

Degradation mechanism of the complementary electrochromic devices with WO₃ and NiO thin films fabricated by RF sputtering deposition

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WO₃ and NiO thin films for electrochromic devices were fabricated by a radio frequency (RF) sputtering deposition method. These thin films were used as working and counter electrodes, respectively. We investigated the performance degradation phenomenon and established the degradation mechanism for both WO₃ and NiO thin films. Based on the long-term cycling tests, the transmittance variation (ΔT) was observed to depend on the cycling number. The electrochromic properties of the full cell with WO₃ and NiO thin films degraded significantly as the cycle number increased. The ΔT increased in the early stages and showed the highest value (25%) at the 200th cycle before gradually decreasing and becoming saturated at the 800th cycle with the lowest value of 5%. Interestingly, while WO₃ thin films showed gradual degradation, NiO thin films were delaminated after 700 cycles, which led to an abrupt degradation in performance. The degradation of WO₃ and NiO thin films is mostly caused by dissolution by H₂O. While WO₃ is directly attacked by H₂O, NiO is chemically converted into Ni(OH)₂, which then converts to NiOOH through an electrochromic reaction during the cycle test; NiOOH is easily dissolved in H₂O.

Key words: Tungsten trioxide, Nickel oxide, Electrochromism, RF sputtering, Degradation mechanism, Thin films.

Introduction

Electrochromic devices have been widely investigated due to their potential applications in smart windows, automobiles, and architectural glazing for energy savings [1-3]. Electrochromism refers to the persistent and reversible change of optical properties caused by an applied voltage pulse. Electrochromic devices are related to a reversible coloration/bleaching process that is accomplished via the simultaneous insertion/extraction of both ions and electrons due to applied voltage. Many transition metal oxides based on W, Ni, Ir, V, Ti, Co, and Mo have been used as electrochromic materials. The coloration of an electrochromic film depends on the materials and the applied electrical field. WO₃, MoO₃, and V₂O₅ become colored under a cathodic electrical field, while NiO_x and IrO_x become colored under an anodic electrical field [4-9].

Electrochromic systems are typically composed of several layers, including an electrochromic layer, ion storage layer, transparent electrode layer, and electrolyte (liquid or solid). Electrochromic systems can be subdivided into three types. The first type is the half system, which has a structure composed of an electrode, electrochromic layer, electrolyte, and electrode. The half system works by receiving ions from the electrolyte. The second type is a full cell, which has an ion storage layer, electrochromic

layer, electrolyte layer, and electrodes. The ion storage layer can store only ions and retains a transparent state. Finally, the complementary system is composed of two electrochromic layers, an electrolyte layer, and electrodes. It is coloration-efficient because the cathodic and anodic electrochromic layers are simultaneously operated, as shown in Fig. 1. WO₃ and NiO are known to be suitable materials for a complementary electrochromic system [10].

Cyclability is the most important of the electrochromic properties. Many researchers have studied degradation mechanisms in attempts to improve the cyclability of electrochromic systems. Previously, degradation mechanisms have been reported in terms of ion accumulation, adhesion, and corrosion in half systems [11-14]. In this study, we investigated the performance degradation phenomenon and established the degradation mechanism for both WO₃ and NiO thin films in a complementary electrochromic system by investigating the dissolution process.

Experimental Procedure

WO₃ and NiO thin films were deposited by radio frequency (RF) sputtering deposition with WO₃ and NiO targets (120 × 550 mm², >99.95%), respectively. Indium tin oxide (ITO)-coated glass, with a sheet resistance of 10 Ω/□ and dimensions of 370 × 5470 mm², was selected as a substrate. Prior to deposition, a pre-sputtering process with only argon gas was carried out in order to eliminate contaminants from the target. The distance between the ITO-glass and the target was 16 mm. The substrate was held at room temperature

