

Electrochromic displays with transition-metal oxide as counterelectrode

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Amorphous WO_3 electrochromic displays (ECD) with transition-metal oxides were investigated to determine fundamental factors for developing all-solid-state ECDs. The oxides examined were CoO , NiO , SnO , Fe_3O_4 , Co_3O_4 , Ir_2O_3 , VO_2 and MnO_2 . Layers of solid electrolyte (tin phosphate) and each oxide were prepared by a spray method. The ECDs with VO_2 , Ir_2O_3 and MnO_2 were found to give excellent characteristics such as high optical coloration efficiency, low threshold voltage for coloration, long memory time and prolonged coloration-erasing cycles. Some reactions are discussed involving dissociation and/or oxidation of the adsorbed water at the counterelectrode.

1. Introduction

Certain materials show possible changes of colour upon application of an electric field. This phenomenon is called "electrochromism" [1], by analogy with "photochromism" and "thermochromism" which describe changes of colour brought about by light and by heat respectively. The colour change of the material caused by a redox reaction in an electric field is used in an electrochromic display (ECD). Such a display is required to satisfy the following conditions:

1. The electrochromic material has a sufficient absorption band of light in the visible region.
2. The change of colour or the coloration-erasing reaction shows good reversibility without non-essential reactions.
3. The contrast of the display is excellent on application of a low voltage at ambient temperature.

Many transition-metal oxides show electrochromic properties. In particular, WO_3 has been studied most extensively [2]. A thin film of amorphous WO_3 (a-WO_3) is able to give a clear image of blue colour, and the display is independent of the viewing angle. However, both the reversibility and the rate of the colour change are not enough at present. The contrast of the display may depend on the structure of the ECD cell which is dominated by the counterelectrode as well as the electrolyte.

We have previously reported all-solid-state ECDs comprising a-WO_3 -solid electrolyte-graphite or metal plate [3-5]. Inorganic ion-exchangers such as tin phosphate and zirconium phosphate were used as the solid electrolyte because of their high protonic conductivities [6]. As the counterelectrode, various metal plates such as silver and nickel were examined.

Further investigation is requisite to improve the characteristics of ECDs. Compared with studies on the electrochromic material and on the electrolyte, the study of the counterelectrode seems to be a little backward in the development of the material [7, 8]. When

a reduction proceeds at the electrochromic electrode on coloration, an oxidation must occur at the counterelectrode, and vice versa on erasing. In this study, transition-metal oxides were chosen as the material for the counterelectrode, since these materials were expected to show reversible changes of their valencies and to follow redox reactions. We examined the actual working characteristics of ECD cells containing powdered oxides and sought the best materials for the counterelectrode.

2. Experimental procedure

An a-WO_3 film (450 nm thick) was deposited by vacuum evaporation on a glass substrate overcoated with a transparent conductive electrode (Indium Tin Oxide, ITO). The deposition was performed at a rate of 15 nm sec^{-1} under a vacuum of $2.7 \times 10^{-3} \text{ Pa}$ on to the substrate held at a temperature lower than 100°C .

Tin phosphate, $\text{Sn}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$, was selected out of several inorganic ion-exchangers (Toagosei Chemical Industry Co. Ltd). A layer of this solid electrolyte (40 to $60 \mu\text{m}$ thick) was formed on the a-WO_3 film mentioned above by spraying a suspension. The suspension was prepared by mixing a powder of tin phosphate ($1.7 \mu\text{m}$ average particle size) with acetone as a dispersing agent under ultrasonic vibration. The schematic layout of the spraying instruments is shown in Fig. 1. The slope of the board and the incline of the spraying nozzle must be carefully adjusted to prepare a uniform layer. The distances from the substrate to the nozzle and to the lamp were determined so as to evaporate acetone at an appropriate rate.

