Electrochromic properties of NiOOH thin films prepared by reactive sputtering in an H₂O atmosphere in various aqueous electrolytes

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Abstract

Nickel oxyhydroxide (NiOOH) thin films were prepared by reactive sputtering using H_2O as a reactive gas, and the electrochromic (EC) properties of these thin films were investigated in alkaline, neutral, and acidic aqueous electrolyte solutions. A stable EC cycling of up to 100 cycles was obtained for the NiOOH thin films in electrolyte solutions with a wide pH range of from 4.1 to 13.5. However, the EC cycling degraded drastically after several tens of cycles in an electrolyte with pH=2.0. In the stable pH region, the NiOOH films exhibited a large transmittance change from approximately 30 to 90%, although the response speed slowed with decreasing pH of the electrolytes.

Keywords

Nickel oxyhydroxide thin film, electrochromic, aqueous electrolyte solution

1. Introduction

The optical properties of electrochromic (EC) materials [1,2] change (darken or lighten) by the application of a small reversible dc voltage, and EC devices are being developed in applications for "smart" energy efficient windows, anti-glare automobile rearview mirrors, sunroofs, and visors [3-8]. A typical EC device consists of a stack of thin films having an EC layer, an ion-conducting layer and an ion-storage layer sandwiched between two transparent conducting oxide layers. A complementary EC device uses a cathodically coloring film (such as W oxide) as an EC layer and an anodically coloring film (such as Ni oxide) as an ion storage layer to improve EC coloration efficiency and to obtain larger color changes with smaller current densities [3,5,7,8].

One of the problems associated with combining W oxide and Ni oxide films is their chemical incompatibility. W oxide is relatively stable in an acidic environment but dissolves in a basic environment. On the other hand, according to the Pourbaix diagram, Ni oxide is relatively stable in a basic environment but is unstable in an acidic enviornment [9]. In order to solve the problem of the chemical incompatibility of W oxide and Ni oxide, non-aqueous or solid electrolytes have been used [3,5,8], and a protective film has also been applied to the films in aqueous electrolytes [10]. Therefore, the EC properties of Ni oxide films in aqueous electrolytes have been generally investigated in alkaline solutions (such as KOH and NaOH) [11-19]. However, there have been few reports on the effects of the electrolytes [20,21]. Lee et $al.$ investigated on the EC properties of NiO/Ta_2O_5 nano-composites using pH neutral KCl aqueous solutions [22], and in a previous study, we reported high EC coloration efficiencies of approximately 30 cm^2/C for sputtered Ni oxide films in dilute acidic solutions [23-25].

Another problem with Ni oxide is that it is necessary to carry out several tens or even hundreds of coloring bleaching cycles before attaining stable EC properties, which is referred to as an activation period. During the activation period, the surface of the NiO grains is covered with a Ni hydroxide layer, which colors and bleaches reversibly [26]. From the viewpoint of productivity, direct formation of Ni hydroxide films by dry processing technologies is preferable. Therefore, in a previous study, NiOOH thin films were deposited by reactive sputtering using H_2O as a reactive gas [27,28]. The NiOOH films showed stable EC cycling from the first cycle in 1 M KOH aqueous electrolyte solution without the activation period.

In the present study, we examined the effects of the pH of aqueous electrolyte solutions on the EC performance of the NiOOH thin films and consider the possibility of using neutral and acidic electrolytes.

2. Experimental

NiOOH thin films with a thickness of 100 nm were deposited on glass substrates coated with a transparent conducting layer of indium tin oxide (ITO) for electrochemical and EC characterizations. These films were deposited from a Ni target (diameter: 2 in., purity: 99.9%) which was sputtered reactively in an H_2O atmosphere using a radio-frequency (RF) magnetron sputtering system as shown in Fig. 1. The H_2O gas flow rate, sputtering gas pressure, RF power and substrate temperature were standardized to 1 cubic centimeter per minute (ccm), 6.7 Pa, 50 W and 10°C, respectively. Plasma emission spectra were investigated in order to determine the active species that contribute to the formation of

the films. The transmittance of the ITO coated glass substrate was higher than 80 % in a visible region and the resistivity of the ITO film was 200–300 $\mu\Omega\cdot$cm.

