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Electrochromism of Niobium Oxide Thin Films Prepared by the Sol-Gel Process

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ABSTRACT

Thin layers of niobium oxide (NbO_x) were accumulated by the sol-gel process, with the sol of NbO_x in ethanol prepared by partial hydrolysis of commercial niobium(V) ethoxide, on glass plates coated with transparent conducting tin oxide. Characterization by x-ray diffraction, differential thermal analysis, and thermogravimetry revealed that the as-prepared film, consisting of fully hydrated amorphous niobium(V) oxide, undergoes dehydration into the partially hydrated form and, finally, crystalline niobium(V) oxide (Nb_2O_5) by calcination at the temperature up to 873 K. The films exhibited electrochromic (EC) properties; the reversible color change was observed between colorless and brown-black by alternating anodic and cathodic polarizations, respectively. Among the films used in this study the crystalline Nb_2O_5 film showed the best EC properties and its spectral change, durability for repeated coloration-decoloration cycles, and retentivity of colored states, *i.e.*, memory characteristics under open-circuit conditions were investigated in detail.

Transition metal oxides, *e.g.*, oxides of tungsten (WO_3), molybdenum (MoO_3), and vanadium (V_2O_5), have been extensively investigated as electrochromic devices in the form of a thin film adhering to a conducting substrate.¹ Among them, niobium oxide (NbO_x) is also expected to show electrochromism, and several studies on NbO_x thin films prepared by thermal oxidation,²⁻⁵ anodization,⁶ sputtering,⁷ vacuum evaporation,⁸ and the sol-gel process⁹ have been reported.

Previous work in this laboratory has shown electrochemical response of WO_3 ,¹⁰ iron(III) oxide (Fe_2O_3),¹¹ and titanium(IV) oxide (TiO_2)¹² films prepared by sol-gel process.¹³ In comparison with the sputtering or vacuum evaporation technique, the sol-gel process is of advantage for preparation without using specialized instruments such as a vacuum chamber. The preparation of NbO_x thin film by thermal oxidation and anodization requires the niobium metal plates of desired size and shape of devices. This might be a limitation to these preparation processes. However, the sol-gel process has no such limitation; it is possible essentially to produce the film on the given substrate material in any size and shape. This paper deals with the preparation of NbO_x thin films by the sol-gel process and the characterization of their properties by x-ray diffraction (XRD), differential thermal analysis (DTA), and thermogravimetry (TG). Their electrochemical (EC) properties are discussed and correlated with the structure.

Experimental

Sol of NbO_x was prepared by partial hydrolysis of niobium(V) ethoxide [$\text{Nb}(\text{OEt})_5$] (Kanto Chemicals) with concentrated hydrochloric acid (HCl; Wako Pure Chemical Industries). Griesmar and co-workers have reported the preparation of clear sol and monolithic gel of NbO_x by the hydrolysis of niobium(V) pentoxide [$\text{Nb}(\text{OPn})_5$] in the presence of acetic acid.¹⁴ As shown below, however, the addition of HCl also enables the preparation of clear NbO_x sol. A portion of $\text{Nb}(\text{OEt})_5$ (0.036 moles) was dissolved in ethanol (Wako, 99.5%, water 0.4%; 1.7 moles) at room temperature and cooled to 273.5 K in an ice bath. To the solution was slowly added under stirring a mixture of ethanol (0.98 mol) and HCl (0.038 mol). Additional stirring overnight at room temperature led to a slightly yellow clear sol containing 0.21 mol dm^{-3} of NbO_x . Glass substrates coated with transparent conducting tin oxide (NESA, $22.3 \Omega/\square$) were supplied from Nippon Sheet Glass Company Limited in a cleaned state and used just after removal of dust by the blowing of dry air. The plates were dipped in and drawn from the NbO_x sol at a constant rate of 0.6 mm s^{-1} . After gelation at room temperature for 10 min, the coated substrates were calcined at 423 K for 5 min in an electric furnace. Further calcination at the higher temperature (T_c) was performed for 2 h for every ten-layer accumulation. Hereafter, the entry of NbO_x films is made with the number

of the layer and T_c , *e.g.*, 20/733 refers to the film consisting of 20 layers calcined at 733 K.

