

# The coloration and degradation mechanisms of electrochromic nickel oxide

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## ARTICLE INFO

### Article history:

Received 15 November 2012

Received in revised form

28 March 2013

Accepted 29 March 2013

### Keywords:

Nickel oxide

Nickel hydroxide

Electrochromic

Coloration

Degradation

## ABSTRACT

Nickel oxide (NiO) is the most common low-cost high-performance anodic electrochromic material that is widely used in the applications for smart windows. The coloration mechanism is, however, still not well understood and we show that this is due to the evolving chemical nature of the film during the electrochromic process. Chemical bath deposited (CBD) NiO was studied using the near-grazing incidence angle Fourier transform infrared spectroscopy (NGIA FTIR) and endurance potential cycling. We will show that the initial hydration of NiO films toward Ni(OH)<sub>2</sub> proceeds gradually through a combination of coloration from hydroxyl (OH<sup>-</sup>) ions and bleaching through H<sup>+</sup> ions. This process increases the optical modulation of the deposited film. However, when the OH<sup>-</sup> ion diffusion is significantly enhanced, OH<sup>-</sup> ion incorporation during coloration will lead to water incorporation. The extensive intercalated networks can then isolate NiOOH grains that results in irreversible coloration and this is commonly reported as degradation. We will propose a model to show that an isolation process can explain this degradation and can be easily reversible by annealing. This understanding of the coloration and degradation mechanisms suggests that an optimum control of hydroxyl ions is critical for both efficiency and durability of NiO electrochromic devices.

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## 1. Introduction

Electrochromic (EC) materials are important for enabling technologies such as smart windows or non-volatile displays [1–4]. The stability of the open-circuit memory can translate to possible energy savings in integrated windows application for indoor comfort [5]. In typical complementary inorganic EC devices, both cathodic and anodic EC materials are needed. Tungsten oxide represents a popular cathodic EC material while nickel oxide (NiO) is a commonly employed anodic EC material in these complementary devices [6,7]. NiO is often preferred because of its demonstrated high coloration efficiency (CE), good cyclic reversibility and low material cost [1,8]. Unlike the coloration mechanism of tungsten oxide, a clear understanding of that of NiO in aqueous electrolyte is still lacking. Part of the reason is the complication due to the existence of different phases for both the bleached ( $\alpha$  and  $\beta$  phases) and colored ( $\gamma$  and  $\beta$  phases) states. In short, it is now understood that these phases simply represent layered octahedron NiO with intercalated water molecules or hydroxyl ions. The difference lies in the distance of the interlayer separation due to the amount of intercalated water [1,9]. We will show that

this ability to incorporate or remove water, in hydrating or dehydrating the film, is critical in understanding the coloration mechanism of NiO. Another complication in studying the coloration mechanism comes from the possibility of multiple reactions in an aqueous electrolyte upon cycling. There are conflicting results on the ions responsible for the coloration where H<sup>+</sup> and OH<sup>-</sup> ions are both reported to be dominant [11,12]. Many works therefore mentioned possibility of both type of reactions involving the two differently charged ions [8,9]. These available explanations therefore appear to lack clarity and consistency, especially between physical-deposited films and solution-based films in the electrochemical reaction [10–14]. A coherent model for the coloration mechanism of NiO that factors in chemical evolution and hydration will be presented in this work. We will show that both ions are responsible at different stages of the hydration that resulted in the changes observed. We will also demonstrate and explain how the mechanism is responsible for the commonly observed activation and degradation stages of a NiO film. Finally, we will show that as expected from our model, this degradation can be reversed.

## 2. Material and methods

The NiO chemical bath deposition (CBD) solution contains 80 ml of 1 M nickel sulfate, 60 ml of 0.25 M potassium persulfate

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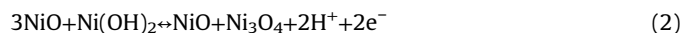
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and 20 ml of aqueous ammonia (25–28%) [8]. ITO-glass substrates with resistivity of 8–12  $\Omega$ /sq were ultrasonically cleaned by acetone and isopropyl alcohol (IPA). Polyimide tape was used to prevent the deposition on the non-conductive sides of the ITO substrates. Growth by CBD was achieved by vertical dipping of the ITO-glass substrates into the freshly prepared solution for 20 min at room temperature. The samples were then washed with deionized water and dried at 75 °C in an oven. The as-deposited samples were annealed at different temperatures (300 °C, 400 °C and 500 °C) for 90 min in an inert argon ambience using a standard horizontal three-zone furnace. The X-ray diffraction (XRD) was performed using a General Area Detector Diffraction system equipped with a Cu X-ray source. The cyclic voltammetry (CV) measurements were carried out using a Gamry series G300 potentiostat with a standard Ag/AgCl reference electrode and a Pt foil counter electrode in a 0.1 MKOH solution. The transmission spectra were measured by the CRAIC micro-spectrophotometer over a wavelength range of 350–800 nm. ITO-glass substrates of identical processing conditions (e.g. anneal temperature and duration) are used as references to eliminate variations of the substrates with annealing. The near-grazing incidence angle Fourier transform infrared spectroscopy (NGIA FTIR) measurements were performed using Bruker FTIR v80 system equipped with reflection stage set at an angle of 70°.