Cyclic voltammetry (CV) and *in-situ* optical transmission measurements were carried out using Ag/AgCl and Pt as reference and counter electrodes, respectively. Here, 0.5 M KOH, 1 M KCl, and mixed solutions of KCl + H_2SO_4 and KCl + KOH were used as aqueous electrolytes. In order to change the pH of the solutions, the concentrations of H_2SO_4 and KOH in the KCl + H_2SO_4 and KCl + KOH mixed solutions were varied, and KCl was added in order to maintain a constant conductivity of the electrolytes of approximately 10 S/m. Cyclic voltammetry measurements were carried out with a voltage scan rate of 20 mV/sec. The upper and lower limits of the potential scan range were changed as a function of the pH of the electrolyte solutions as shown in Fig. 2 corresponding to the Nernst equation [21]. The transferred charge density was calculated by integrating the current density of the CV curves. EC coloration efficiency (η) was calculated using the following equation:

$$\eta = \Delta OD / \Delta Q,$$

where ΔOD is the change in optical density ($\Delta OD = \log_{10}(T_b/T_c)$, where T_b and T_c are bleached and colored transmittances) and ΔQ is the transferred charge density. *In situ* optical modulation was measured using a multi-channel charge coupled device (CCD) detector. The total transmittance of the samples with a NiOOH/ITO/glass structure was calculated using a quartz glass cell filled with the aqueous electrolytes as the reference sample.

3. Results and discussion

The plasma emission spectrum during sputter deposition of the NiOOH films is shown in Fig. 3. Emission peaks due to H and O atoms and OH radicals are clearly observed, and these active species are thought to be incorporated into the films. The formation of NiOOH films was confirmed by electrical and optical measurements and Fourier transform infrared spectroscopy (FTIR) as described in a previous paper [27].
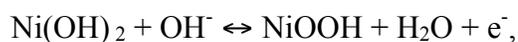
The electrochromic properties of the NiOOH films in various electrolyte solutions were investigated by cyclic voltammetry, and the CV curves in various electrolyte solutions are shown in Fig. 4. The shapes of the CV curves in alkaline and acidic solutions (pH = 13.5 and 2.0) are triangular, whereas those in nearly neutral and dilute acidic solutions (pH = 6.3 and 4.1) are rectangular. No remarkable change of the CV curves was observed up to 100 cycles except for the sample cycled in an acidic solution of pH = 2.0, which exhibited a drastic decrease in current density after several tens of cycles due to the dissolution of the NiOOH film. The changes in transferred charge density and EC coloration efficiency at a wavelength of 600 nm are shown as functions of pH of electrolyte solutions in Fig. 5. The coloration efficiency was found to be approximately independent of the pH, and the values of approximately 30 cm^2/C are comparable to the values reported for Ni oxide films in aqueous electrolyte solutions [12,14,16-19,21,24]. The largest transferred charge density of approximately 14 mC/cm^2 was obtained in alkaline solutions with pH=13.5. However, this value decreases with decreasing pH of the electrolyte solutions and becomes 3 to 5 mC/cm^2 in acidic and nearly neutral electrolyte solutions.

Next, the transmittance changes of the NiOOH thin films were investigated under a constant applied voltage in various electrolyte solutions. Figures 6(a) and 6(c) show the

bleached and colored transmittance spectra of the NiOOH films in electrolytes with pH=13.5 and 4.1, respectively. No remarkable difference in the spectra was observed in the alkaline and acidic electrolyte solutions. The similarity of the transmittance spectra and EC coloration efficiency of the NiOOH films in various electrolyte solutions indicates that valance change of Ni ions, Ni^{2+} (bleached state) $\leftrightarrow$ Ni^{3+} (colored state), is the underlying mechanism for the optical modulations of the NiOOH films in the entire pH range of the electrolyte solutions. Figures 6(b) and 6(d) shows the transmittance change at a wavelength of 600 nm under constant applied voltages. Large transmittance changes of from approximately 30 to 90% were obtained in both the alkaline electrolyte with pH=13.5 and the dilute acidic electrolyte with pH=4.1.