Electrochemical measurements were performed with an HA-301 potentiostat/galvanostat, an HB-104 function generator, and an HF-202D coulometer (Hokuto Denko). A Pyrex cell with flanges in opposite sides was used. An NbO_x -coated substrate and a Pyrex glass plate were fixed on the flanges in parallel each other with fluorinated rubber (Vyton) gaskets. Through these two parallel plates passed the light beam for optical absorption measurements (a Shimadzu UV-200S spectrophotometer). A plane platinum counterelectrode and an Ag/AgCl reference electrode were fixed in the positions outside the light beam. Electrolyte solutions, 1.0 or 9.0 mol dm^{-3} aqueous formic acid solution or 0.5 mol dm^{-3} sulfuric acid in the cell were deaerated by bubbling nitrogen for at least 20 min before and during the measurements.

X-ray diffraction patterns of NbO_x films on NESA glass substrate were recorded on a Mac Science MXP18 diffrac-

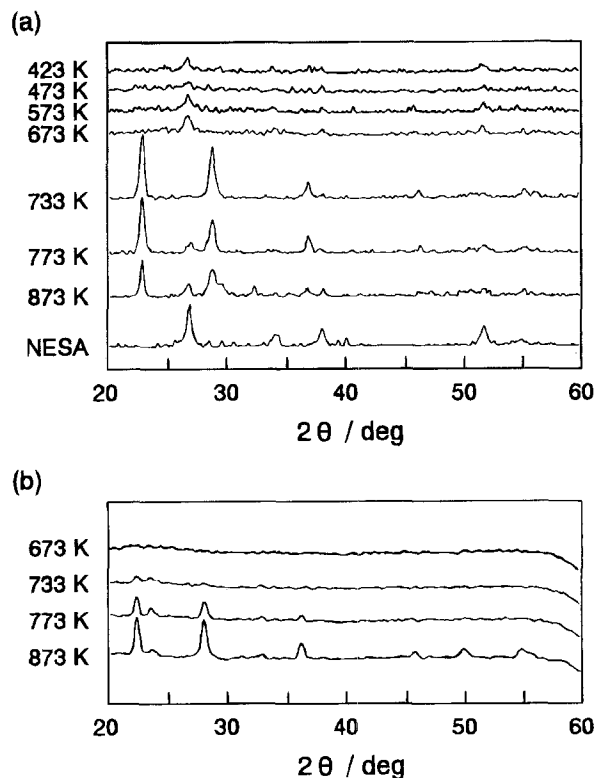


Fig. 1. Parts of XRD patterns of NbO_x in the form of (a) films and (b) powders.

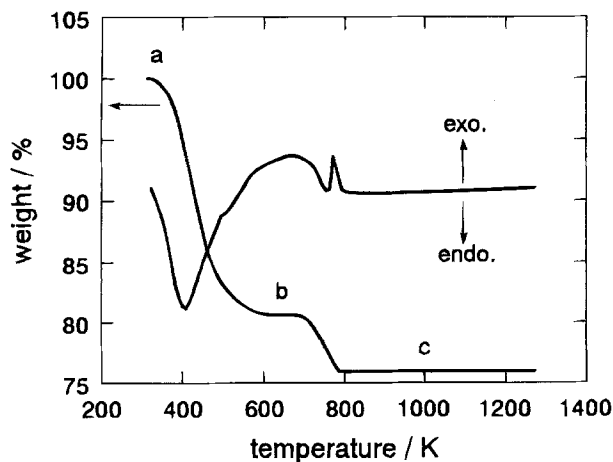


Fig. 2. DTA and TG of NbO_x powder.

