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## IN-SITU SPECTROSCOPIC STUDIES OF ELECTROCHROMIC HYDRATED NICKEL OXIDE FILMS

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## ABSTRACT

In this investigation, in-situ spectroscopic studies of anodically deposited electrochromic hydrated nickel oxide electrodes were performed by visible/near-infrared spectroscopy and Fourier-Transform Infrared (FTIR) spectroscopy. All measurements were taken while the nickel oxide thin films were switching between the bleached and colored states, where the electrodes were not removed from the electrochemical cell. Optical transmittance measurements of the nickel oxide film relative to tin oxide coated glass varied during coloring from the integrated solar spectral transmittance,  $T_s=101\%-54\%$ , and average near-infrared transmittance,  $T_{nir} = 101\%-83\%$ . The photopic transmission was  $T_p = 101 - 31\%$ . Transmittance measurements versus time were also performed at selected wavelength values, ranging from 375 to 1100 nm. Also different scan rates (10-100 mV/s) were investigated at each of these wavelengths, where optimum switching rates could be determined. All changes in optical density were achieved by continuously cycling between a potential range of -500 to +800 mV. Coloration occurs at a faster rate than bleaching of the films at every switching rate selected. Also, maximum and minimum transmission measurements at 420 nm do not correspond to the cathodic and anodic peak current densities. Instead these transmission measurements correspond to the regions past the peak current densities. From these optical experiments, plots of transmission (%) versus voltage (mV) and transmission (%) versus total extracted charge (mC) were obtained. For FTIR spectroscopic experiments, chemical identification of the 10-20 nm thick films showed that the films exhibit different bonding environments for both the colored and bleached states. There exist surface hydroxyl groups associated with nickel oxide in the region of 3600-3800  $\text{cm}^{-1}$  wave numbers. Fundamental water vibrations are also found at 3200-3500  $\text{cm}^{-1}$  and at 1600-1700  $\text{cm}^{-1}$  wave numbers. The nickel oxygen vibration region is at 400-525  $\text{cm}^{-1}$  for both states. The comparison of bleached and colored states exhibits distinctive molecular vibrational states, which correspond to  $\text{Ni}(\text{OH})_2$  and  $\text{NiOOH}$  respectively.

## 1. INTRODUCTION

Electrochromic materials have shown great promise for future window and information display applications. These reversible optically switching materials offer dynamic control of solar radiation with long memory times. An important property of electrochromic materials for window displays is the ability to control illumination levels as well as glare and heat gain or loss. These features are particularly desirable for large-scale architectural glazing. There are many transition metal oxides that exhibit this phenomena.<sup>1</sup> The most widely studied is tungsten oxide,  $\text{WO}_3$ , which exhibits a transparent to blue coloration. However, there are other materials, such as hydrated nickel oxide that demonstrate such promise.

Electrochromism is defined as reversible optical switching of a material to a colored, bleached or intermediate state as a result of dual ion and electron insertion/removal under a low applied voltage (Fig. 1). As a result of this injection/ejection, color centers are formed in the material, producing optical absorption principally in the visible wavelength region, although near-infrared (NIR) absorption is possible.<sup>2</sup> These changes in optical density, between the colored and bleached states, represent both chemical and structural changes in the material.

Electrochromic device configurations for application in architectural glazing can be envisioned as symmetric structures consisting of up to five distinct layers (Fig. 2). These layers consist of a transparent conductive coated substrate, an electrochromic material (working electrode), a polymeric ion conductor (which can also serve as a lamination material), an electrochromic material (counter electrode), and another transparent conductive substrate. By applying a low potential (1-3 V) between the working and counter electrodes, protons/ions are shuttled from the ion conductor into the electrochromic materials causing the desired effect of coloration or bleaching. For in-situ spectroscopic studies, the polymeric ion conductor was replaced by a liquid electrolyte. Before fabricating such a device, it is important to fully understand the optical properties and switching mechanism of the electrochromic material. In our prior studies of hydrated nickel oxide all of the optical measurements and chemical identification have been analyzed in the ex-situ mode.<sup>3,4</sup> To more realistically analyse how electrochromic hydrated nickel oxide changes chemically as well as optically, in-situ spectroscopic techniques were utilized. Chemical identification of the thin films in the colored and bleached states was achieved by Fourier-Transform Infrared (FTIR) spectroscopy and changes in optical density were measured by a dual-beam spectrophotometer. The information obtained by these experiments, along with our prior work, will ultimately lead to our development of a working electrochromic device.

