1. Introduction

Intercalation or insertion metal oxide systems are very important ionic host compounds that possess key technological applications in lithium ion batteries and electrochromic devices [1–6]. Many studies have been focused on intercalation kinetic mechanisms, most of them based on frequency response techniques [7–11]. The application of these techniques is very useful, since insertion or intercalating host compounds exhibit a complex and difficult pattern involving different processes [7.9–11]. However, due to their complexity, it is not possible to separate exactly all the existing kinetic processes, even with frequency analysis [11.12–14]. For instance, a remarkable feature is related to a low frequency dispersion linked to a complex capacitive behavior, i.e., capacitive dispersion response [7,10,11]. Another feature is the appearance of a resistive component in the diffusion region [12].

Therefore, investigations have been conducted with the main goal of coming up with good physical interpretations for experimental observations, ranging from interfacial roughness [10] to solid-state guest diffusion in the host oxide matrix accompanied by reactions between host and guest [8,15,16], which are normally metal alkali ions such as Li⁺, K⁺ and Na⁺, etc. In order to gain a clearer picture of the processes involved during ionic insertion in electrochromic systems, electro-optical measurements have been applied successfully [12–14,17–20].

Also based on the aforementioned picture, impedance responses considering a diffusion-trapping approach have been discussed theoretically in various papers [16,21]. The theory is based on the fact that some experimental evidence suggests the existence of a solid-state kinetic process slower than ionic diffusion. This aspect, for instance, was first proposed by Gabrielli et al. [17], i.e., the existence of a slower step that controls the coloration rate during the solid-state incorporation of Li ions inserted into optically active entities in the WO₃ metal oxide host. Similar processes have also been proposed to describe electrochromic properties in polymer films [22].

Although very interesting descriptions of the impedance patterns expected for intercalation systems have been published [15,21,23], so far there is still a lack of experimental results to support such ideas, i.e., diffusion accompanied by solid-state reactions [15,21]. Furthermore, a realistic explanation of such a slower kinetic process, described as a coloring ionic trapping process (e.g., solid-state reaction), i.e., a solid-state reaction controlling the coloring sites in electrochromic devices, has still not been clearly proposed.

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ABSTRACT

Complex electro-optical analysis is a very useful approach to separate different kinetic processes that occur during ionic insertion reactions in electrochromic oxide materials. In this paper, we use this type of combined technique to investigate ionic and optical changes in different oxide host systems, i.e., in two oxide hosts, specifically WO₃ and Nb₂O₅. A comparison of their electro-optical responses revealed the presence of an ionic trapping contribution to the kinetics of the coloring sites, which was named here as coloring ionic trapping state. As expected, this coloring trapping process is slower in Nb₂O₅ since the reduction potential of Nb₂O₅ is more negative (more energy is needed for a higher degree of coloration). A phenomenological solid-state model that encompasses homogeneous charge transfer and valence trapping was proposed to explain the coloring ionic trapping process. Basically the model is able to explain how ionic dynamics at low frequency region, i.e., the slower kinetic step, controls the coloring kinetics, i.e., how it is capable to regulate the coloration rates.

Optical transient analyses demonstrated the possibility of the presence of more than one coloring ionic trap, indicating the complexity of the processes involved in coloration phenomenon in metal oxide host systems.

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Coloring ionic trapping states in WO₃ and Nb₂O₅ electrochromic materials

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This paper specifically proposes this possibility with regard to metal oxide host compounds.

The main purpose of this paper, therefore, is to show the correlation between the ionic trapping feature and the coloring sites in metal oxide electrochromic device systems. To this end, complex electro-optical measurements were made, i.e., experiments capable of following the ionic and optical changes in the oxide host systems.

Two different oxide hosts were tested, i.e., WO₃ and Nb₂O₅. By comparing their electro-optical response, which is the main goal of the paper, it was possible, considering the ionic trapping interpretation [15,16,21,24], to identify the ionic trapping dynamics of these different hosts and to infer how the reduction potential of the host are related to coloring characteristic frequency. Both kinetics and thermodynamic aspects are responsible for the differences between hosts concerning their reduction potential level. Therefore, as expected, the trapping process is slower in Nb₂O₅ since the reduction potential of Nb₂O₅ is more negative (more energy is needed for a higher degree of coloration as will be discussed on this text).