tometer (Cu K_α ; 50 kV, 200 mA) with a fixed incident angle of x-ray to the films at 0.3 deg.¹⁵ For comparison, NbO_x powder was prepared by gelation of the sol at ambient temperature, dried at 383 K, and calcined in a furnace of elevated temperature up to 1273 K at a rate of 20 deg min^{-1} . The powder XRD patterns were measured *in situ* by a Shimadzu XD-D1 diffractometer (Cu K_α ; 40 kV, 40 mA) with conventional scanning procedure. Thermogravimetry (TG) and DTA were performed in air with the temperature range of room temperature to 1273 K at a heating rate of 10 deg min^{-1} by using a ULVAC HPC-5000 equipped with an infrared image furnace.

Results and Discussion

Figure 1 shows parts of XRD patterns of NbO_x films (a) and powders (b) prepared by the gelation of NbO_x sol and subsequent heat-treatment. Only less intense peaks corresponding to the NESAs layer (2 θ : 27.0, 38.0, 52.0 deg) appeared in the pattern of films calcined at <733 K, suggesting their amorphous structure. Similar amorphous structure was observed in the case of powder. Heat-treatment at higher temperatures (≥ 733 K) led to the crystallization of NbO_x as seen for both films and powders; intense peaks (2 θ : 22.5, 28.0, 37.0 deg) are assigned to Nb_2O_5 crystallites.¹⁶ The relatively smaller intensity of the powder at 733 K may be due to the shorter duration (5 min) of heat-treatment during the *in situ* XRD measurement compared with that for films (2 h). Calcination at further elevated temperature (773 to 873 K) reduced the intensity of Nb_2O_5 peaks for the film, while it enhanced them for powder; peaks (2 θ : 46.0, 50.0, 55.0 deg) newly appeared. These facts suggest the partial decomposition of NESAs layer occurring at the higher temperature. Thus, the NbO_x layer obtained by calcination at the lower temperature consists of amorphous oxide, and of crystalline Nb_2O_5 at the higher (≥ 733 K) temperature.

Such a structural change was followed by TG and DTA of NbO_x powders (Fig. 2). On heating up to 550 K, the weight of the powdered NbO_x sample decreased to ca. 81% of the original (a), accompanied by a significant endothermic DTA peak with the maximum at ca. 400 K. The weight loss due to the elimination of water is most plausible. Subsequent heating up to 700 K induced negligible change in the weight of sample, suggesting the metastable structure of NbO_x in this temperature region (b). Further weight decrease was observed at around 750 K. Characteristic exothermic peak appeared at 780 K. Neither change in weight nor DTA shift was observed at the temperature region higher than 800 K (c). The total weight loss during the heating from room temperature to 1273 K was 24%. On the assumptions that NbO_x consists of Nb_2O_5 and that only the dehydration causes the weight loss, the composition a of $\text{Nb}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$ [or $\text{Nb}(\text{OH})_5$] and b of $\text{Nb}_2\text{O}_5 \cdot \text{H}_2\text{O}$ [or $\text{NbO}_2(\text{OH})$] account for the results in TG. At present we have no experimental results to distinguish the hydrated

oxides ($\text{Nb}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$ and $\text{Nb}_2\text{O}_5 \cdot \text{H}_2\text{O}$) from the hydroxides [$\text{Nb}(\text{OH})_5$ and $\text{NbO}_2(\text{OH})$]. The NbO_x gel prepared from $\text{Nb}(\text{OPn})_5$ ¹⁴ showed a similar, but somewhat shifted (to higher temperature), DTA curve. However, the above-mentioned double-step TG curve is a unique characteristic of NbO_x sol from $\text{Nb}(\text{OEt})_5$; sharp decrease in weight could be seen between 473 and 523 K for the gel from $\text{Nb}(\text{OPn})_5$.

On the basis of the results of XRD, TG, and DTA, the structure of NbO_x could be described as follows. The as-prepared gel (a) in a fully hydrated amorphous phase is dehydrated by the calcination at lower than 550 K into a metastable amorphous phase of partly hydrated oxide. Further dehydration into crystalline Nb_2O_5 proceeds at temperature higher than 700 K. The exothermic peak in DTA at 780 K may correspond to the accompanying amorphous-crystal transition.