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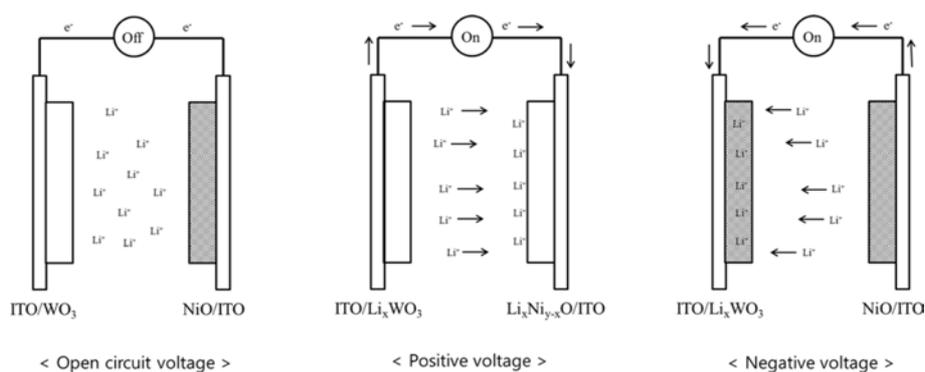


Fig. 1. Schematic illustration of the operation of a complementary electrochromic system.

Table 1. Deposition conditions of the RF sputtering method for WO₃ and NiO thin film fabrication.

Target	RF power (W)	Working pressure ($\times 10^{-3}$ Torr)	Gas atmosphere		Scan rate (mm/s)	Scan count (count)
			Ar (sccm)	O ₂ (sccm)		
WO ₃	800	15	90	10	2.8	24
NiO	800	15	90	10	5.6	4

during the deposition. The applied power, working pressure, gas atmosphere, scan rate, and scan count are shown in Table 1. By controlling the scan rate and scan count, the thicknesses of the WO₃ and NiO thin films were kept constant at about 100 and 50 nm, respectively.

The deposited WO₃ and NiO thin films were cut to $2 \times 3 \text{ mm}^2$ in order to evaluate the electrochromic performance. WO₃ and NiO thin films were used as electrodes in electrochromic devices and spaced out at a distance of about 1 cm in an electrolyte of 1 M LiClO₄ in propylene carbonate (PC). In addition to the electrochromic performance tests with a He-Ne laser (632.8 nm), transmittance measurements were carried out with a DC power of $\pm 2 \text{ V}$. Field emission scanning electron microscopy (FE-SEM, S-4800, Hitachi) and atomic force microscopy (AFM, Bruker) were performed to compare the morphology and thickness of WO₃ and NiO thin films before and after the transmittance measurements. The AFM data scales were fixed at 200 nm and 50 nm for WO₃ and NiO, respectively. An inductively coupled plasma mass spectrometer (ICP-MS, Agilent 7500a, Agilent) was used to quantitatively analyze the content of the dissolved or delaminated WO₃ and NiO after transmittance measurements.

Results and Discussion

Fig. 2 shows the transmittance values and transmittance variation (ΔT) under $\pm 2 \text{ V}$ of continuous DC power over a period of approximately 24 hrs. The ΔT is the difference in the transmittances of the film in the bleached (T_{bleached}) and colored (T_{colored}) states. Based on the variation of the ΔT value, the degradation

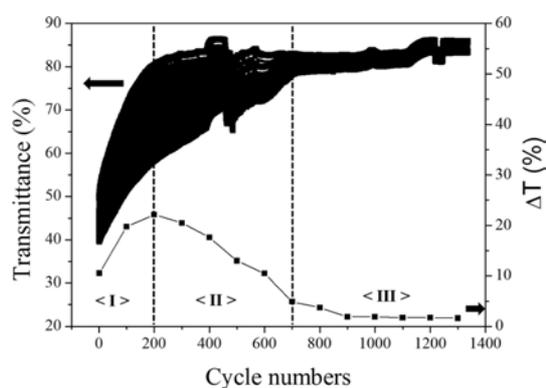


Fig. 2. Transmittance and ΔT variation in the WO₃/NiO complementary electrochromic system as a function of cycle number.

