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Coloring ionic trapping states in WO_3 and Nb_2O_5 electrochromic materials

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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 WO_3 and Nb_2O_5. 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 Nb_2O_5 since the reduction potential of Nb_2O_5 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 coloring 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.

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 [1,12–14]. 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 WO_3 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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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., WO_3 and Nb_2O_5. 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 Nb_2O_5 since the reduction potential of Nb_2O_5 is more negative (more energy is needed for a higher degree of coloration as will be discussed on this text).

2. Experimental procedure

WO_3 and Nb_2O_5 host layers of about 250 nm were prepared by the traditional sol–gel route. For combined electro-optical measurements, WO_3 and Nb_2O_5 homogeneous films were deposited on ITO substrates by dip-coating. The WO_3 film was heat-treated at 300 °C for 4 h, while the Nb_2O_5 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 $LiClO_4$ dissolved in an acetonitrile solution. Prior to the electrochemical measurements, the cell was purged with dry N_2 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., WO_3 and Nb_2O_5, 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].

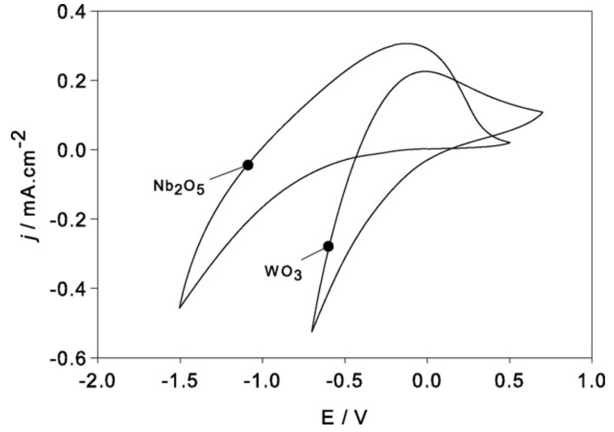

Fig. 1. Classical cyclic stabilized (after about 10 cycles) voltammetric pattern for WO_3 and Nb_2O_5, evidencing the higher reduction potential for the Nb_2O_5 host in comparison to the WO_3 host system. The scan rate used was of 30 mV s^{-1}. The quasi-reference electrode was a silver wire.

3. Results and discussions

Fig. 1 shows the typical stable (after about 10 cycles) cyclic voltammetric pattern for both WO_3 and Nb_2O_5 metal oxide host systems. The most important feature to be observed in Fig. 1 is the reduction potential of Nb_2O_5, which is comparatively more negative than the one observed in WO_3 hosts, which is classically known. Basically, this is an indication that it is easier to reduce W^{6+} metal valence state to W^{5+} in WO_3 hosts than to reduce Nb^{5+} valence state to Nb^{4+} in Nb_2O_5 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 Nb_2O_5 than in a WO_3 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 Nb_2O_5 with ionic trapping accompanied by valence trapping is more difficult in such host comparatively to WO_3 host).

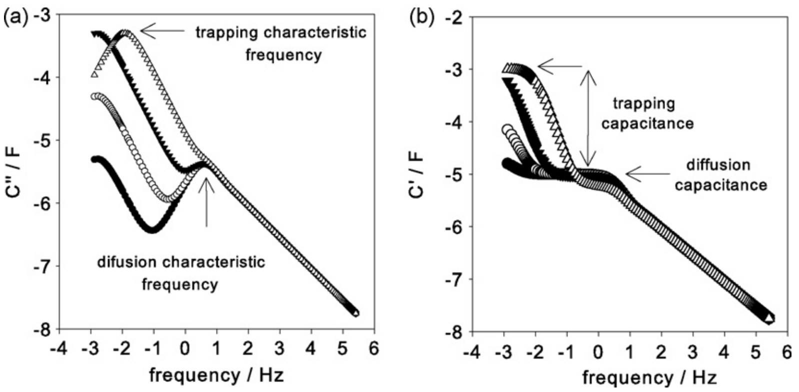

Fig. 2. Bode capacitance spectra illustrating the influence of the charging of trapping states, i.e., trapping capacitance: (a) imaginary and (b) real parts. For this simulation it was considered that the trap has a characteristic frequency of $\omega_t = 0.01$ rad s^{-1} and a resistance $R_t = 1/\omega_t C_t$ with C_t changing from $C_t = 0.1C_0$, $C_t = C_0$, $C_t = 10C_0$ and $C_t = 10^2C_0$. C_0 = has a value of 10 μF.