The coloring and bleaching response times were defined as the time required to obtain a 90% transmittance change from the fully colored state to the fully bleached state, and vice versa, (inset in Fig. 6(b)), and the response times are shown in Fig. 7 as functions of the pH value of the electrolyte solutions. The coloring and bleaching times are found to increase with decreasing pH in the alkaline region. The longer response times in the neutral and acidic region correspond well to the decrease in the transferred charge density during the CV measurement, as shown in Fig. 5. The rate of ion diffusion in the hydroxide layer is thought to have decreased in the neutral and acidic region, and the EC reaction was incomplete under the relatively high voltage scan rate of 20 mV/s. In the neutral and acidic regions, the coloring time tends to decrease slightly with decreasing pH, and the bleaching time becomes approximately constant. The shorter response time for bleaching, as compared to that for coloring is thought to be caused by the lower electron conductivity of the Ni hydroxide layer in the bleached state.

The reaction mechanisms for Ni oxide films remain unclear [7, 20,21], and the following reaction schemes have been proposed:

$Ni(OH)_2 \leftrightarrow NiOOH + H^+ + e^-$,

$NiO + Ni(OH)_2 \leftrightarrow Ni_2O_3 + 2H^+ + 2e^-$,

$Ni(OH)_2 + OH^- \leftrightarrow NiOOH + H_2O + e^-$,

$NiO + OH^- \leftrightarrow NiOOH + e^-$.

Although the ion species that contribute to the coloration of the Ni oxide films cannot be derived from this experiment, the importance of the concentration of OH^- ions is clearly demonstrated. The increase in the reaction rate for NiO_x films has also been reported by Wruck *et al.* [12] using KOH + KCl aqueous solutions. The complex behavior of the transferred charge density and the response times in neutral and acidic electrolytes suggests that concentrations of H^+ and K^+ ions should also be taken into consideration for the EC reaction rate of Ni oxide.

4. Conclusions

A stable EC cycling of up to 100 cycles was obtained for the NiOOH thin films in electrolyte solutions with a wide pH range of from 4.1 to 13.5. Although the response speed slowed in acidic and neutral solutions, large transmittance changes were obtained in the stable pH region. The NiOOH films are expected to be usable in various aqueous electrolyte solutions except for low-pH acidic solutions.

Acknowledgement

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10

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Figure captions

Fig. 1. Schematic diagram of the sputtering system used in the present study.

Fig. 2. Potential scan rage as a function of pH of the electrolyte solutions used in the present study.

Fig. 3. Plasma emission spectrum during sputtering using H_2O gas.

Fig. 4. Cyclic voltammograms of the NiOOH films measured in various electrolyte solutions. The voltage scan rate was 20 mV/s.

Fig. 5. Transferred charge density and EC coloration efficiency as functions of pH of the electrolyte solution.

Fig. 6. Transmittance spectra of the NiOOH thin films in bleached and colored states, and transmittance change during the application of a constant voltage in electrolytes with pH=13.5 and 4.1. The response time is defined in the inset in of (b).

Fig. 7. Bleaching and coloring response times as functions of pH of the electrolyte solutions.