2. Experimental procedure

WO₃ and Nb₂O₅ host layers of about 250 nm were prepared by the traditional sol–gel route. For combined electro-optical measurements, WO₃ and Nb₂O₅ homogeneous films were deposited on ITO substrates by dip-coating. The WO₃ film was heat-treated at 300 °C for 4 h, while the Nb₂O₅ was heat-treated at 500 °C for 2 h. These heat treatments resulted in crystalline films, as confirmed by X-ray diffraction analyses. All the electrochemical experiments were performed in a three-electrode cell arrangement. The counter electrode was a platinum foil and the quasi-reference electrode was a silver wire. The electrolyte was 0.1 M LiClO₄ dissolved in an acetonitrile solution. Prior to the electrochemical measurements, the cell was purged with dry N₂ gas. An electrochemical cell transparent to visible light was used for the electro-optical measurements. Complex electro-optical measurements were taken in a single-beam, linear arrangement using monochromatic light at ~543.5 nm.

The frequency response measurements were taken in a frequency interval of 1 mHz to 10 Hz and 1 mHz to 10 kHz for optical and electrical transfer function analyses, respectively. The transient absorbance versus time analysis was made at different reduction potential (−0.75, −1.00, −1.25 and −1.5 V) using a monochromatic light at ~543.5 nm.

It is important to stress that the criteria used to select the steady-state potential to investigate the complex electro-optical response for each oxide host, i.e., WO₃ and Nb₂O₅, was based on finding a potential, for each material, in which it was possible to better visualize the trapping characteristic frequency for each of them without coupling parallel irreversible reactions. The simulations and the fitting to the experimental data were done considering the appropriate models [15,16,21,24]. However, concerning the ionic trapping approach, a specific physical interpretation was discussed herein for electrochromic hosts whose detailed theory is discussed and presented elsewhere [24].

3. Results and discussions

Fig. 1 shows the typical stable (after about 10 cycles) cyclic voltammetric pattern for both WO₃ and Nb₂O₅ metal oxide host systems. The most important feature to be observed in Fig. 1 is the reduction potential of Nb₂O₅, which is comparatively more negative than the one observed in WO₃ hosts, which is classically known. Basically, this is an indication that it is easier to reduce W⁶⁺ metal valence state to W⁵⁺ in WO₃ hosts than to reduce Nb⁵⁺ valence state to Nb⁴⁺ in Nb₂O₅ hosts. As will be demonstrated here by means of electro-optical measurements and considering the ionic trapping state scheme, the latter aspect is related to the fact that ionic trapping (or better coloring ionic trapping) is more difficult in Nb₂O₅ than in a WO₃ host structure (higher energy is necessary to access the site, or in other words, and in agreement to the phenomenological model developed here, it means that polarization of the Nb₂O₅ with ionic trapping accompanied by valence trapping is more difficult in such host comparatively to WO₃ host).

![Fig. 1](image1.png)

**Fig. 1.** Classical cyclic stabilized (after about 10 cycles) voltammetric pattern for WO₃ and Nb₂O₅, evidencing the higher reduction potential for the Nb₂O₅ host in comparison to the WO₃ host system. The scan rate used was of 30 mV s⁻¹. The quasi-reference electrode was a silver wire.

![Fig. 2](image2.png)

**Fig. 2.** Bode capacitance spectra illustrating the influence of the charging of trapping states, i.e., trapping capacitance: (a) imaginary and (b) real parts. For this simulation it was considered that the trap has a characteristic frequency of ωₜ = 0.01 rad s⁻¹ and a resistance Rᵣ = 1/ωₜCᵣ with Cᵣ changing from Cᵣ = 0.1C₀, C₀ = 10C₀ and Cᵣ = 10²C₀. C₀ has a value of 10 μF.
Fig. 2 shows the theoretical Bode diagrams (from Eqs. (1)–(3)) for capacitance transfer function, \( C'(\omega) = C + j\omega C'' \), considering that diffusion characteristic frequency \( \omega_d = D/l^2 \), in which \( D \) is the diffusion coefficient and \( l \) is the thickness of the host (this is considered for simplification since what is more common is the occurrence of a displacement of this characteristic frequency to higher frequencies due to the increasing of \( D \) with insertion degree) and the occupation of trap sites (i.e., the trapping capacitance \( C_t \)) is increasing relatively to that of free diffusion sites (i.e., the diffusion capacitance \( C_0 \) which dictate the occupation of free diffusing sites). This picture means that with the increasing of intercalation degree or concentration more species are being trapped, as discussed in many references \([3,4,8,11,15,16,21]\). Note that \( C_0 \) and \( C_t \) accounts for the amount of species in the host’s volume.