The transition-metal oxides examined were CoO , NiO , SnO , Fe_3O_4 , Co_3O_4 , Ir_2O_3 , VO_2 and MnO_2 , where two kinds of MnO_2 were used: one was electrolytic manganese dioxide (EMD) and the other chemical manganese dioxide (CMD). The counterelectrode (10 to $20 \mu\text{m}$ thick) was formed on a graphite plate (1 mm thick) in the same way as the formation of the

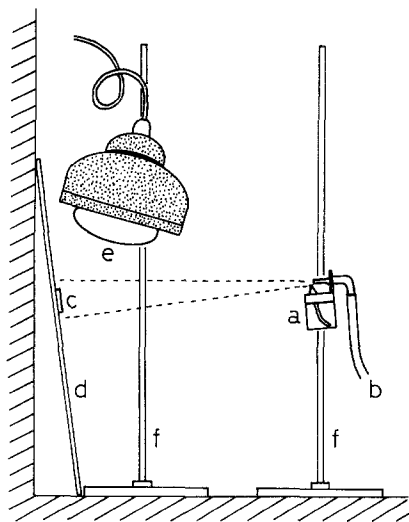


Figure 1 Instruments for the spray method: (a) suspension holder with nozzle, (b) nitrogen gas for carrier (80 to 100 kPa), (c) substrate, (d) supporting board, (e) infrared lamp, (f) stand.

electrolyte layer. The suspension containing the oxide powder was prepared by using ethyl alcohol as the dispersing agent.

The configuration of thin films and layers in the ECD cell is shown in Fig. 2 without the glass substrate. A d.c. constant voltage or current was supplied to the cell from a function generator and a d.c. current source. The change of colour was measured in the reflection mode using a tungsten lamp and a photodiode. The change in the optical density, ΔOD , was detected in the logarithmic form of the ratio of the potential drop, V_0/V . The values V_0 on erasing and V on coloration are observed across a resistor connected in series with the photodiode. All the measurements were carried out at room temperature.

3. Results and discussion

3.1. Sprayed layers

The sprayed layer of the electrolyte was observed by using a scanning electron microscope. The fractured cross-section is shown in Fig. 3. The layer had a nearly uniform thickness. The particle size observed on the surface and in the fractured cross-section came up to as large as $30 \mu\text{m}$. This fact suggested that the pulverized particles coagulated at the spray and that the apparently bulky particles accumulated on the thin film of $\alpha\text{-WO}_3$. In the case of the oxide layer, coagulation was observed as in the case of the electrolyte. The packing was not always dense. If the powders of the samples are prepared to be as uniform as possible and coagulation is suppressed, the packing densities of the

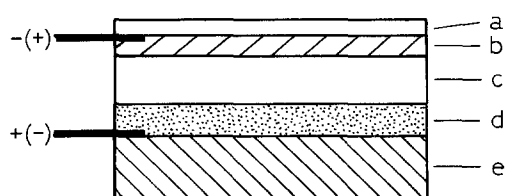


Figure 2 Schematic diagram of the ECD cell: (a) ITO, (b) $\alpha\text{-WO}_3$, (c) solid electrolyte, (d) transition-metal oxide as the counterelectrode, (e) graphite substrate.

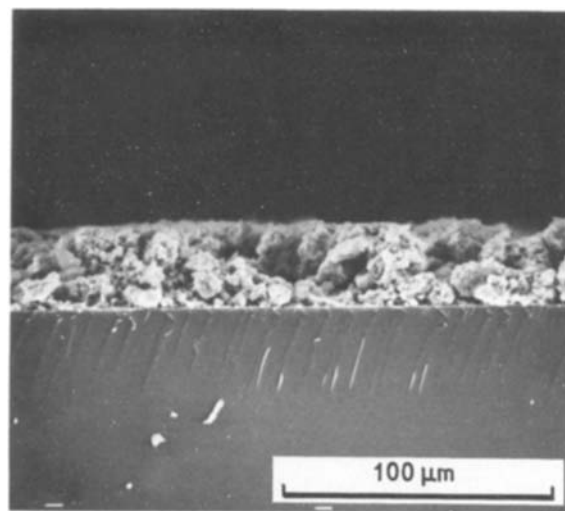


Figure 3 SEM photograph of fractured cross-section of solid electrolyte on ITO glass.

layers will be raised. The problem of coagulation must be solved as soon as possible.