Cooling system (10°C)

Flow meter

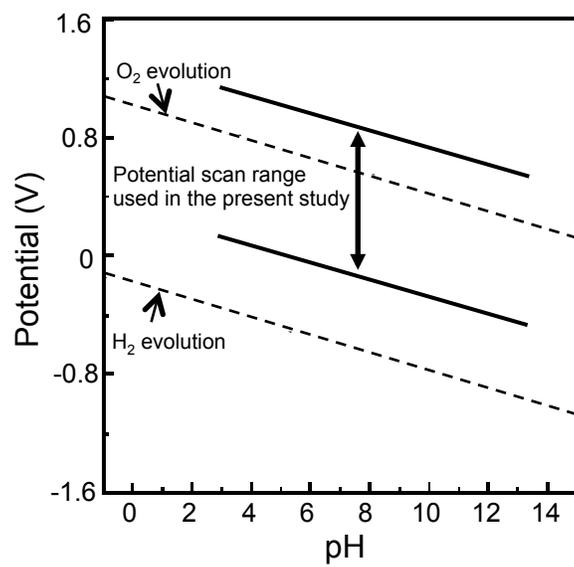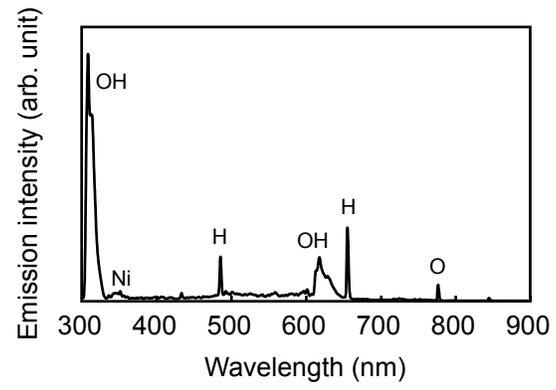Substrate

Ni target

Vacuum pump
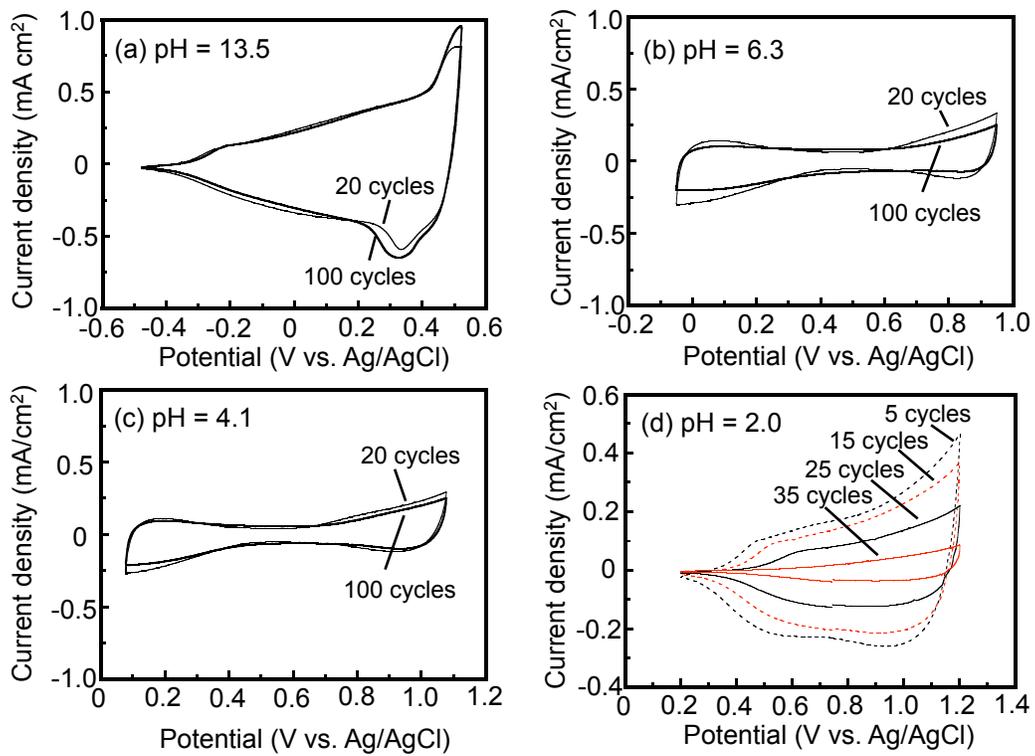
Water tank

Sputtering chamber

Water bath (20 °C)

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7