When \( C_t = 10^2 C_0 \) it is possible to clearly observe the characteristic frequency of the trapping state as indicated in Fig. 2. This simulation demonstrates that the coloration sites must be sufficiently occupied to access the trapping or coloring characteristic frequency in the electro-optical experimental data.

The final theoretical impedance function that was used to make the simulations of Fig. 2 and fittings of the experimental results further herein in Figs. 3 and 4 is \([16,21,24]\)

\[
Z_b = R_d \left[ \frac{D_t/l^2}{j\omega} \right]^{1/2} \left[ \coth \left( \frac{j\omega}{(D_t/l^2)} \right) \right]^{1/2}
\]

(1)

in which

\[
D_t = \frac{dC_t^b/dV}{dC_t^b/dV + C_t^b D_{ch}},
\]

and

\[
R_d = \frac{L}{AeD_{ch}dC_t^b/dV}.
\]

(2)

(3)

in which \( D_{ch} \) is the chemical diffusion coefficient and \( dC_t^b/dV \) is the amount of species able to freely diffuse along the electrode thickness due to the potential applied on the electrode, i.e., it is equivalent to \( C_0 \) under certain steady-state conditions. \( A \) is the geometric area of the electrode and \( e \) is the elementary charge.

The modulation of the optical density can be given by the Lambert–Beer law. Considering that just the \( C_t^b \) \([24]\) (equivalent to \( C_t \)) of the inserted ions contributes to the coloration, i.e., that only the ionic trapping concentration contributes to the coloring, the Lambert–Beer law for our problem shall be given by

\[
\ln \frac{T}{T_0} = \kappa \int_0^{L} C_t^b(x) dx,
\]

(4)

in which \( \kappa \) is the molar absorption coefficient of the host material. The \( T_0 \) is the reference transmittance in a way that \( T/T_0 \) is the relative modulated transmittance, in which the tilde represents the modulation of the transmittance. Note that \( x \) indicates the unidirectional way of diffusion, i.e., from the electrode/electrolyte surface to the bottom of the working electrode, i.e., substrate/oxide host material surface. The limits of the integration is then from \( 0 \) to \( L \), i.e., from the electrode/electrolyte surface to the electrode/current collector surface, over which the oxide host materials was deposited.

Figs. 3 and 4 show the experimental complex electro-optical measurements for Nb2O5 and WO3, respectively. These figures give a comparative view of the frequency response data for WO3 and Nb2O5 host materials, showing the impedance \( Z'(\omega) = Z' + jZ'' \) (in the inset), capacitance \( C'(\omega) = C + jC'' \) and transmittance \( T'(\omega) = T' + jT'' \) transfer functions in Nyquist diagram (parts a and b) and (parts c and d) in Bode representation. In general, and in agreement with an analysis of the literature \([12]\), one can see that an increase in the degree of insertion causes the low frequency processes – here associated with trapping and coloring sites – to slowly decrease in both host materials at high degree of insertion, i.e., after coloring states.

Fig. 3. (a) and (b) shows, respectively, the Nyquist complex capacitance (\( C' = C + jC'' \)) and Nyquist complex transmittance (\( T' = T' + jT'' \)) diagrams of the Nb2O5 host system. (c) and (d) are Bode diagram representations for \( T' \) (•) and \( C' \) (○). The impedance pattern is shown in the inset of (a). All the frequencies indicated here are in Hz (m stands for mHz and k for kHz). Steady-state reduction potential of \(-750 mV\). The axis in (c) and (d) shows the exponent of the base of logarithm scale, i.e., \( 10^x \) where \( x \) is indicated in the axis. The gray line indicates the fitting to the diffusion-trapping scheme, i.e., experimental results were fitted to Eq. (1).
being extensively occupied. However, the frequency related to this process is always lower in the Nb$_2$O$_5$ host (see Figs. 3 and 4), which will be explained in detail furthermore here based on a higher energy for reduction in this host than in WO$_3$. It is important to note that the trapping characteristic frequency $\omega_t$ is obtained at the maximum of a $C''$, according to the references $[3,4,8,11,15,16,21]$. In the present case, Fig. 3 shows the electro-optical transfer function measurements at a reduction potential of $-750$ mV $[18–20]$, in which it is still possible to detect the characteristic frequency of the relaxation process involved with coloring and trapping (see Fig. 3c). It is important to note that, at this steady-state, the insertion process is in its beginning for Nb$_2$O$_5$ (see also Fig. 1). At higher reduction potentials the process is slower, falling to frequencies lower than 1 mHz, which are undetectable in the frequency range used in this work. Because of this, the ionic trapping process can be described as a solid-state reaction and the physical interpretation of this tendency is naturally related to the increase in the concentration of trapping states (see simulations presented in Fig. 2), which is caused by a decrease in the trapping rate with a concomitant increase in the release reaction rate.