The NbO_x films were almost colorless and transparent. An example is shown in Fig. 3. This spectrum was recorded in transmission mode, not in reflection mode, and therefore included the concurrent absorption by a NESAs glass substrate. The undulations seen in a whole range of spectrum are the interference pattern due to reflections of the front and back surfaces of the film. Difference in such optical characteristics due to the calcination temperature was not so marked. The films exhibited negligible change in these ultraviolet and visible range spectra by the contact with an aqueous formic acid solution (9.0 mol dm^{-3}).

Cathodic polarization in acidic electrolyte induced the change in color. The NbO_x film turned brown or black and was bleached readily by anodic polarization. As Fig. 3 shows, an almost constant increase in absorption by cathodic polarization was observed in visible to the near infrared region. Thus, the thin films of NbO_x exhibited the EC activity. Early studies^{2,17} suggested that electrochromism of Nb_2O_5 is based on simultaneous injection of cations (proton, H^+) and electrons, thereby reversible change occurs between Nb_2O_5 and $\text{H}_x\text{Nb}_2\text{O}_5$. Although the color blue in the reduced form was reported previously, a somewhat different result was obtained in the present experiments. These facts might suggest a different morphology of NbO_x films related with the method of preparation.

Although the NbO_x film exhibited the above EC properties, unrelated with T_c , the degree of coloration under given conditions of cathodic polarization depended considerably on T_c as shown in Fig. 4. The change in absorbance (ΔOD) by the cathodic polarization was monitored at 700 nm and plotted against T_c . The as-prepared film (T_c 423 K) showed larger ΔOD , which was reduced by elevating T_c up to 700 K. At $T_c > 700$ K, ΔOD was drastically enhanced to attain its maximum at 733 K, and gradually decreased by the further calcination at higher T_c . In several experiments of different potentials of cathodic polarization, similar dependences

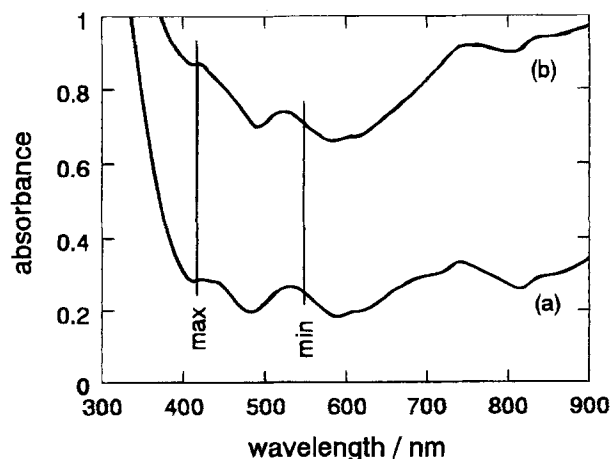


Fig. 3. Absorption spectra of NbO_x -coated NESAs glass (20/733) immersed in an aqueous formic acid solution (1.0 mol dm^{-3}), (a) before and (b) after polarization at -0.9 V.

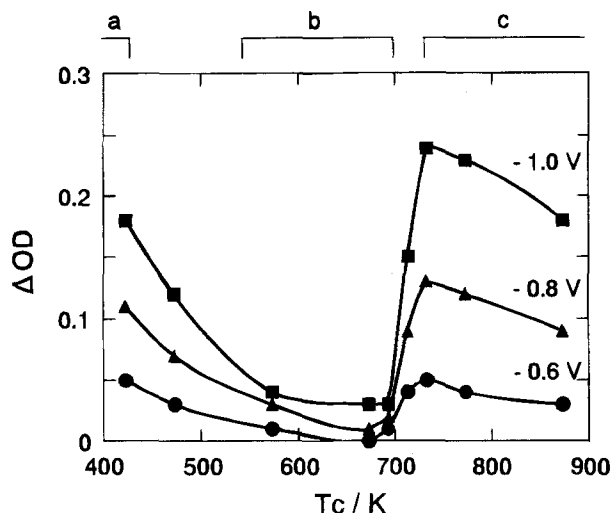


Fig. 4. Dependence on T_c of ΔOD by cathodic polarization at given potentials for 20 s in 9.0 mol dm^{-3} aqueous formic acid solution.