3.2. Optical coloration efficiencies

Representative curves of the optical density changes (ΔOD s) are shown in Fig. 4. These data were obtained by charge-injection to the ECD cells at a constant current of $700 \mu\text{A}$ per cell. Independent of the material used as the counterelectrode, the individual cell was anticipated to display a uniform ΔOD value at a certain charge. However, the forms of the curves are different from each other.

To estimate the characteristics of the ECD, the optical coloration efficiency is defined as $E_{\text{opt}} = \Delta OD/Q$ which is the optical density change divided by the injected charge per unit area in units of $\text{cm}^2 \text{C}^{-1}$ [9]. In this experiment, the charge required to achieve $\Delta OD = 0.5$ was used for estimation of the E_{opt} value. The values are summarized in Table I below together with

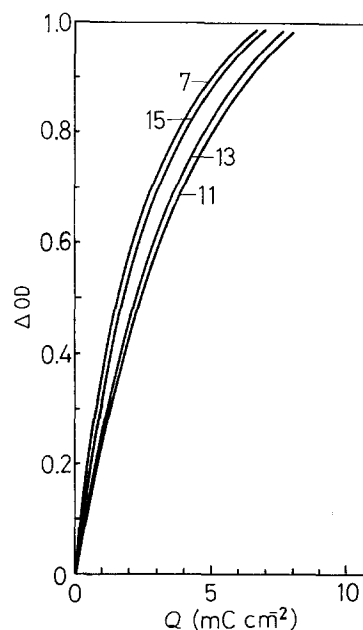


Figure 4 Optical density changes as a function of injected charge. Number cited corresponds to the ECD cell number shown in Table I.

TABLE I Characteristic values for ECDs with transition-metal oxides used as the counterelectrode

ECD cell No.	Oxide	E_{opt} ($\text{cm}^2 \text{C}^{-1}$)	Threshold value (V)	ΔOD 1 sec after start	Memory time (h)	Repeating cycles
4	NiO	200	1.9	0.13	82	7000
5	NiO + Ni(OH) ₂	135	1.2	0.06	88	20 000
6	SnO	143	1.5	0.15	0.5	> 55 000
7	MnO ₂ (EMD)	294	1.5	0.23	82	2000
9	MnO ₂ (CMD)	167	2.0	0.06	21	6000
10	CoO	238	1.2	0.07	35	3000
11	Co ₃ O ₄	200	2.7	0.04	> 170	3000
12	Fe ₃ O ₄	227	2.3	0.13	12	> 10 000
13	Ir ₂ O ₃	217	1.5	0.23	52	> 100 000
15	VO ₂	263	0.5	0.38	65	> 58 000

other characteristic parameters of the ECDs. The E_{opt} values, except the values for Cells 5, 6 and 9, are considerably larger than those reported in previous papers [9–11].

The efficiency decreases at higher injected charge, as is seen in Fig. 4. Tell [9] indicated that the decrease could be due to the coloration depth becoming greater than the optical penetration depth. In addition to his supposition, we made the following guess concerning electrochemical polarization.

The decrease in E_{opt} at higher charge may be related to the difference in the overvoltage applied to generate the constant current. Under the application of a d.c. voltage in the coloration process, the concentration of the H^+ ion in the solid electrolyte will vary to bring about a density gradient. The density of the H^+ ion is high at the a-WO₃-electrolyte interface because of the sufficient supply from the electrolyte. On the other hand, the density is low at the electrolyte-counter-electrode interface due to the deficient supply from the counterelectrode. When a number of H^+ ions are accumulated at the a-WO₃-electrolyte interface, some of them migrate back to the electrolyte and do not always take part in the formation of the H_xWO₃ bronze. Otherwise, as the overvoltage increases, the probability of a direct reaction of the H^+ ion with

an electron may increase at the a-WO₃-electrolyte interface. These H^+ ions cannot contribute to the formation of the bronze.