This could be better evaluated considering the characteristic frequency of the trapping $\omega_t$ as given by $[15,16,21]$: 

$$\omega_t = k_t \bar{n} + k_f$$

in which $k_t$ and $k_f$ are kinetic constant for trap and release, $\bar{n}$ is the equilibrium concentration of free inserted lithium ions, i.e., concentration of ions that are not binding or trapped, whereas $N_t$ is the density of trapping sites. Still according to reference $[16]$ the ratio between $k_t/k_f$ as function of binding energy (i.e., $E_b$, the energy for an ion to bind from a free diffusion to a trapped site or state), is given by:

$$\frac{k_t}{k_f} = \frac{N_b}{N_t} \exp \left( \frac{-E_b}{k_BT} \right)$$

in which $k_B$ is the Boltzmann constant. The $N_b$ is the density of free diffusing sites. Combining Eqs. (5) and (6) it is possible to observe directly the influence of binding or trapping energy on the trapping frequency:

$$\omega_t = \frac{k_t}{N_t} \left( \bar{n} + N_0 \exp \left( \frac{-E_b}{k_BT} \right) \right)$$

From Eq. (7) it is possible to observe that when $E_b$ increases the characteristic frequency of the trapping decreases. The Eq. (7) involves kinetic and thermodynamic aspects. Kinetic aspects are involved with the term $k_t$ and when the kinetic constant for trapping increases, the trapping characteristic frequency due to the higher occupancy of the trapping sites increases (see Fig. 2). On the other hand, the thermodynamic aspect of the problem comes from $E_b$ and consequently from the energy of the specific chemical system considered (WO$_3$ or Nb$_2$O$_5$).

Another important aspect of the Nb$_2$O$_5$ host is that the complex patterns are strongly influenced by the diffusion process, i.e., the free diffusion of the lithium ions contributes considerably to this pattern because the insertion process is still at the beginning. According to Eq. (7) this means that $\bar{n}$ is low, implying that $\omega_t$ is at very low frequency with the frequency response dominated by the diffusion process, comparatively to what is observed for WO$_3$ system. This fact can be also inferred from the discrepancy between capacitance and transmittance, which is interpreted by assuming an additional and more intense, non-coloring relaxation (both $C$ and $C''$ should rise toward low frequencies), i.e., ionic diffusion.

On the other hand, the freely diffusing lithium has a lower contribution to the WO$_3$ system, i.e., the trapping contributions...
dominate the response. This aspect is better explained by analyzing the capacitance spectra shown in Fig. 4 for a proper comparison with the transmittance spectra. In a previous work [12], it was found that practically there is a coincidence (within the experimental error) between the location of the peak loss of $C^d$ and the maximum of the $T'$ spectra for WO$_3$ system, specially for high reduction potentials (more negative potentials). A similar tendency is also observed here for WO$_3$, i.e., there is a tendency of coincidence of potentials (more negative potentials). In other words, at the steady-state of $-200 \text{ mV}$, the response of the WO$_3$ host is highly determined by the trapping mechanism, even for crystalline systems, comparatively with the response of the Nb$_2$O$_5$ electrochromic host. It is important to stress that in the present work the most important to be discussed and to be emphasized is the comparison between WO$_3$ and Nb$_2$O$_5$ electro-optical frequency response patterns, this gives important information concerning the coloration kinetics and its relationship with metal oxide structures, i.e., the nature of atomic structural energy framework that dictates the bounding energy in Eq. (7). In both cases, to make a better comparative analysis, it was chosen steady-state potential at the beginning of the lithium insertion process for both host oxides.