**ELECTROCHROMIC REACTION IN NICKEL OXIDE**

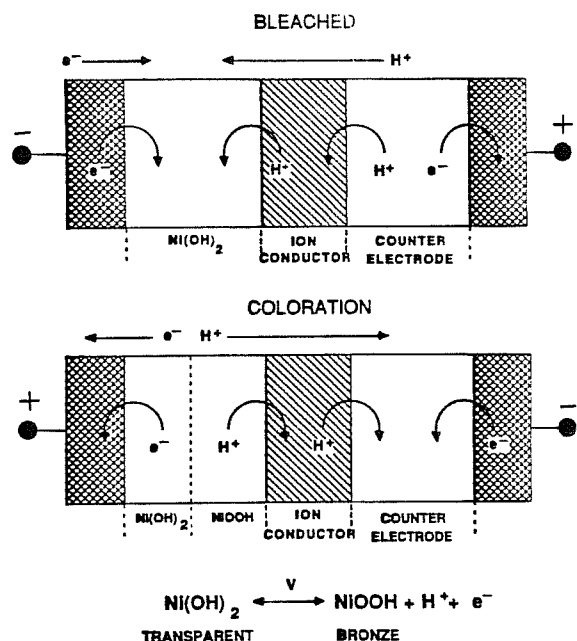
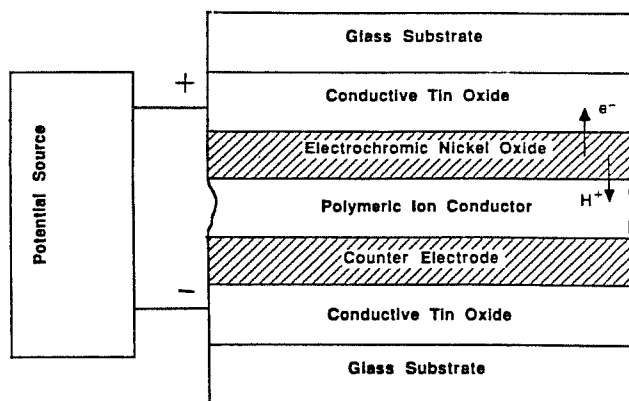


Fig. 1. Simplified diagram of bleaching and coloration of a nickel oxide switching device showing the migration of electrons and protons.

**SYMMETRIC ELECTROCHROMIC DEVICE CONFIGURATION**



-- XBL 874-1940 --

Fig. 2. Schematic of an electrochromic device utilizing a polymer ion conductor as a lamination layer.

**2. EXPERIMENTAL PROCEDURES**

Thin films of hydrated nickel oxide were anodically deposited onto conductive sheets of tin-oxide coated glass by electrochemical techniques described in our prior work.<sup>3,4</sup> The anodic technique was used because cathodically deposited films have been shown to be unstable.<sup>5</sup>

A scanning potentiostat, Princeton Applied Research Model 273, was used to form the nickel oxide films, with the voltage range set at -500 mV to +1500 mV. The current range was +100 mA, and the scan rate was 20 mV/s. The electrochemical bath was identical to those described in previous studies.<sup>3,4</sup> After growth of 10-20 nm thick films, the electrodes were removed from the deposition bath and rinsed in distilled water. They were then placed in an electrolyte solution of potassium hydroxide to investigate their switching properties (Fig. 3). For the visible/near-infrared experiments, the electrolyte was 0.05M KOH and for FTIR spectroscopy studies, it was 1M KOH. The switching properties were monitored by an X-Y recorder, Hewlett Packard Model 70005B.

**ELECTROCHEMICAL CELL**

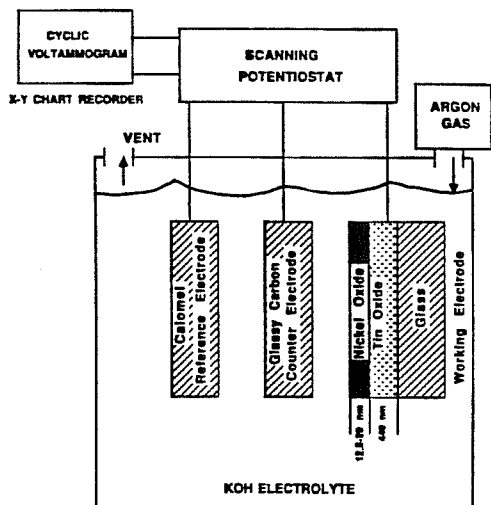


Fig. 3. Schematic of the electrochemical cell used in the voltammetry studies.

**IN-SITU SPECTROELECTROCHEMICAL CELL FOR FTIR STUDIES**

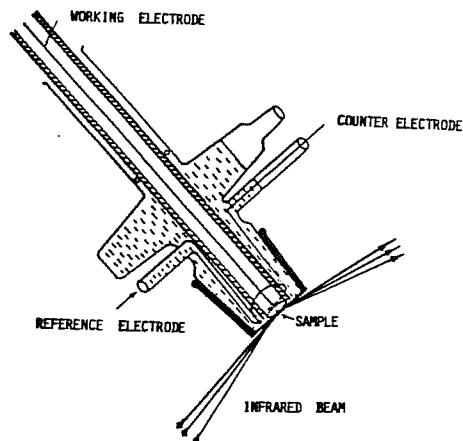


Fig. 4. Diagram of the In-situ spectroelectrochemical cell used in the FTIR studies. The incident infrared beam is at a 80-85° angle with respect to normal.