3.3. Threshold voltages for coloration

Fig. 5 shows typical ΔOD curves obtained at various voltages for 5 sec duration. The three cells Nos. 15, 13 and 7 coloured in the fairly low-voltage region of 0.5 to 2 V. Some cells containing other oxides such as Fe₃O₄ did not colour so much at 2 V. The minimum voltage at which distinct coloration could be noticed was defined as the threshold voltage for coloration. The threshold voltage was found from the point of intersection of two straight lines which were drawn on a ΔOD against applied voltage curve in a lower ΔOD region and in a higher ΔOD region. The ECD cell with VO₂ had the very low value of 0.5 V, as is shown in Table I. Most of the cells had threshold values of 1.2 to 2.0 V which were lower than the values (1.7 to 3.5 V) for cells with counterelectrodes of metal plate [5]. This is one of the excellent characteristics obtained in this study.

3.4. Coloration and erasing rates

The coloration rate of the ECD can be compared by measuring either the time necessary to achieve a certain ΔOD value or the ΔOD value obtained at a certain duration of coloration under a constant voltage. In this work, the ΔOD values 1 sec after the start of coloration at 3 V were read from ΔOD against time curves, as shown in Fig. 6. Cells 7, 13 and 15 showed values higher than $\Delta\text{OD} = 0.20$. It is worthy of notice that these cells had high E_{opt} values and relatively low threshold voltages (Table I). In contrast, Cells 5 and 10 did not colour so fast as the rate expected from the low threshold voltage, 1.2 V.

All the cells except Cell 13 showed an erasing rate higher than the coloration rate. The erasing curve of ECD No. 13 is unique, but the reason for this phenomenon could not be clarified. In any case, the coloration and the erasing rates obtained in this work were not always as high as the response speeds reported by other investigators [10–12].

3.5. Memory features

A prolonged memory time is one of the excellent characteristics of all-solid-state ECDs with a-WO₃. The ΔOD against time curves of several cells are indicated in Fig. 7. The memory feature was judged in this

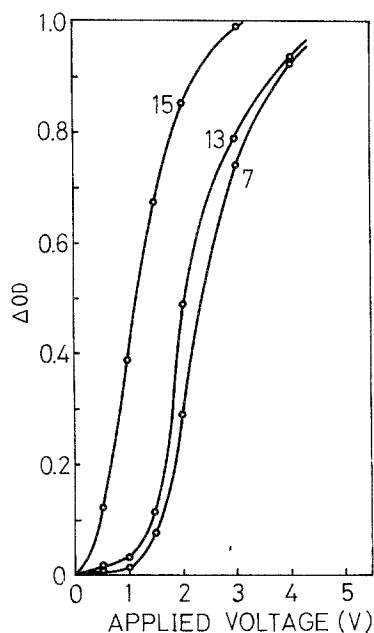


Figure 5 Optical density changes at various applied voltages (see Table I).

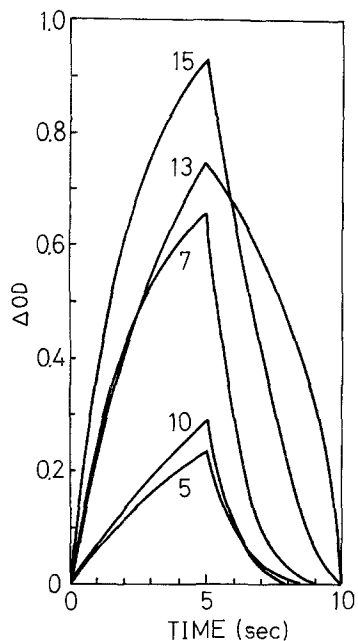


Figure 6 Coloration-erasing rate under an applied voltage of ± 3.0 V (see Table I).

work by the duration from the initial state of coloration immediately after the injection of 6 mC cm^{-2} to the state corresponding to a decay by half of the initial ΔOD value [13]. The durations are shown in Table I. These cells held a clear image for more than 50 h.