In general, this comparison of the WO$_3$ and Nb$_2$O$_5$ metal oxide host systems, considering the reduction potential and ionic trapping frequency differences, allows one to infer that the ionic binding energy (which leads to ionic trapping inside these hosts) must be higher in the Nb$_2$O$_5$ than in the WO$_3$ metal oxide system. In other words, the mechanism of the coloring ionic trapping state must be coupled to the reduction potential (that in electronic/ionic coupling terminology will be here named as valence trapping). Hence, the Li$^+$ oxygen binding must induce the reduction of W$^{4+}$ metal valence state to W$^{5+}$ in WO$_3$ hosts and of Nb$^{5+}$ valence state to Nb$^{4+}$ in Nb$_2$O$_5$ hosts. The energy of Li$^+$ oxygen binding must be higher in Nb$_2$O$_5$ than in the WO$_3$ system.

Based on the complex electro-optical comparison of WO$_3$ and Nb$_2$O$_5$ host and clearly and explicitly assuming that the ionic trapping states are responsible for the coloring kinetics (which is not considered in the models proposed in references [16,21]), i.e., that the existence of a solid-state kinetic process slower than ionic diffusion, as firstly proposed by Gabrielli et al. [17], controls the coloring kinetics we will now propose a solid-state structural interpretation for this process that correlates the electronic and ionic aspects. We believe that such structural interpretation, valid especially for oxide host, is capable to give a realistic interpretation for the coloration process (which is not only a question of discussing about diffusion and ionic trapping but also correlates the ionic trapping to the coloring sites, i.e., coloring trapping sites) in terms of ionic guest dynamics in trapping state modes. Indeed, the proposition emphasizes that the ionic guest dynamics in trapping state modes is related to the electronic valence change of the almost adjacent metal atoms in the surrounding structural environment.

In general, the differences of the physical mechanisms accessed by the impedance and electro-optical techniques has rarely been addressed and raise difficulties in the interpretation of the data [12]. Indeed, the impedance spectrum (electric transfer function) is due to chemical diffusion and ion transport/trapping, while the complex optical absorption (optical transfer function) is due to electronic transitions. Therefore, the novelty in the interpretation given here is to propose a coupled ionic and electronic solid-state picture capable to correlate the impedance spectrum. This will explain how transport/trapping or, in other words, ionic dynamics might be correlated to electronic transitions or how ionic dynamics controls the electronic transitions, which is, in turn, the cause of the optical absorption.

To start addressing this analysis it must be emphasized that both impedance and complex optical absorption spectrum have, at low frequency region, a relaxation pattern that is very similar to the most known dipolar relaxations (Cole–Cole dielectric pattern [25], for instance). From this point of view it is possible to assume that the ionic dynamics in the structure of the host oxide is likely a consequence of the local interaction of the guest ion, i.e., Li$^+$ in the present situation, with the oxygen that is preferentially bonded to it. In this picture, the diffusion (that can be also denominated as shallow intercalation states) and trapping states can be only differentiated by its level of energy in the structure (see Fig. 5). However, as indicated in Fig. 5, the local polarization that causes a change from the diffusion, or shallow intercalation state, to trapping state is the polarization of the guest ion in the structure concomitantly to a most probable electronic location of the electron around this environment. Hence, the environment around the ionic polarization, causes per se a valence change (or valence trapping) of the adjacent metal atoms to the oxygen, in which the Li$^+$ is bonded.

Differently of the traditional polarization modes [25], in which the potential cause a displacement of the local charge center due to the atomic displacement, in the present situation the oxide structure is suffering two kinds of modifications: one due to the electronic valence change (valence trapping—also referred as coloring center) and the other due to the internal effect of the applied electrochemical potential that cause the concomitant ionic coupled polarization. Let us now explore more this phenomenological view of the process. From literature [16,21] it is considered that the ionic trapping can be described as a reversible solid-state reaction [16]. Such aspect is totally in agreement with our coloring trapping picture of the electrochromic process. However, the models considered in references [16,21] are very general from physical point of view and not specifically adapted to electrochromism, i.e., coloring or absorption effects due to electrochemical ionic intercalation. The optical aspect and its correlation with ionic trapping
is the purpose of such phenomenological model developed here. Therefore, the most clear and important difference is that in our view, as shall be detailed in the next paragraphs, the electronic trapping states are correlated and linked with the valence change of the metal adjacent to the electronic trapping site and the coupled effect can be described as electron trapping states. The valence change (or valence trapping) can be described as a specific kind of electronic trapping and electronic polarization mode. In more explicit words, the electrochemical potential, mainly for intercalation reactions, causes an ionic and electronic modification in the structure of the material. The electronic change, coupled with ionic dynamic change, causes a valence change (or valence trapping) and this is the main effect responsible for light absorption, according to complex electro-optical analysis. Indeed, this is the essence of the electrochromic reactions but in solid-state terms, i.e., a solid-state chemical reaction that, after ionic intercalation step (faster than the coloration step), causes a specific optical absorption (in the visible electromagnetic region). The optical absorption is a consequence of the electronic change around the sites where the solid-state chemistry occurs, i.e., where Li+ guest ions are bonded with oxygen and that is the lower step process than that of intercalation per se.