phenomenon can be divided into three steps. Before the cycle test, the transmittance of the electrochromic system was measured to be about 37% because of the dark brown color of the as-deposited NiO thin film. The electrochromic system gradually became transparent because the bleached transmittance (T_{bleached}) of the NiO thin film increased via the continuous electrochromic reaction. Consequently, ΔT increased up to 200 cycles; this is indexed as Step I. In Step I, the electrochromic reaction was accelerated by the conversion of NiO to Ni(OH)₂, which subsequently converts into NiOOH ($\text{NiO} + \text{H}_2\text{O} \rightarrow \text{Ni(OH)}_2 \text{ (bleached)} \leftrightarrow \text{NiOOH} \text{ (colored)} + \text{H}^+ + \text{e}^-$) [14]. This conversion step depends on the cycle number. The thickness of the electrochromic layer is the most important factor that determines the electrochromic properties because the transmittance variation depends on the thickness of the electrochromic layer. The thicker is the electrochromic layer, the larger is the number of ions that can be stored. The ΔT declines from 25% to 5% in Step II. This means that the thickness of the WO₃ and/or NiO layers was decreased. The degradation phenomenon terminated at about 700 cycles, after which ΔT was constant at 5%; this is indexed as Step III. The important point of Step III is that the electrochromic system shows a high transmittance state. After 700 cycles, the bleached transmittance (T_{bleached}) remained

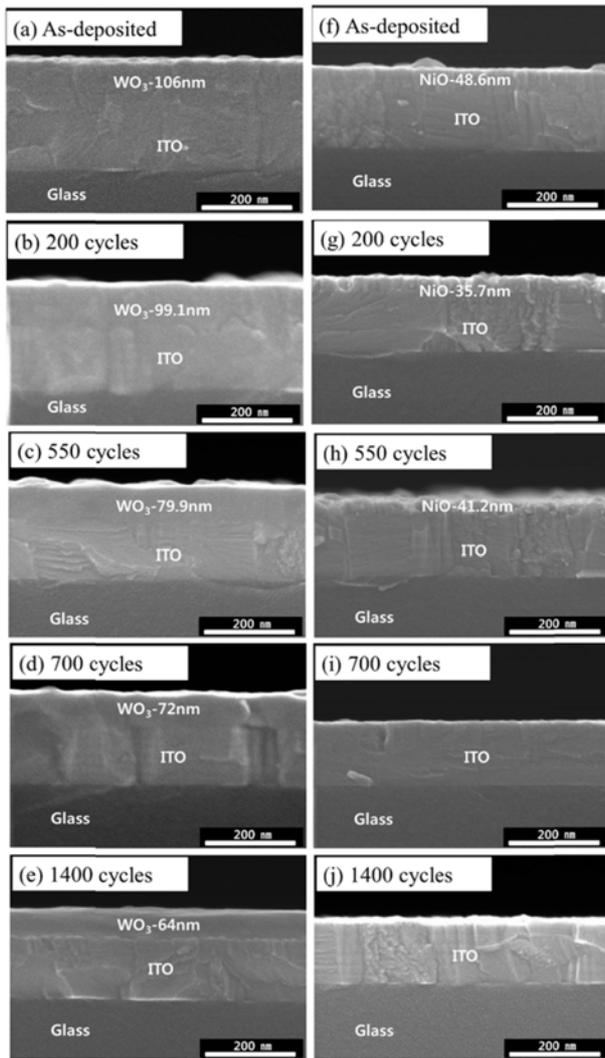


Fig. 3. Cross-sectional FE-SEM images of the WO₃ and NiO thin films after transmittance measurements for various cycle numbers ((a)-(e): WO₃ and (f)-(j): NiO).

high because the NiO thin film lost its original dark brown color. This indicates that the NiO film could no longer act as an electrochromic layer. Usually, the degradation phenomenon of electrochromic devices is caused by both irreversible reactions and mechanical defects. In this study, the irreversible reactions were caused by NiO conversion. Alternatively, the WO₃ thin film was more greatly affected by mechanical defects than by the irreversible reaction.