The decrease in the ΔOD value with time may be caused by the oxidation of W^{5+} ions in H_xWO_3 . One reason for the oxidation will be disappearance of the H^+ ions from H_xWO_3 . The H^+ ions are accumulated in the a- WO_3 film in the colouring reaction. Upon elimination of the electric field, the a- WO_3 -electrolyte interface charges in positive charge due to the H^+ ions accumulated, while the electrolyte-counter-electrode interface charges in negative charge. This results in the production of an inverse electromotive force, by which the H^+ ions in the a- WO_3 film will back-diffuse to the electrolyte [14]. Another reason for the oxidation will be the oxidation of H_xWO_3 . Oxygen gas is taken into the a- WO_3 film on assembling the ECD cell. H_xWO_3 is oxidized by the oxygen, and W^{5+} ions will change to W^{6+} ions [9]. The H^+ ions exhausted from H_xWO_3 will become hydrogen atoms or molecules [15].

3.6. Repeating cycles

One more characteristic should be examined in the

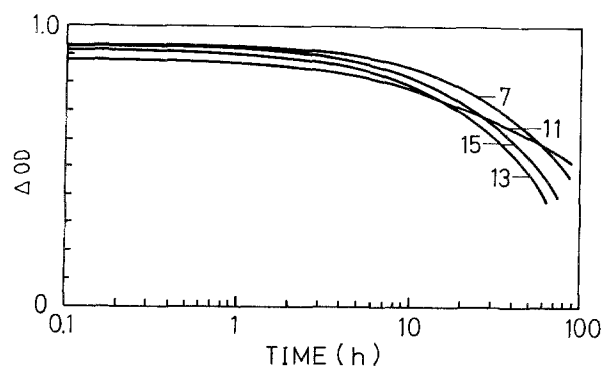
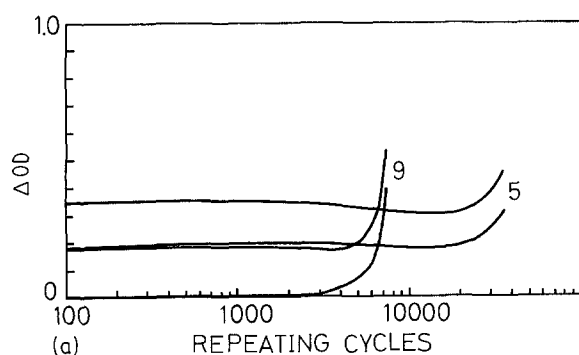


Figure 7 Optical density changes with time under open-circuit condition (see Table I).

study of ECDs. It is the repeating cycle of coloration-erasing at a certain current or voltage. Fig. 8 shows the ΔOD against repeating-cycle curves obtained at a constant current of $700 \mu\text{A}$ per cell and a period of 0.1 Hz. Under the working condition of constant current, most of the coloration-erasing curve showed an abrupt breakdown as is seen in Fig. 8a. In some cells such as Nos. 5 and 15, the colour was not clearly bleached in cycles beyond some dozens of times after the start of cycling. As is shown in Fig. 8b, Cells 13 and 15 had comparatively long lives. The repeating life of the ECD was defined as the cycling number at which a clear discrimination between the coloration and erasing states became impossible. The repeating life of each cell is summarized in Table I.

The breakdown may be caused by the remaining H^+ ions in the a- WO_3 film in the erasing state. The H^+ ions injected into the a- WO_3 film gradually diffused into the bulk of a- WO_3 apart from the a- WO_3 -electrolyte interface, and they would not reversibly return to the electrolyte under bleaching conditions. In addition to this irreversibility, some positive ions other than H^+ ions such as Na^+ would be fixed in the a- WO_3 film [16].