In-situ spectral transmittance experiments were performed using a 2.54 cm x 2.54 cm x 3.81 cm polystyrene cuvette to accommodate a three-electrode system, the nickel oxide electrode, the calomel reference electrode and a glassy carbon counter electrode. The electrolyte used for all measurements was 0.05M KOH (pH=12.8). Transmission measurements were restricted to wavelengths of 300-1300 nm due to the polystyrene cuvette being transparent in only this region. All data measured was in reference to an identical polystyrene cuvette containing the same electrolyte and a blank tin-oxide transparent substrate, 2 cm<sup>2</sup> in size. Initial spectral experiments involved optical transmittance measurements of the hydrated nickel oxide thin film in its colored and bleached states. Upon completion, six wavelengths (375, 420, 525, 600, 725, and 1100 nm) representing different absorption characteristics were chosen to be further analyzed in a cyclic time mode. This mode involved observing the film reversibly switching from the colored to the bleached state in a cyclic mode as a function of transmission and time. In addition, for each wavelength measured, scan rates of 10, 20, 50, and 100 mV/s were used. FTIR spectroscopy was performed on the nickel oxide films using an IBM-98 spectrometer with liquid nitrogen cooled mercury cadmium Telluride (MCT) detectors. The IR spectra were collected at 4 cm<sup>-1</sup> resolution and 500 scans. In-situ measurements were made to help identify the chemical compounds of the material in its bleached and colored states in the near- and middle-infrared regions (4000-400cm<sup>-1</sup> 2.5-25 μm). The films were analyzed in a reflection-absorption mode at 80-85° to normal to the electrode surface, as shown in Fig. 4, but the data was converted to effective single-pass transmittance by computer simulation. The measurements were taken relative to an uncoated substrate in the same conditions. The atmospheric conditions of the chamber were 1.33 x 10<sup>-1</sup> Pa in a nitrogen environment. The electrolyte used in the chamber was 1M KOH (pH=13.8, 22 °C), where the nickel oxide substrate was a circular disk 1 cm in diameter.

### 3. RESULTS AND DISCUSSION

Characterization techniques using in-situ spectroscopy have provided a more realistic understanding of the behavior of electrochromic hydrated nickel oxide. Optical measurements showed the change of transmission in the bleached and colored states. The switching properties of nickel oxide were also studied, indicating that the anodic coloration occurs faster than the cathodic bleaching. Infrared spectroscopy revealed the chemical identification of the compounds in the system during its colored and bleaching states.

### 4. OPTICAL SPECTROSCOPY

After deposition of the nickel oxide film, the electrode was submerged in the cuvette filled with 0.05M KOH (pH=12.8) and allowed to complete five cycles before in-situ data was taken. All of the optical experiments were recorded by the X-Y chart recorder. A typical cyclic voltammogram generated for these experiments is shown in Figure 5. The film thickness was identical to those in previous studies.<sup>4</sup> The optical spectra of the hydrated nickel oxide layer in its colored and bleached state is shown in Figure 6 for the spectrum.

Cyclic Voltammogram of Nickel Oxide in 0.05 M KOH

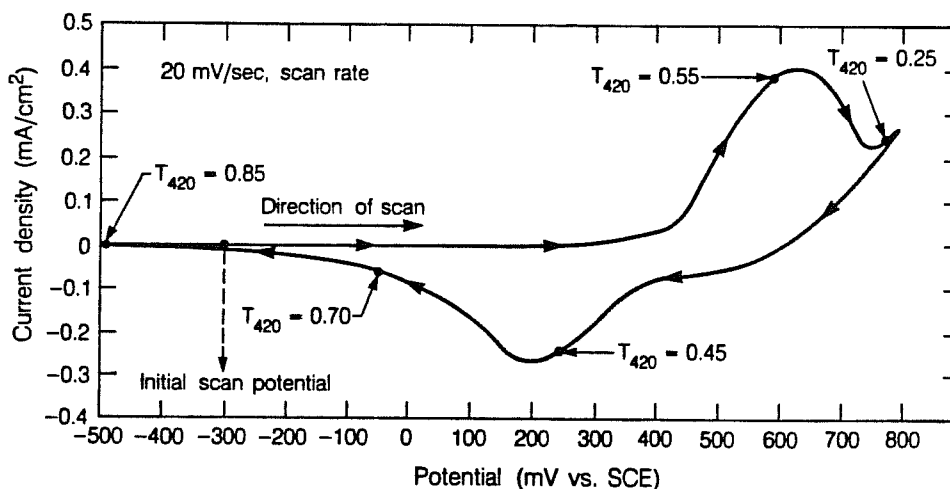


Fig. 5. Cyclic voltammogram of nickel oxide in 0.05 M KOH electrolyte. Transmittance data at 420 nm is given for various points.

The spectral data was obtained relative to an uncoated substrate in the same cell configuration. Integrating with respect to the solar (AM2) and the photopic spectrum the transmittances are  $T_s(\text{bleached})=101\%$ ,  $T_s(\text{colored})=54\%$ ,  $T_{\text{vis}}(\text{bleached})=101\%$ ,  $T_{\text{vis}}(\text{colored})=83\%$ ,  $T_p(\text{bleached})=101\%$ , and  $T_p(\text{colored})=31\%$ , respectively.<sup>6</sup> The high transmittance values for the bleached states are a result of the adsorption being low for the hydrated nickel oxide thin films. The