were observed (Fig. 4). Comparison of these T_c dependents with the presumed structure of NbO_x indicates that the fully hydrated amorphous oxide (a) showed relatively higher EC property and it was reduced by dehydration into partly hydrated form (b). Further dehydration and crystallization (c) enhanced the EC property markedly. The lower EC property of the (b) state, assigned to be $\text{Nb}_2\text{O}_5 \cdot \text{H}_2\text{O}$, should be correlated with its poor electronic and ionic conductivity.¹⁸

Figure 5 shows the variations of ΔOD , current, and potential as a function of time during the repeated potential stepping at intervals of 20 s between -0.6 and $+1.0$ V. Reversible change in ΔOD was observed, and its maximum was kept almost constant during a few tenths of cycles. A relatively large cathodic current, which induces the coloration, was seen just after the step of potential to -0.6 V and gradually decreased. Appreciable residual cathodic current flowed even at 20 s after the cathodic step. On the contrary, the decay of anodic current was rather sharp; both ΔOD and current became negligible within 5 s. This behavior of cathodic and anodic currents seems to depend on neither the potential nor the concentration and kind of electrolytes (data not shown). Figure 6 shows relationship between ΔOD and passed charge, the latter of which was

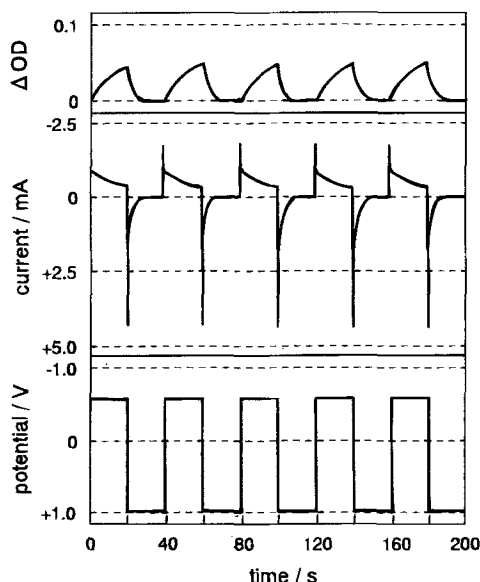


Fig. 5. Results of repeated potential stepping by every 20 s between -0.6 and $+1.0$ V of NbO_x film (10/733) immersed in 1.0 mol dm^{-3} aqueous formic acid solution.

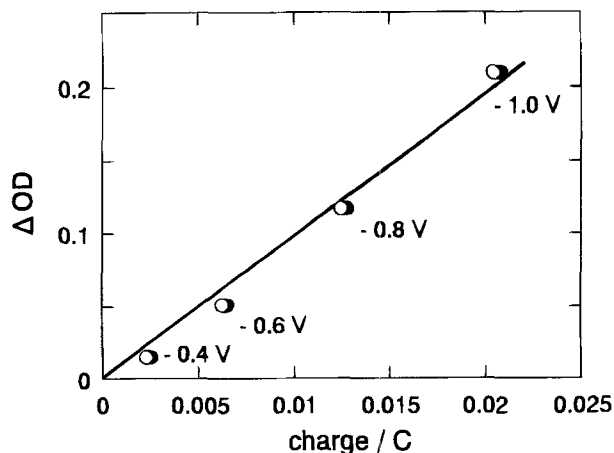


Fig. 6. Relationship between ΔOD and passed charge during coloration: (○) figures denote the potential and (● +1.0 V) bleaching processes of 10/733 film immersed in a 1.0 mol dm^{-3} aqueous formic acid solution.