A practical reliability has not been obtained in the ECD cells, as can be seen in Fig. 8 and Table I. However, the cycling feature was improved compared with that of a cell containing only graphite as the counter-electrode [3]. Moreover, the actual working hours of the ECD cells such as Nos. 13 and 15 under these working conditions correspond to some long-life operations in high-rate ECDs [10, 11]. The working duration of 10^5 cycling times at 0.1 Hz is as good as the actual duration of 10^7 cycles at 10 Hz.

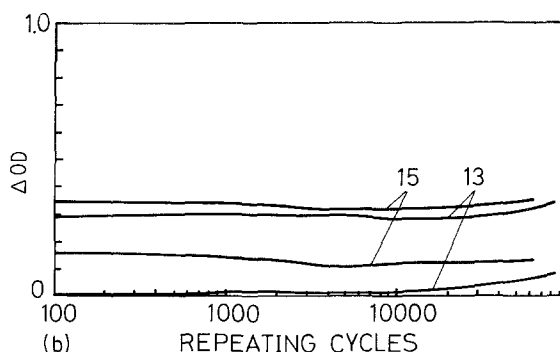
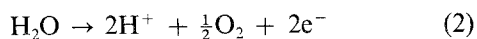


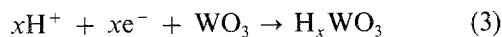
Figure 8 Coloration-erasing cycles at 0.1 Hz. Upper curves show the coloration states and the lower ones show the erasing states. (a) ECD cells Nos 5 and 9, (b) ECD cells Nos 13 and 15.

3.7. Reactions in the counterelectrode

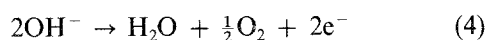
The H^+ ion taking part in the electrochromic reaction must be formed by dissociation and/or oxidation of the adsorbed water at the electrolyte–counterelectrode interface:



This H^+ ion formed at the interface moves into the electrolyte, and at the same time the H^+ ion in the electrolyte is injected into the a- WO_3 film together with electrons from the ITO electrode [17]:



The OH^- ions formed by the dissociation of water may be oxidized to produce oxygen gas [5]:



Oxygen gas (Equations 2 and 4) may adhere to the surface of the counterelectrode to disturb an essential reaction taking place at the electrode. On the other hand, when the OH^- ion reacts with some metal (M) hydroxide, the metal ion in the hydroxide is oxidized to produce a second hydroxide as follows:



Such reactions are known to occur in ECDs with rhodium or iridium hydroxide as the counterelectrode [18, 19].

The material used as the counterelectrode in this study is not a metal hydroxide but a metal oxide. The reaction written by Equation 5, however, is able to proceed at the surface of the transition-metal oxide on the coloration process. The surface of a metal oxide generally contains a little adsorbed water. The adsorbed water dissociates, adsorbs to the oxide and forms a surface hydroxyl group [20]. This surface hydroxyl group on the transition metal will act as a kind of metal hydroxide. The reaction with the OH^- ion may be similar to Equation 5. In practice, the two reactions (Equations 4 and 5) would have taken place in the counterelectrode treated in this work.

4. Conclusion

The transition-metal oxides showed potential ability as materials for the counterelectrode of an ECD. All the characteristics of the ECDs with VO_2 , Ir_2O_3 and MnO_2 were better than those of the cells with other oxides. These characteristics are related to the reactions at the counterelectrode. The H^+ ion necessary to form H_xWO_3 bronze was supposed to occur by

dissociation and/or oxidation of the adsorbed water at the counterelectrode. The OH^- ion produced by dissociation was able to be oxidized to yield oxygen gas. In addition, the dissociation of the adsorbed water followed by hydroxylation was considered to proceed reversibly and smoothly at the surface of the oxide. Such a surface state will differ with the nature of the oxide, its preparation method, the treatment condition of the sample, etc.

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