The dissolution test for the WO₃ and NiO thin films was carried out in order to understand the degradation mechanism. When the WO₃ and NiO thin films were dissolved into the electrolyte, the thickness of the WO₃ and NiO layers changed due to the dissolution. The thickness variation of the WO₃ and NiO thin films after the cycle test was investigated by FE-SEM, as shown in Fig. 3. The thickness variation corresponds to the variation of ΔT , as shown in Fig. 2. The thicknesses of

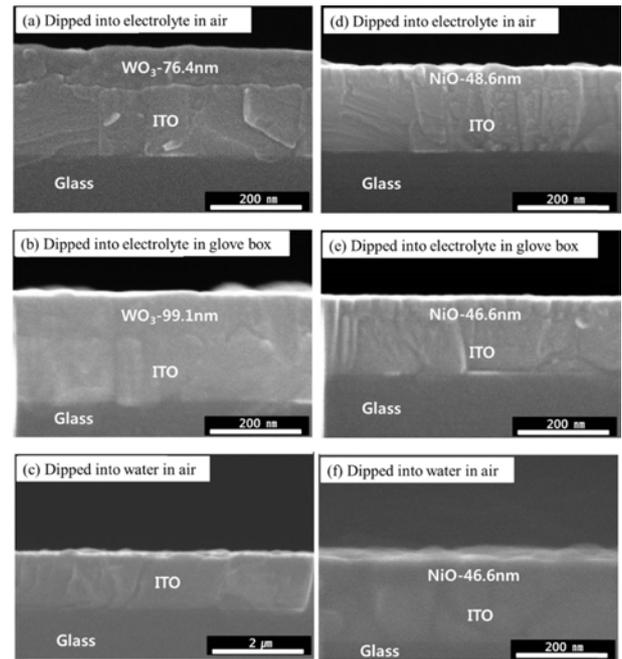


Fig. 4. Cross-sectional FE-SEM images of the WO₃ and NiO thin films before and after the dissolution test.

the as-deposited WO₃ and NiO thin films were measured to be 106 and 48.6 nm, respectively. As the cycle number was increased, the thickness of the WO₃ thin film gradually decreased. Additionally, the NiO thin film disappeared completely after 700 cycles. From this result, it can be determined that the WO₃ thin film was dissolved by the electrolyte, and the NiO thin film was delaminated due to the conversion of NiO into NiOOH, which was caused by the recursive electrochromic reaction.

Fig. 4 shows the morphology change of the WO₃ and NiO thin films after the dissolution test under various conditions. As shown in Figs. 4(a) and (d), the thickness of the WO₃ layer decreased from 106 nm to 76.4 nm after the dissolution test in the electrolyte (1 M LiClO₄ in propylene carbonate) in air for 24 hrs without the electrochromic reaction. The decrease in thickness of the WO₃ thin film was much higher than that in the NiO thin film during a similar dissolution test. Alternatively, there was no change in the thicknesses of the WO₃ and NiO layers during the dissolution test in the electrolyte in a glove box for 24 hrs, as shown in Figs. 4(b) and (e). Interestingly, after the dissolution test in D.I. water in air for 24 hrs, the WO₃ layer disappeared completely, but the NiO layer maintained its thickness, as shown in Figs. 4(c) and (f). Based on these results, it can be inferred that water in both the electrolyte and air can strongly affect the degradation phenomenon of the WO₃ layer in electrochromic devices. While NiO itself is not dissolved in water, the NiOOH that is converted from NiO during the electrochromic reaction can be dissolved in water [14]. When NiO was exposed to water, there was