calculated by integration of the current profile, for both cathodic (coloration) and anodic (bleaching) processes. The linear relation for both processes at various cathodic potential clearly shows that the EC property of the present NbO_x films is attributed to a unique reversible electrochemical reaction. From the slope of the linear plot, ΔOD per unit charge density, corresponding to efficiency of coloring, is estimated to be $38 \text{ C}^{-1} \text{ cm}^2$ (at 700 nm). This coulombic efficiency is superior to that reported for Nb_2O_5 thin film via the sol-gel process ($6 \text{ C}^{-1} \text{ cm}^2$ at 800 nm)⁹ and sputtering ($<10 \text{ C}^{-1} \text{ cm}^2$).¹⁹ However, the efficiency is ca. four times smaller than that for a WO_3 film prepared by sol-gel process ($167 \text{ C}^{-1} \text{ cm}^2$ at 800 nm).¹⁰

Stability of NbO_x films was studied in prolonged periods as shown in Fig. 7. In these experiments, the duration of anodic potential ($+1.0$ V) step was expanded to 180 s to bleach completely. In the experiment with the duration of a given cathodic potential (-1.2 V) for 40 s, the maximum ΔOD after the 104th cycle was considerably decreased

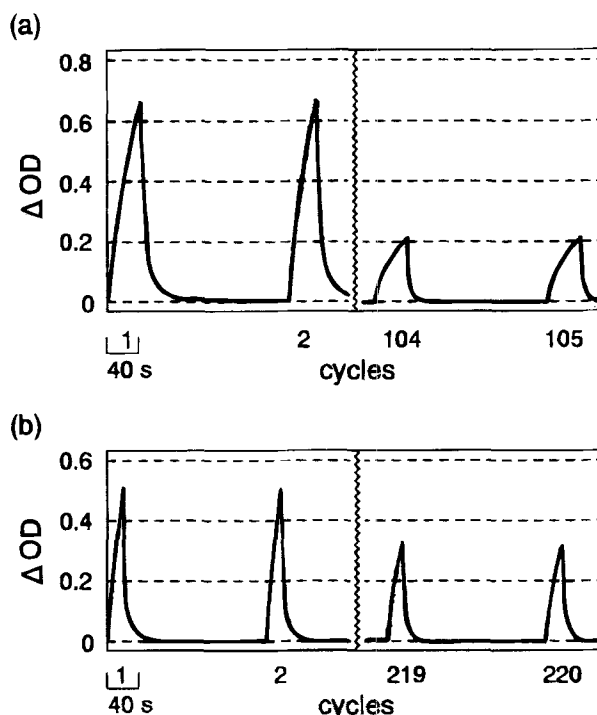


Fig. 7. Parts of time course of ΔOD of 30/733 film in repeated polarization [-1.2 V for (a) 40 s and (b) 20 s and $+1.0$ V for 180 s] in 1.0 mol dm^{-3} aqueous formic acid solution.

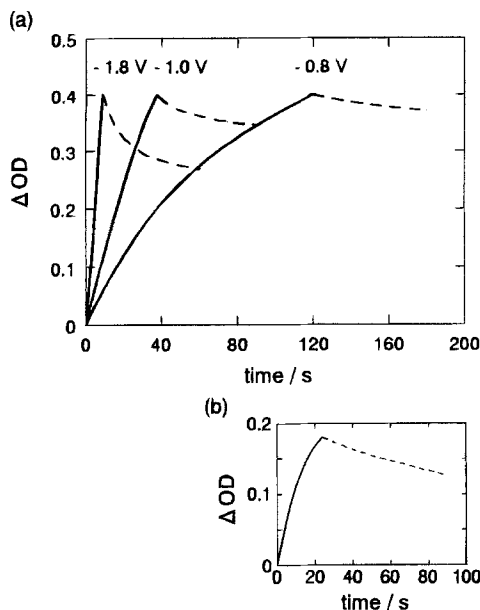


Fig. 8. Memory characteristics of 30/733 film immersed in (a) 1.0 mol dm⁻³ aqueous formic acid and (b) 0.1 mol dm⁻³ acetonitrile solution of lithium fluoroborate. In the experiment in aqueous electrolyte (a), the film was cathodically polarized (solid lines) to attain ΔOD 0.4, and the circuit was opened (dashed lines).