### 3. Results and discussion

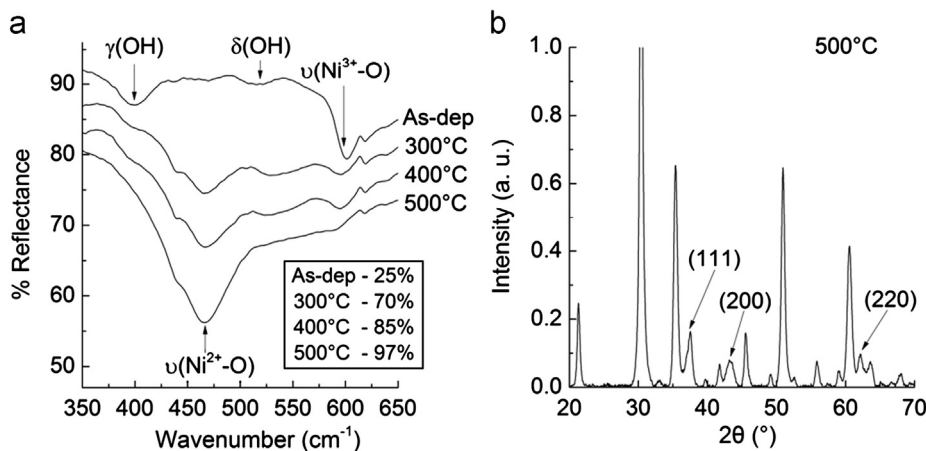
We investigated CBD NiO films with different post-deposition annealing temperature. The NGIA FTIR spectra for the CBD films at the respective annealing conditions are shown in Fig. 1(a). The inset in Fig. 1(a) shows the measured transmittance of the film at a wavelength of 550 nm. The lower wavenumber region from 350 to 650  $\text{cm}^{-1}$  represents the Ni-related vibrational modes. These are useful to identify the presence of different phases or even valency and we based the shown peak assignments mainly on solution-deposited films for consistency [15,16]. The as-prepared solution deposited film is quite hydrated, as Fig. 1(a) shows the presence of bending vibration modes of both  $\alpha$  and  $\beta$  Ni(OH)<sub>2</sub> at 400  $\text{cm}^{-1}$  ( $\gamma$ (Ni–OH)) and 520  $\text{cm}^{-1}$  ( $\delta$ (Ni–OH)). Higher valence (3+) Ni–O stretching vibration mode  $\nu$ (Ni<sup>3+</sup>–O) can also be observed at 600  $\text{cm}^{-1}$ . The presence of higher valency modes gives the as-deposited film a brownish color appearance and this is also shown by the significantly lower transmittance indicated in the inset. XRD studies show the presence of only Ni(OH)<sub>2</sub> and therefore suggest that the higher valence NiOOH are of a more

disordered form. The presence of NiOOH is also supported by recent findings from XRD investigations using filtered powder from the bath solution [8]. As the annealing temperature increases, the vibrational mode at 465  $\text{cm}^{-1}$  appears and gradually increases with annealing temperature. We attribute this broad peak to the lower valence (2+) Ni–O stretching vibration mode  $\nu$ (Ni<sup>2+</sup>–O) and the presence of NiO grains can also be observed using XRD through the appearance of NiO crystal peaks as shown in Fig. 1 (b). This shows the gradual dehydration of the film and the reduction in the higher valency oxides with increased annealing temperature that also increases the transmittance of the film significantly from 25% to 97% as indicated. The cyclic voltammetry (CV) and NGIA FTIR of the 300 °C annealed samples are shown in Fig. 2(a–c). There is only a slight change in the sheet resistivity of the ITO ( $\sim$ 0.4  $\Omega$ /sq) after the 300 °C anneal and in any case, the focus is on the variations with cycling rather than the absolute peak positions. The good optical modulation of our films are consistent with previous studies on CBD films [8]. The NGIA FTIR measurement shows the presence of NiO and Ni(OH)<sub>2</sub> after the 300 °C anneal. When these are present in close proximity, coloration can reportedly proceed via the following reactions [1],[10]:



However, if reactions (1) and (2) are the key mechanisms where H<sup>+</sup> is the only diffusing ion and the higher valence state is either the defective Ni<sub>2</sub>O<sub>3</sub> or Ni<sub>3</sub>O<sub>4</sub>, the cyclic reversibility should be highly stable. We do not observe these structures from our XRD measurements and the cyclic stability is not observed in the CV plot as shown in Fig. 2(a). The current density of the oxidation and reduction current peaks is observed to increase gradually with cycling. This increase in peak intensity and separation then reaches a pseudo-maximum at around the 90th potential cycle. Thereafter, the CV plot shows a slight decrease in current density as the reduction–oxidation (redox) peaks shift toward more positive potential. A similar phenomenon has been previously observed [17–19] and here we will explain the underlying mechanism.

The key instability observed from the CV measurements is the evolving chemical nature of the EC material that can be better understood from the NGA FTIR spectra shown in Fig. 2(b) and (c). An increase in  $\beta$ -Ni(OH)<sub>2</sub> after repeated cycling can be observed from the  $\delta$ (Ni–OH) bending vibration mode in Fig. 2(b) and the O–H stretching vibration mode ( $\nu$ (O–H)) at 3640  $\text{cm}^{-1}$  in Fig. 2(c).



**Fig. 1.** (a) The FTIR reflectance spectra of the as-deposited CBD film after post-deposition annealing at 300 °C, 400 °C and 500 °C. Inset shows the transmittance of the respective films at a wavelength of 550 nm. (b) XRD spectrum of the CBD film after 500 °C post-deposition anneal. Labeled peaks show the different crystal orientation of NiO cubic structure while the remaining peaks that are contributed by the ITO.

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