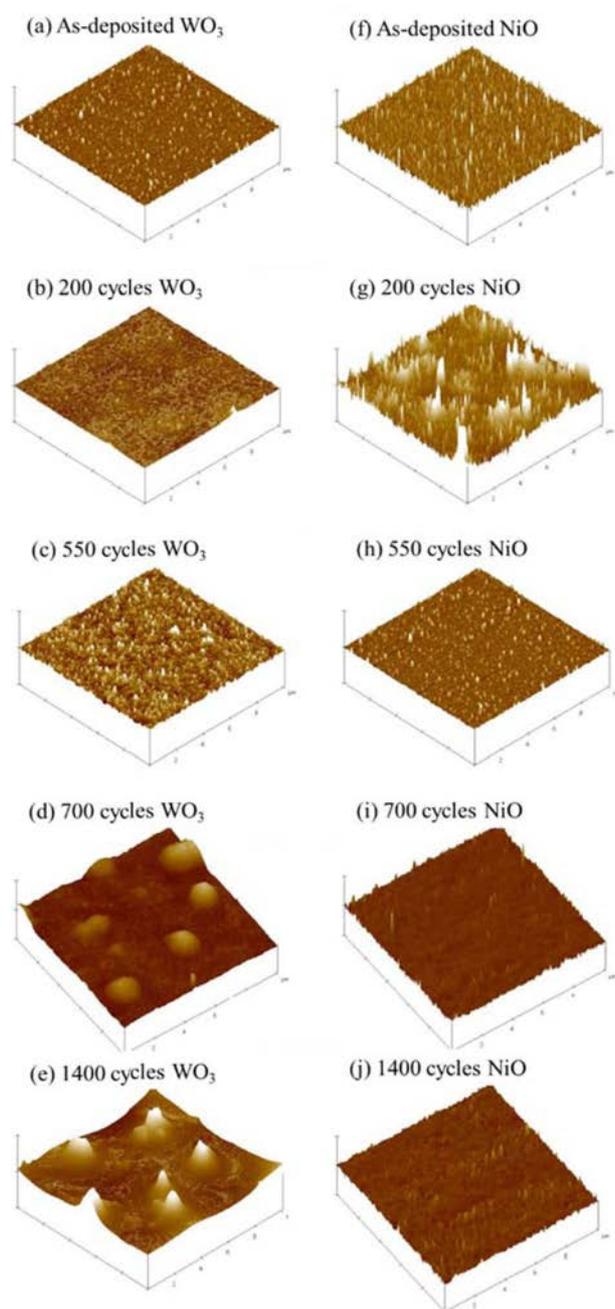


Fig. 5. AFM images of the WO_3 and NiO thin films after transmittance measurements for various cycle numbers.

no change in the morphology, as shown in Fig. 4(d). Under the electrochromic reaction, the NiO layer delaminated due to the conversion and consequent dissolution of NiOOH , as shown in Figs. 3(i) and (j).

The surface morphologies of both WO_3 and NiO thin films are shown in Fig. 5. In order to observe the surface morphology of the films, the z-axes of the WO_3 and NiO films were fixed at 200 nm and 50 nm, respectively. The surface roughness of the WO_3 thin film increased as the cycle number increased. After 200 cycles, the WO_3 thin film was flatter than the as-deposited WO_3 thin film. It appears that WO_3 was

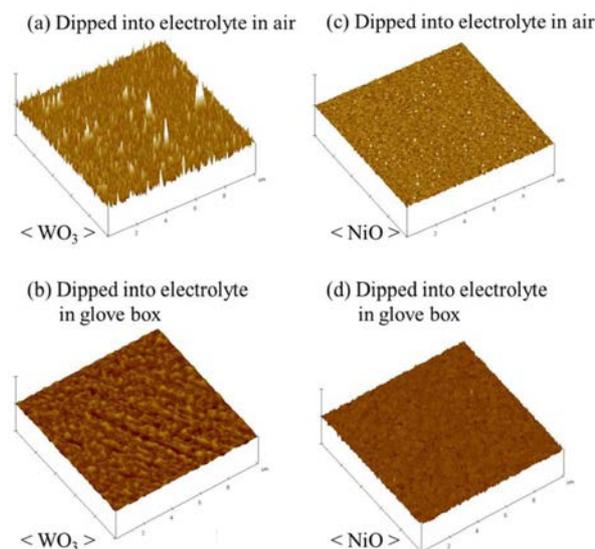


Fig. 6. AFM images of the WO_3 and NiO thin films before and after the dissolution test.

preferentially dissolved from the prominent area. After 700 cycles, the surface of the WO_3 thin film gradually roughened, as shown in Figs. 5(c-e). Alternatively, the surface of the NiO thin film was smooth after 700 cycles. The NiO samples changed dramatically because the NiO layer was no longer present after 700 cycles, as shown in Fig. 5.