It is very important to stress, in the picture of the process detailed here, the presence of two kinds of charge transfer process during the whole intercalation reaction occurring in oxide electrophotonic hosts. The first kind of charge transfer process are able to cause mass change (and it can be better studied with the aid of mass transfer function combined with impedance spectrum, as shall be detailed discussed in a forthcoming paper of the theory for oxide hosts [24], but some examples can be accessed into references [9,17]) and the second kind of charge transfer process does not cause any mass change (although current can be detected, as will be discussed in the forthcoming paper [24] by using combined mass, electrical and optical transfer function) and can only be better studied by means of optical transfer function combined with impedance spectrum (which is the approach that is being addressed in the present paper, but details of the theory will be given in a forthcoming paper because here we are just interested in the comparison between the two different charge processes already previously and in introduce the concept of coloring trapping state for electrochromic systems). In the second kind of charge transfer to be considered it is then possible to consider a homogeneous or solid-state charge transfer, i.e., an internal ionic and electronic rearrangement that does not cause mass change (that will also be demonstrated in a general forthcoming paper).

The picture addressed in last paragraphs is also in agreement with the charge transfer between valences and polaron models [26], which are the two most accepted models for explanation of electronic aspect of the electrochromism phenomenon. Our approach here is capable to joint these theories and its phenomenological aspects with the ionic dynamic aspect addressed in the interpretation of diffusion/trapping scheme of the intercalation reactions so that it gives a more realistic picture of the coloring reaction in terms of ionic trapping phenomenon.

Therefore, according to charge transfer between valence and polaron models [26], the optical absorption is a consequence of valence changes of a metal atom in an oxide host that are distributed and resonates between different metal atoms. In our picture of the process such an electronic state can be addressed as \( M^{n+1} \rightarrow M^n \rightarrow M^{(n-1)+} \), which represents the valence state distributed between different metal atoms in the oxide host structure. Note that \( M^+ \) states for the metal atom in the host structure with its respective valence state. But such energy state is not capable to cause optical change when the ions, in turn, occupy the shallow trapping states (see Fig. 5). The electronic charge transferred (heterogeneous charge transfer reaction) to the materials firstly resonates occupying such kind of electronic state. Concomitantly, to maintain the electroneutrality of the system an ion is intercalated in the structure occupying the diffusion shallow states and just after this ionic species starts to diffuse in the host structure throughout the ionic shallow sites. Therefore, as can be seen there are sites for electrons and ions. It is explicitly assumed that the injected electron occupies a \( M^{(n+1)+} \rightarrow M^n \rightarrow M^{(n-1)+} \) kind of site and that such kind of sites does not cause visible absorption (see Fig. 5). It is assumed that such step of the intercalation kinetics does not cause a color change and the corresponding ionic species that balance the electronic counterpart are free to diffuse throughout the host structure. In the frequency response pattern (impedance spectrum, for instance) this step is identified at higher frequency region followed by an ionic diffusion process in intermediate frequencies [7,10,11,21]. The ionic species at this step is located in the shallow intercalation sites or states.