(29% of the original). It should be noted that the current profile (data not shown) remained almost unchanged after such prolonged experiments. As a result, the efficiency of coloring was ca. 25% of the original (35 to 8.7 C⁻¹ cm²). On the other hand, reduction of cathodic duration to 20 s improved the stability of NbO_x film, though the maximum ΔOD was a little decreased in the first stage of experiments. Even after the 219th cycle, 67% of ΔOD could be obtained. Also in this case, the current profile was kept almost constant, and the coloring efficiency was in proportion to ΔOD [ca. 68% (36 C⁻¹ cm²) after 219 cycles; in the first cycle, 53 C⁻¹ cm²]. The reason for such decrease in the coloring efficiency is ambiguous at present. As a possibility, it is assumed that certain structural changes are induced during the repeated alternating polarization cycles to enhance the hydrogen (H₂) liberation rather than the coloration, though we have at present no experimental evidence for this. Further assumption that the longer the cathodic polarization the more the structure changes is consistent with the fact that durability under 40 s cathodic duration is inferior to that under 20 s duration, as described above.

Memory characteristics of once-colored NbO_x films under open-circuit conditions were examined (Fig. 8); the film was cathodically polarized to attain prescribed ΔOD (0.4) and time dependence of ΔOD was measured thereafter. As clearly seen in Fig. 8, bleaching proceeded spontaneously without the flow of the current through the electrode. Such phenomenon of the spontaneous bleaching has been reported for Nb₂O₅ films prepared by anodization⁶ and thermal oxidation.⁴ In these reports, the phenomenon has been interpreted in terms of oxidation of the reduced moiety (H_xNb₂O₅) by oxygen dissolved in the electrolyte or by water in the film. In this relation, Mohapatra²⁰ reported that memory characteristics of WO₃ thin film could be improved by using argon-saturated cell instead of oxygen-saturated one and by replacement of aqueous electrolyte by aprotic organic solvent containing lithium salt. However, in our experiment, a negligible effect of nitrogen bubbling could be seen. Furthermore, the use of acetonitrile solution of 0.1 mol dm⁻³ lithium fluoroborate was also unsuccessful for eliminating spontaneous bleaching (Fig. 8). It is noticeable that the rate of bleaching depends strongly on the preceding cathodic potential which determines the rate of coloration. The faster the cathodic coloring, the faster the

color bleached; the decrease in ΔOD of NbO_x film colored at the potential of -0.8 V was negligibly small. On the assumption that the EC properties of NbO_x in the present study are also based on the reversible electrochemical reaction between Nb₂O₅ and H_xNb₂O₅, the spontaneous bleaching under open-circuit conditions should be caused by the oxidation of H_xNb₂O₅. The reason for its dependence on the preceding cathodic potential is unknown at present. However, it is possible to assume that difference in distribution, i.e., depth profile of reduced moiety (H_xNb₂O₅), depending on the cathodic potential, gives considerable influence on the oxidation of H_xNb₂O₅. Research along this line is now in progress.

Conclusion

Thin film of NbO_x was prepared on NESAs glass substrates by the sol-gel process. The optimum EC properties were obtained for the film consisting of crystalline Nb₂O₅. Its stability in repeated polarization cycles depended on the cathodic polarization time. The NbO_x films prepared by the sol-gel process in this work have higher coulombic efficiency than the other NbO_x films in previous reports. However, the spontaneous bleaching proceeds under open-circuit conditions. Clarification of the reason for this poor memory characteristic and improvements are necessary for the practical use of this NbO_x film as the electrochromic material.

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