Figure 6 shows the surfaces of WO_3 and NiO thin films after the dissolution test without chemical reaction. The surface morphologies of WO_3 and NiO thin films after the dissolution test experienced less change than those after the cycle test, as shown in Fig. 5. Although the thickness of WO_3 was maintained after the dissolution test in the Ar -filled glove box (Fig. 4), the surface morphology of WO_3 was changed. This might be due to the lithium salt-containing crystal water in the electrolyte. However, there was no significant morphological change, which is in accordance with the results shown in Fig. 4. The root mean square (RMS) values, which indicate the degree of roughness measured via AFM, are listed in Table 2. There are two reasons for the increase in surface roughness. The first reason is due to the structural deformation of the film itself. The initial amorphous film, which is very unstable, deformed via the ionic effect during intercalation/de-intercalation of Li -ions. The second reason is due to the dissolution and delamination caused by the chemical reaction.

ICP-MS measurements were carried out to quantitatively analyze the amount of dissolved WO_3 and NiO ; these results are shown in Table 3. The amounts of W and Ni dissolved into the electrolyte during the dissolution test increased with longer dipping time. After the dissolution test in D.I. water, relatively large amounts of W and Ni were dissolved (compared to the amounts dissolved in the electrolyte). When the WO_3 samples were dipped into D.I.

Table 2. Root mean square (RMS) values of the WO₃ and NiO thin films after transmittance measurements for various cycle numbers and after the dissolution test.

Sample	RMS (nm)						
	As-deposited	200 cycles	550 cycles	700 cycles	1400 cycles	Dipped in air for 24 h	Dipped in glove box for 24 h
WO ₃	4.568	2.291	6.273	16.799	24.514	2.476	4.187
NiO	2.496	6.065	8.301	2.434	2.139	3.722	1.507

Table 3. ICP-MS data after the dissolution and cycle tests.

Solution	Atmosphere	Time (h)	W (ppb)		Ni (ppb)	
			After dissolution test	After cycle test	After dissolution test	After cycle test
1 M LiClO ₄ in PC	Air	24	4	34	12	299
1 M LiClO ₄ in PC	Air	48	15	34	18	350
D.I. water	Air	24	7134	-	192	-
1 M LiClO ₄ in PC	Argon	24	2	-	6	-

water for 24 hrs, a large amount of W was detected. The amount of detected elements from the WO₃ and NiO samples was decreased by 50% in the H₂O-free conditions. For 100% water, all of the WO₃ layers were dissolved. However, the WO₃ layer was partially soluble in the electrolyte containing a small amount of water. This means that the degree of dissolution of WO₃ depends on the amount of water in the system. In the NiO film, NiO itself was not dissolved by water during the dissolution test; however, NiO was critically affected by the conversion reactions that occurred during the electrochromic process.

Conclusions

Both WO₃ and NiO thin films in the complementary electrochromic system showed degradation as the cycle number increased. The thicknesses of the WO₃ and NiO thin films depended on the number of cycles. While the WO₃ film gradually decreased with cycle number, the NiO film became delaminated after 700 cycles. The roughness of both WO₃ and NiO thin films also increased with cycling. In the NiO thin film, however, the film surface became smoother after 700 cycles due to delamination. The ICP-MS data clearly showed that both W and Ni were dissolved by H₂O; this dissolution phenomenon can be accelerated by electrochromic cycling. Consequently, the degradation of WO₃ thin films was mainly caused by the dissolution of W, which is attacked by H₂O. In the NiO thin film, the cycling effect (accompanied by chemical conversion and partial dissolution) is the critical factor that influences degradation.

Acknowledgments

This research was financially supported by the Ministry of Knowledge Economy (MKE) and Korea Institute for Advancement of Technology (KIAT) through the Research and Development for Regional Industry.

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