The process at low frequency is the most interesting process and is the main focus of the present paper. The phenomenological solid-state physical mechanism will be proposed now. The adjacent environment of the shallow intercalation state can be represented by \( M^{(n+1)+} \rightarrow O \rightarrow Li^+ \) (oxidized valence state of the metal atom, representing a cluster in the structure) and around of it a homogeneous charge transfer can occur. Note that by considering such a framework, as the intercalation proceeds, the probability of ionic structural polarization increases due to the applied potential and also due to the net interaction effect between the guests and the host, facilitated by structural configuration aspects, which is very well known aspect from a solid-state chemistry point of view [25]. Therefore, the \( M^{(n+1)+} \rightarrow O \rightarrow Li^+ \) local environment is the precursor for the rises of coloring ionic trapping states. As a consequence, after the homogeneous charge transfer occurs, the coloring ionic trapping state can be described as \( M^n \rightarrow O \rightarrow Li^+ \), in which the symbol “-” represents the change on the lithium ion dynamics as a consequence of more strongly locally interaction due to structural polarization (note that the symbol are also able to represent the formation of a dipole), perhaps forming chemical bonds, with the oxygen of the net. This kind of homogeneous charge transfer, i.e., ionic and electronic coupled charge transfer, is kinetically slower than that described previously. The change from \( M^{(n+1)+} \rightarrow O \rightarrow Li^+ \) state to \( M^n \rightarrow O \rightarrow Li^+ \) state implies energy change accompanied by coloring, as exemplified in Fig. 5. Note that albeit the electronic sites are considered to explain the coloring effects in the oxide host, this is an aspect that does not invalidate the fact that the coloring kinetics is controlled by ionic dynamics. Here, ionic dynamics are fundamental for the control of the valence trapping, i.e., the electronic change that causes the optical absorption. In other words, the coupled valence trapping process follows the rate of ionic trapping and is dictated by the latter. Note that the whole picture is named here as coloring ionic trapping scheme.

As a consequence of this interaction, in which the oxygen electronic cloud is displaced and oriented in favor of the lithium ionic guest, it must lead to a valence change on the adjacent metal, i.e., electronic charge transfer to rearrange locally the energy of the cluster and to distribute the local charge in the cluster. Therefore, from this point of view it is possible to observe an explicit correlation between the electronic and ionic dynamics. The ionic and electronic processes, are strongly dependent, although kinetically controlled by the ion movement. Fig. 5 shows the specific situation in which \( W_5^+ \rightarrow O \rightarrow Li^+ \) and \( Nb_5^+ \rightarrow O \rightarrow Li^+ \) represents the coloring trapping states for \( WO_3 \) and \( Nb_2O_5 \) hosts, respectively. The shallow diffusion states are represented by \( W_5^+ \rightarrow O \rightarrow Li^+ \) and \( Nb_5^+ \rightarrow O \rightarrow Li^+ \), respectively.

The possible existence of more than one ionic trapping state (\( Li^+ \) oxygen binding energy) cannot be discarded in the picture given here for the coloring ionic trapping process. For instance,
Fig. 6 shows various absorbance versus time patterns for the Nb2O5 system, i.e., it represents the transient charging of coloring sites at a given reduction potential applied to the system. Accordingly, after about four minutes, the absorbance stabilizes at a plateau, indicating that the steady-state situation is reached. As expected, the value of the absorbance plateau increases with the reduction potential, evidencing the increased concentration of the occupied ionic coloring trapping sites. However, after about seven minutes at the reduction potential of 1.5 V (indicated by an arrow in Fig. 5), a new increase in the absorbance occurs. The concentration of coloring ionic trapping sites probably saturates and, at this potential level, there is sufficient energy to occupy other ionic coloring trapping sites. Indeed, Fig. 6 combined with Figs. 1–4 provides a clear evidence of the coloring ionic trapping state framework in metal oxide electrochromic host systems, reinforcing the complex plane analysis.

4. Conclusions

By using complex electro-optical analysis it was possible to identify the presence of ionic trapping states contributing to the coloration kinetics in two different oxide hosts, i.e., WO3 and Nb2O5. The trapping state characteristic frequency is lower in Nb2O5 indicating that the mean energy need to the occupation of mentioned energetic state is higher. This observation is in agreement to the fact that the reduction potential of Nb2O5 is more negative compared to that found in WO3 systems (more energy is needed for a higher degree of coloration in Nb2O5 host). Optical transient analyses clearly confirms the interpretation based on the ionic trapping state approach and the possibility of the presence of more than one coloring ionic trapping state, indicating the complexity of the processes involved in coloration in metal oxide systems.

A phenomenological solid-state model was proposed. It is capable to give specific analysis of the ionic trapping scheme in the case of electrochromic systems. The fact that the ionic dynamics controls the electronic transitions capable to generate the color centers was here denominated coloring ionic trapping state.

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