to $2.5 \times 10^{-3}$ emu/cm$^2$ and coercive fields of 300 Oe. This high magnetization agrees with the presence of magnetite found by Raman spectroscopy.

3.6. Insights of the coloration mechanism of iron oxide films

In accordance with the characterization presented in this work, the as-deposited hematite films transform gradually to a transparent state at cathodic potentials, which is unstable in air. The quick transformation of the bleached state in open atmosphere gives the same compound that the obtained at anodic potentials, which was identified as $\delta$-FeOOH. A typical synthesis of $\delta$-FeOOH nanopowders involves a quick oxidation of Fe(OH)$_2$ with H$_2$O$_2$ at high pH (＞14) [20,23]; also, its formation can be favored if the rate of air supply is high [27]. Fe(OH)$_2$ is a white powder, and its band gaps lie in the UV region of the spectrum [20]. The transformation of Fe(OH)$_2$ to $\delta$-FeOOH is a topotactic redox reaction, where an
electron and ion transference take place. In the reaction each Fe\(^{3+}\)(OH)\(_{6}\) octahedron becomes a Fe\(^{2+}\)(OH)\(_{4}\) octahedron while the hexagonal structure is conserved [20,28,29]. According to the optical properties of the bleached state in the electrochromic films, it is feasible that Fe(OH)\(_{2}\) causes the bleaching. Additionally, in an interesting mass-balance diagram of the transformation of Fe(OH)\(_{2}\) to δ-FeOOH, magnetite is reported as an intermediate state [28]; remembering the double electrochromic behavior, the darkish hue may be due to the presence of magnetite (see Figs. 4 and 5). The presence of magnetite in thicker films was demonstrated by Raman spectroscopy.

Once the phases responsible for different color states in the films were identified, a coloration mechanism of iron oxide films can be formulated. First, the reduction of hematite to a mixture of Fe(OH)\(_{2}\) and Fe\(_{3}O_{4}\) takes place, identified as double electrochromism. For subsequent IC/DIC cycles, the reduction to Fe(OH)\(_{2}\) gains more importance, because the topotactic reduction is favored vs. the change in the structure that is necessary for the transformation to magnetite. The IC/DIC of charge can be schematized as follows:

At cathodic potentials:

\[
2\text{Fe}_{3}\text{O}_{4} + 2\text{H}^{+} + 2e^{-} \rightarrow 3\text{FeOOH} + \text{Fe(OH)}_{2}
\]

Orange \(\rightarrow\) darkish \(\rightarrow\) transparent

\(\delta\)-FeOOH + H\(^+\) + e\(^-\) \(\rightarrow\) Fe(OH)\(_{2}\)

Yellow \(\rightarrow\) transparent

(2)

At anodic potentials:

\[
\text{Fe(OH)}_{2} + e^{-} + \text{H}^{+} \rightarrow \delta\text{-FeOOH}
\]

Transparent \(\rightarrow\) yellow

(4)

The first half redox reaction that forms magnetite is not-topotactic. The reaction of (2) seems to be irreversible, because the hematite structure can only be restored if the films are annealed at temperatures above 200 °C. The complete transformation of δ-FeOOH to hematite is at 200 °C [29]. The coexistence of both phases and the absence of other phases such as goethite have been reported at temperatures as low as 100 °C [29,30]. For thinner films, (2) is important at early cycles (double electrochromic behavior) and involves a change in the morphology of the iron oxide particles. The reactions (3) and (4) are more significant at long terms (anodic coloration), while the morphology of the particles is conserved. Through kinetic studies, it was found that the morphological changes from round shaped nanoparticles to a platy morphology take long times. It is in contrast to the topotactic transformations shown in (3) and (4) that are faster.

4. Conclusions

According to the structural characterization, all as-prepared films exhibited the presence of hematite. After a process of intercalation/deintercalation of charge, the presence of the δ-FeOOH phase was determined by different characterization techniques. The thickness of the films is an important parameter for the observance of color changes at featured times, because the coloration process is mediated by the diffusion of charge. Typically, thinner iron oxide films exhibit coloration changes at shorter times. It was found that the anodic coloration is attributable to topotactic transformations from the initial α-FeOOH to the transparent state attributed to the Fe(OH)\(_{2}\) phase and subsequently to the δ-FeOOH phase (yellow state). Otherwise, it was found that the double electrochromic behavior that was observed for short times is due to two different transformations; e.g., the topotactic one jointly with the formation of magnetite.

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