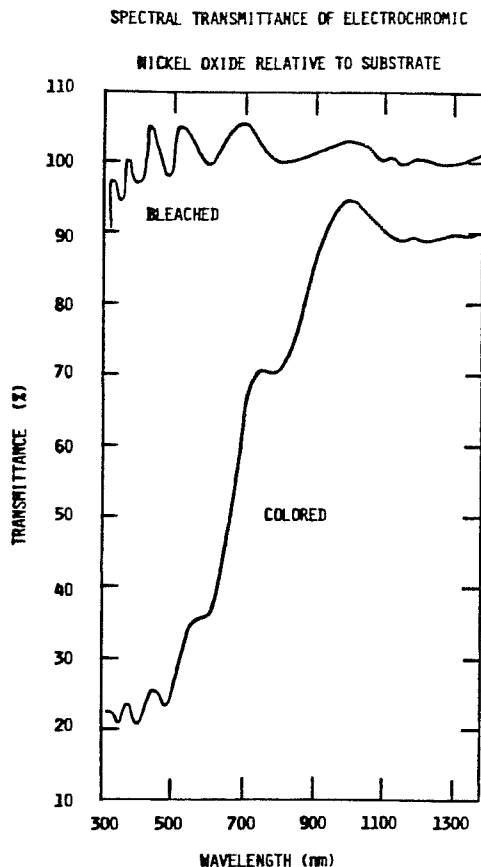
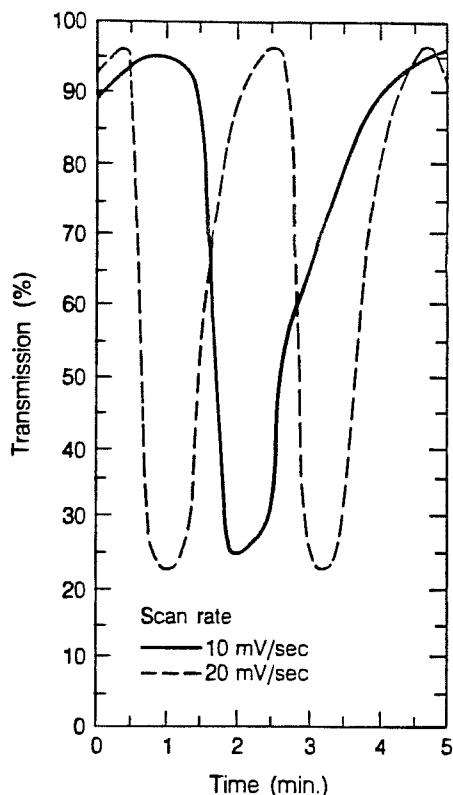


Fig. 6. Spectral transmittance of electrochromic hydrated nickel oxide/tin oxide/glass for both bleached and colored states. This data is taken relative to a tin oxide/glass substrate.

antireflection effect caused by the hydrated NiO layer on the surface causes an increase in the transmission over that of the uncoated substrate. Other optical experiments performed involved transmittance measurements versus time at six different wavelengths, 375, 420, 525, 600, 725, and 1100 nm. Various scan rates (10, 20 50, 100 mV/s) were investigated at each of the wavelengths, where optimum switching rates could be determined. Due to the enormity of the data accumulated, figures 7 and 8 are representative of measurements taken at 420 nm at each of the aforementioned scan rates. The data was tabulated into three regions, region 1 being the colored sequence and regions 2 and 3 representing the bleached sequence. A linear relationship was found for each of the coloration and bleaching regions by curve fitting. Table 1 depicts equations for these three regions at different scan rates. The usefulness of such equations allows for predicting the transmittance of the film as well as the rate it takes to change its optical density. One can also find the potential that corresponds to the transmittance value, all of which are dependent on the scan rate. From these equations, it is important to note the magnitudes of the slopes for each region. For coloration at slow scan rates (10 or 20 mV/s) the slopes are much larger than those of both bleaching regions. One can physically observe coloring occurring faster than bleaching. For the faster scan rates (50 or 100 mV/s), the occurrence is still apparent. One also notes that at these rates residual coloration is evident as the film changes in optical density.

From the experiments performed in the time-drive mode, three important graphs (the absorptive peak) were extrapolated from the data, where the wavelength of adsorption was 420 nm and the scan rate was 20 mV/s. Figure 9 shows a plot of transmission versus applied voltage. This graph shows experimental and theoretical lines representing the coloration and bleaching sequences. To obtain 25% transmittance, complete coloration, the applied potential is 782 mV, and for 85% transmittance, complete bleaching, the applied potential is -500 mV. It is important to note that the transmission measurements do not correspond to the maximum/minimum peak current densities on the cyclic voltammogram (Fig. 5). Maximum and minimum transmission is achieved past the cathodic and anodic peaks. Figure 10 depicts transmission versus total extracted charge for both the colored and bleached states. The total extracted charge to obtain a 25% transmittance coloring effect is 300 mC and for a 85% transmittance bleaching effect is -93 mC.

Transmission (%) vs. Time (min.)  
for Nickel Oxide



Transmission (%) vs. Time (min.)  
for Nickel Oxide

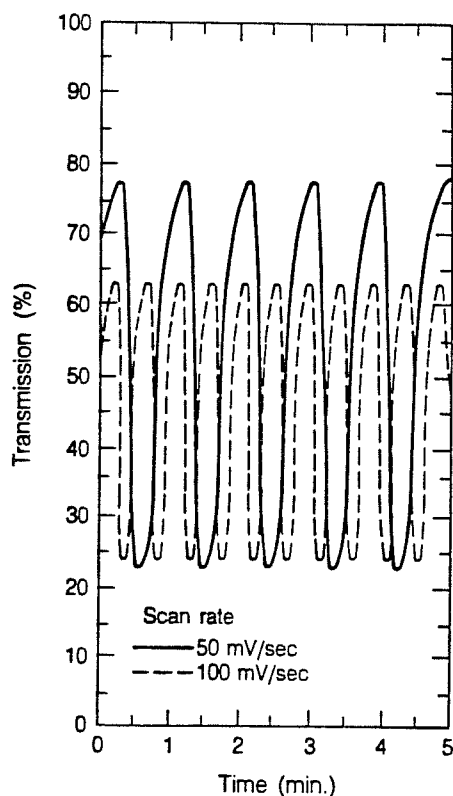


Fig. 7. In-situ dynamic transmittance at 420 nm of electrochromic switching film. Note that coloring occurs more rapidly and follows a single function. Bleaching occurs less rapid and follows two functions. A triangle wave is used as the driving potential for 10, and 20mV/s scan rates.

Fig. 8. In-situ dynamic transmittance at 420 nm of electrochromic hydrated nickel oxide. A triangle wave is used as the driving potential for 50, and 100 mV/s scan rate.

Table 1. Modeled equations for bleaching and coloring for different scan rates for 3 regions of the dynamic transmittance curves.

Scan Rate (mV/s)	Region1 (colored)	y values (%)
10	$y=390-200x$	30-90
20	$y=203.5-198x$	25-90
50	$y=210.5-194x$	25-70
100	$y=106.5-192x$	25-60
Scan Rate (mV/s)	Region 2 (bleached)	y values (%)
10	$y= -175+84x$	35-60
20	$y= -74+86x$	35-60
50	$y= -107.55+100x$	30-55
100	$y= -9.06+104.2x$	30-45
Scan Rate (mV/s)	Region 3 (bleached)	y values (%)
10	$y=10+25x$	60-85
20	$y=5+40x$	60-85
50	$y= -13+83x$	55-70
100	$y=13+83x$	45-57.5

$y=$  % transmittance  
 $x=$  time (minutes)

The switching phenomenon of nickel oxide involves first anodization (coloration) and then cathodization (bleaching). Internally, it is a diffusion process where protons are being shuttled into and out of the  $\text{Ni}(\text{OH})_2$ , or  $\text{NiOOH}$  lattice. The hydroxyl ions also play an important role in this process.<sup>4</sup> By using a triangular potential sweep, the complete coloration of the electrode to 25% transmittance takes 54 s at a scan rate of 20 mV/s. To obtain a 45% transmittance value (in the bleached region) at the same scan rate, the time is 83 s. For a total bleaching effect, 85% transmittance, the time required is 120 s. It is important to note that the electrode response time is characteristically much faster when using a D.C. potential source.

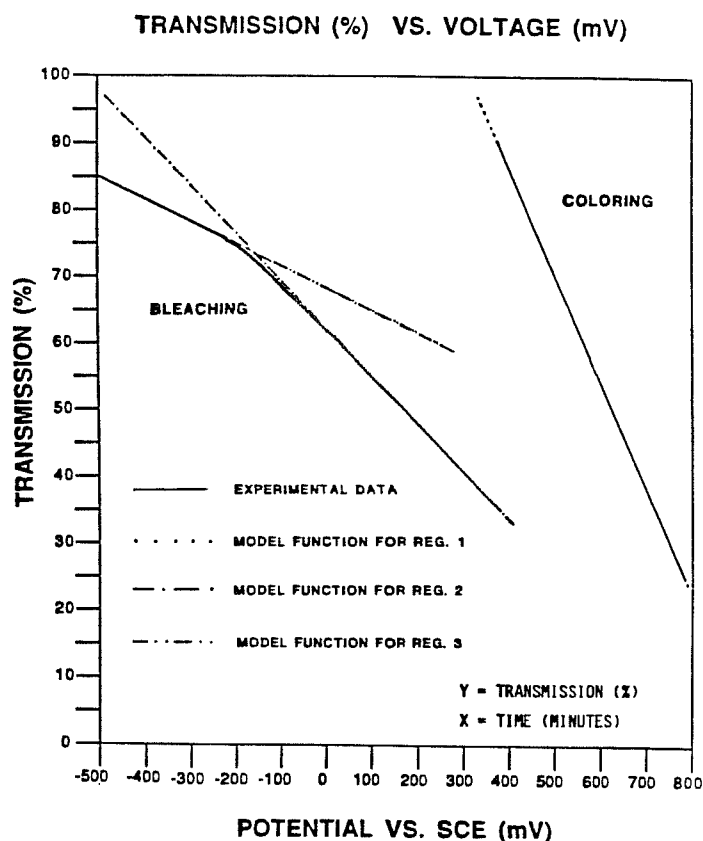


Fig. 9. Example relationship between transmittance at 420 nm and applied voltage for both bleaching and coloring. Model functions are shown for various regions. The scan rate is 20mV/s. Table 1 shows modeled functions for other scan rates.

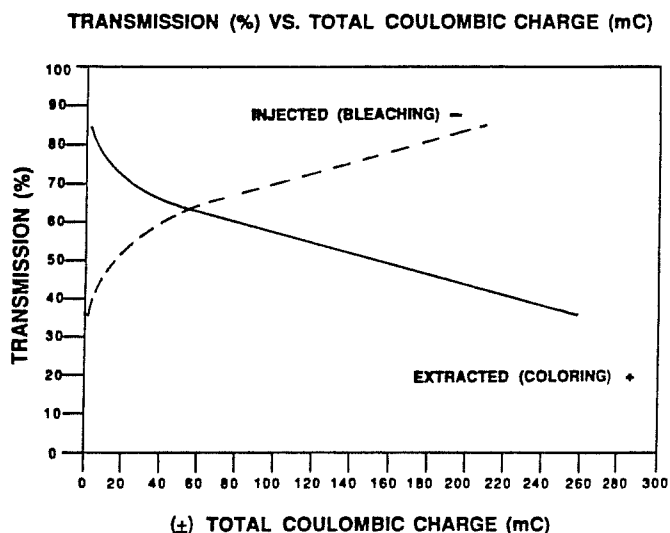


Fig. 10. Relationship for transmittance as a function of injected or extracted charge for hydrated nickel oxide. Data is for a 20mV/s scan rate.

### 5. FOURIER-TRANSFORM INFRARED SPECTROSCOPY

In-situ spectroscopic studies involved characterizing the bleached and colored states through the identification of the molecular vibrational stretches. A nickel oxide thin film was grown under conditions identical to those described in our prior work.<sup>3,4</sup> After deposition the film was rinsed in distilled water. Then the electrode was placed in a cell containing a 1M KOH (pH=13.8 at 22 °C) electrolyte, where the cell was purged with nitrogen under a vacuum of  $1.33 \times 10^{-1}$  Pa. The cyclic potential range was set from -500 to +700 mV at a scan rate of 50 mV/s.

Figure 11 shows spectra of the near- and middle-infrared regions in both the bleached and colored states. In tables 2a and 2b are tabulated comparative vibrational spectra and assignments. Figure 11 depicts identifiable vibrational stretches of surface hydroxyl groups of nickel oxide and fundamental water and carbon dioxide vibrations. Infrared spectra of hydroxyl groups on the surface of nickel oxide generally consist of several absorption bands, with the wave number and relative intensity dependent on the type of oxide and degree of dehydroxylation.<sup>7</sup> Also, there are distinct types of surface hydroxyl groups in nickel oxide as a result of the different coordination bonding of oxygen atoms to nickel atoms. These groups are evident in Figure 11 for both the bleached and colored modes in the wave number regions of  $3600\text{--}3800\text{ cm}^{-1}$ . The location of the experimental vibrational stretches are in agreement with those noted by other investigators, but the peak-by-peak identification of each stretch is dependent on sample preparation and test conditions.<sup>7-16</sup>



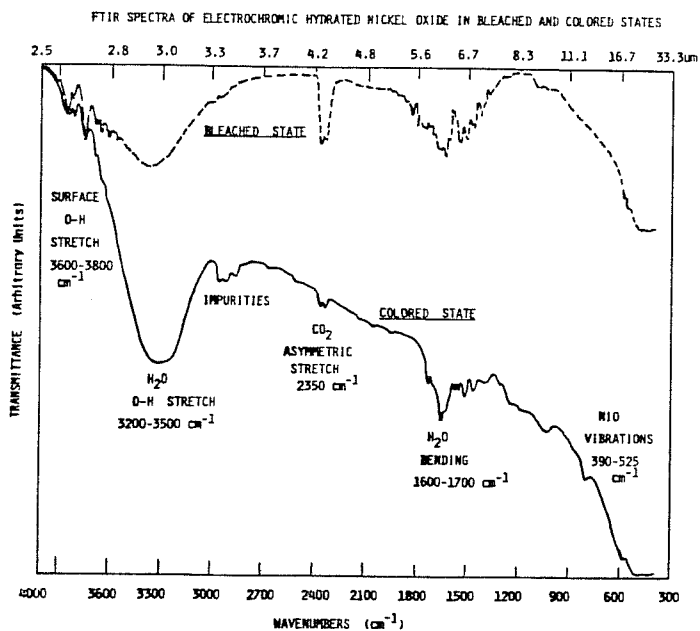


Fig. 11. In-situ FTIR spectra for electrochromic hydrated nickel oxide showing characteristic molecular vibration regions. These regions are correlated in Table 2a-b for both the bleached and colored states.

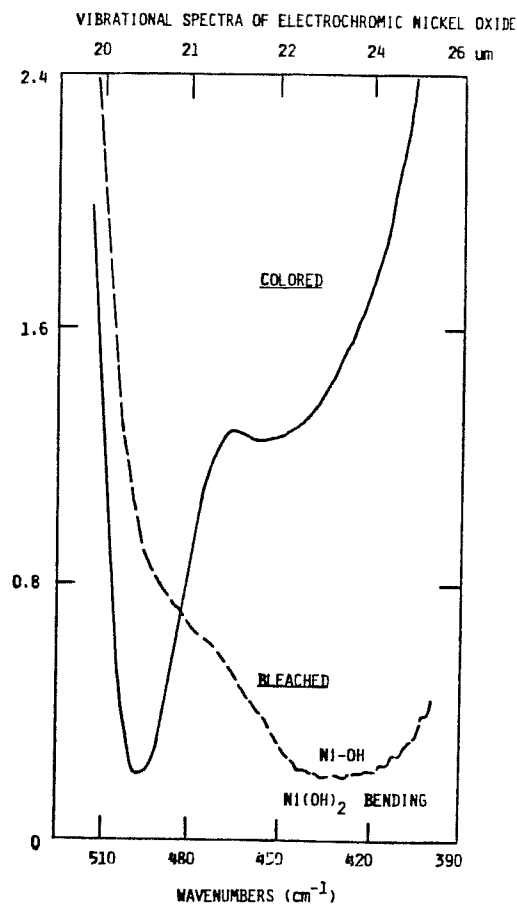


Fig. 12. In-situ FTIR spectra for electrochromic hydrated nickel oxide in the Ni-O vibration region. Both bleached and colored states can be seen.

Fundamental water vibrations are noted in Figure 11 in the wave number regions of  $3200\text{--}3500\text{ cm}^{-1}$  and  $1600\text{--}1700\text{ cm}^{-1}$ . Thus, both spectra indicate lattice water as a part of the nickel oxide's structure in its bleached and colored states, i.e., water molecules trapped in the crystal lattice by weak coordinate-covalent bonds to the nickel ions.<sup>8</sup> Other investigators have noted that the broad band having a center at  $3450\text{ cm}^{-1}$  and absorption at  $1620\text{ cm}^{-1}$  can be attributed to the stretching mode and the bending mode of the lattice water, respectively.<sup>12-15,17</sup> Fundamental  $\text{CO}_2$  vibrations are also evident in both spectrums at  $2350\text{--}2370\text{ cm}^{-1}$  in good agreement with its asymmetrical stretching ( $\nu_{\text{as}}\text{ CO}$ ) at  $2350\text{ cm}^{-1}$ .<sup>16,18</sup> The symmetric stretching vibration of  $\text{CO}_2$  is inactive in the infrared because there is no change in the dipole of the molecule.<sup>8</sup> shows the nickel-oxygen vibration region occurring at  $400\text{--}525\text{ cm}^{-1}$  for the bleached and colored states. Identification of the bleached state shows a broad vibrational stretch occurring in the wave number region of  $400\text{--}510\text{ cm}^{-1}$  with the central band at  $430\text{ cm}^{-1}$  and shoulder at  $483\text{ cm}^{-1}$ . Comparison of this stretch to those in the literature does show a correlation.<sup>8,10,12-16,19,20</sup> The  $430\text{ cm}^{-1}$  absorption may be the Ni-OH stretching vibration for  $\text{Ni}(\text{OH})_2$  and  $483\text{ cm}^{-1}$  may be the -OH group bending vibration but the assignment of our experimental stretch is lower than those reported by others at  $500\text{--}550\text{ cm}^{-1}$ .<sup>7,8,10-16</sup> This difference could be caused by preparation differences and the nature of the applied voltage. Both can affect the rate of charge injected or ejected into the electrode system, which as a result causes shifts in the vibrational stretches in the infrared spectrum.<sup>8</sup> For the colored state, vibrational stretches again occur in the same wave number region of  $400\text{--}510\text{ cm}^{-1}$  with a band at  $496\text{ cm}^{-1}$  and shoulder at  $458\text{ cm}^{-1}$ . They are also in agreement with those reported.<sup>9,10,15,19,20</sup> At  $496\text{ cm}^{-1}$  the Ni-O vibration can be identified for  $\text{NiOOH}$ .<sup>19</sup> From these experiments, it is clear that the molecular analysis of amorphous electrochromic nickel oxide by FTIR spectroscopy is a very complex process. Recent work has indicated that coatings similar to ours can be characterized by angle-resolved FTIR spectroscopy.<sup>10</sup> For crystalline films, a proposed layer structure resulted from their study. On the surface is an open layer of  $\beta\text{-Ni}(\text{OH})_2$  and hydroxyl groups with free water, under which are a compact layer of  $\alpha\text{-Ni}(\text{OH})_2$  and bound water layers. As the electrode is oxidized or switched to the colored state the film transforms to an open surface layer of  $\beta\text{-NiOOH}$  with free water over a compact layer of  $\gamma\text{-NiOOH}$  and bound water. However, there is a lack of direct physical evidence for these layers. As further studies are performed, we expect to gain a better understanding of the nature of electrochromism and its relationship to structural and chemical changes in nickel hydroxide.

Table 2a. IR Vibrational Frequencies and Assignments for Discharged Nickel Hydroxide - Ni(OH<sub>2</sub>)

Species	Assignment	Vibrational Frequencies cm <sup>-1</sup>								
		Ours								
Ni(OH <sub>2</sub> )	Ni-OH bend			354					340m	350s,sh
Ni(OH <sub>2</sub> )	-						400(β)			
Ni(OH <sub>2</sub> )	-						405(α)			
Ni(OH <sub>2</sub> )	Ni-OH stretch	420-450b	450	475	450w	450, 433	457(β)w	458w	450b	430(β)
Ni(OH <sub>2</sub> )	-OH group bend	483sh, 568w	500-550	530	540s	525-549	470(α), 513(β)	525s	540-550s	530(β)
Ni(OH <sub>2</sub> )	-	607w	640				625(α)			
Ni(OH <sub>2</sub> )	-		690-700				680(α)			
Ni(OH <sub>2</sub> )	-		780-790							
CO <sub>3</sub> <sup>2-</sup>	Ni-O-CO <sub>2</sub>									840
CO <sub>3</sub> <sup>2-</sup>	Ni-O-CO <sub>2</sub>	1020								1025
NO <sub>3</sub> <sup>-</sup>	-	1103w								1110
NO <sub>3</sub> <sup>-</sup>	-									1380
CO <sub>3</sub> <sup>2-</sup>	-	1450w						1450		1430
H <sub>2</sub> O	Lattice water H <sub>2</sub> O bend	1650b		1640	1620-1650			1640		1630
CO <sub>2</sub>	Assymmetric CO <sub>2</sub> stretch	2350- 2370								2350
Organic	C-H	2800, 2850								2840
Organic	C-H	2900								2910
H <sub>2</sub> O	Bound H <sub>2</sub> O stretch	3400b	3400b			3400	3400b(α)	3460w		3420
H <sub>2</sub> O	Inner O-H stretch					3550	3500(α)			3570
H <sub>2</sub> O	Free O-H stretch		3650- 3670	3650	3546	3610	3650(β)		3650, sh	3635
<b>Sample Type:</b>		n.s.p.	n.s.p.	n.s.p.	n.s.p.	n.s.p.	p	s.p.	s.p.	p
<b>Reference:</b>		This Work	10	11	12	13,14	10	15	9	16

Codes: Phases (α), (β), (γ), nickel sulfate precipitation: n.s.p., sintered powder: s.p., powder: p weak: w, broad: b, strong: s, shoulder: sh, medium: m.

Table 2b. IR Vibrational Frequencies and Assignments for Charged Nickel Hydroxide - NiOOH

Species	Assignment	Vibrational Frequencies $\text{cm}^{-1}$								
		Ours								
NiOOH	-						430( $\beta$ )			
NiOOH	-	458sh, w	440-455				440( $\gamma$ ), sh			
NiOOH	Ni-O bend	496s	490				485( $\beta$ )	470w	450	
NiOOH	Ni-O stretch	580	600			560-570	570( $\beta, \gamma$ )	580s	580	
NiOOH	-	616w	640sh, w			620-630( $\gamma$ )		625sh		
NiOOH	-		670w							
NiOOH	-						700( $\gamma$ )			
NiOOH	-		720-760							
NiOOH	-		790				790( $\beta, \gamma$ )			
$\text{CO}_3^{2-}$	Ni-O- $\text{CO}_2$	800						770w		
$\text{CO}_3^{2-}$	Ni-O- $\text{CO}_2$	1040								
$\text{CO}_3^{2-}$	-	1450						1450w		
$\text{H}_2\text{O}$	Lattice water $\text{H}_2\text{O}$ bend	1650				1620- 1650		1640		
$\text{CO}_2$	Assymmetric C-O stretch	2350- 2370								
Organic	C-H	2800								
	-	2850								
Organic	C-H	2900								
$\text{H}_2\text{O}$	$\text{H}_2\text{O}$ stretch	3300b	3350-3400				3350-3370	3480w	3450s, b	
$\text{H}_2\text{O}$	$\text{H}_2\text{O}$ stretch								3580b	
<b>Sample Type:</b>		n.s.p.	n.s.p.	n.s.p.	n.s.p.	n.s.p.	p.	s.p.	s.p.	p.
<b>Reference:</b>		This work	10	11	12	13, 14	10	15	9	16

## 6. CONCLUSION

In-situ spectroscopic measurements were performed on hydrated nickel oxide thin films. Optical transmission studies of the switching of a hydrated nickel oxide film relative to an uncoated substrate gave the following values:  $T_s=101\%-54\%$  and  $T_{\text{air}}=101\%-83\%$ . The photopic transmission response was  $T_p=101\%-31\%$ . Transmission measurements versus time indicated that there exists a linear relationship for both bleaching and coloring. From this relationship, one can predict the time it takes to change its optical density, the percent transmittance, and the applied cyclic potential. Maximum and minimum transmission measurements were found not to correspond to the cathodic and anodic peak current densities. Experimental data indicated that these transmission values were past the peak current densities. Infrared spectroscopic studies showed that the films have different bonding environments in both the bleached and colored states. Surface hydroxyl groups of nickel oxide are found at  $3600\text{-}3800\text{ cm}^{-1}$  wave numbers. Fundamental water vibrations are at  $3200\text{-}3500\text{ cm}^{-1}$  and at  $1600\text{-}1700\text{ cm}^{-1}$  wave numbers. For the nickel oxide region, vibrational stretches occur at  $400\text{-}525\text{ cm}^{-1}$  in both states. From these vibrations the coloration reaction appears to be  $\text{Ni}(\text{OH})_2 \rightarrow \text{NiOOH}$ , consistent with our prior work, and the electrode is expected to have a layered structure. From these in-situ spectroscopic investigations, a more realistic analysis of how electrochromic hydrated nickel oxide behaves optically and chemically has been achieved. This information, along with our prior work<sup>3,4</sup> will aid us in future studies of device technology.

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