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On a Solid-State ECD, WO_3/Solid Electrolyte/Metal

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Electrochromic display (ECD) was investigated using WO_3 as the electrochromic material and metals as the counter electrode. WO_3 was vacuum-evaporated on a glass substrate coated with indium tin oxide. A film of solid electrolyte, $Sn(HPO_4)_2 \cdot H_2O$, was prepared by means of the spray method on the thin film of WO_3. ECDs with metal electrodes were examined from the points of view of the change in optical density, the current-wave forms, and the response speeds in coloring and bleaching processes. ECD cells with noble metals indicated comparatively high optical density changes on coloration at a constant-voltage operation. The cell with Ag showed a high coloration speed compared with the cells containing graphite and other metals.

Much attention has been paid to the electrochromic display (ECD) since Deb reported on the electrochromic properties of WO_3.[1] The ECDs with WO_3 are classified into the following groups:

WO_3/liquid electrolyte[2,3] (I)

WO_3/dielectric material[4,5] (II)

WO_3/solid electrolyte (super ionic conductor)[6–10] (III)

The first group has been investigated extensively. A few devices in this group have come to practical use because of their excellent performance, especially their distinct image and high response speed, but various problems remain to be solved such as the leakage of liquid electrolytes, the dissolution of the WO_3 film, and the evolution of gases. In the second group, since the dielectric material must adsorb some water in order to have ionic conduction, the performance of the ECD is affected by moisture in the atmosphere. The solid electrolyte in the third group originally contains a mobile ion in its own structure, but the ionic conductivity is not always so high as that of the electrolytic solution. The poor response speed has prevented the ECDs from satisfactory development, although the devices are hopeful because of their stable memory, long life-cycle, and maintenance-free operation.

In previous papers,[11,12] the ECDs were investigated using several inorganic ionexchangers as the solid electrolyte, and an ECD cell with $Sn(HPO_4)_2 \cdot H_2O$ (hereinafter to be referred to as SPA) was found to display the best behavior on coloration. The proton conductivity ($\approx 10^{-5}$ S cm^{-1} at room temperature) of the electrolyte[13] is not high enough for the ECD, but is not affected so much by the temperature as by the humidity in the atmosphere. Therefore, SPA has the possibility of providing an ECD with stable performance.

WO_3 films were studied from various points of view, such as the effect of adsorbed-water, the packing density, and the degree of crystallizatio.[14–16] However, counter electrodes for the ECD had scarcely been examined at all in previous papers. Yoshimura et al. reported that the spontaneous coloration of ECD was suppressed by the use of metal as a counter electrode,[10] and Sakamoto et al. reported the electrochromic behavior to be influenced by the material of the counter electrode.[17] In this paper, we wish to report on solid-state ECDs containing metals as the counter electrode. The performances of the ECDs have been evaluated in comparison with those of the ECD containing graphite as the counter electrode.

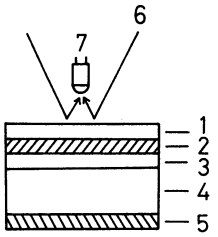

Fig. 1. Schematic diagram of the ECD cell and the experimental set up. 1: glass substrate, 2: ITO electrode, 3: WO_3, 4: $Sn(HPO_4)_2 \cdot H_2O$, 5: counter electrode, 6: tungsten lamp, 7: photo transister.

Experimental

The configuration of the components in the ECD cell is shown in Fig. 1. WO_3 film (450 nm thick) was deposited on an ITO-coated glass substrate by means of vacuum evaporation at a rate of 15 nm s^{-1} and under a vacuum of 2.66×10^{-3} Pa. SPA (Toagosei Chemical Industry Co. Ltd.) was used as the solid electrolyte, and its layer (40—60 μm thick) was formed by spraying the suspension which had beed prepared by mixing SPA fine powder with acetone under ultrasonic vibration.

Metal plates and graphite plate (0.1—0.8 mm thick and 3.29 cm^2) were used as the counter electrode. The metals were Ag, Al, Au, Cu, Fe, Ni, Pt, Pt black, Sn, Ti, Zn, and Zr. The surfaces were polished with tapping film and cleaned with trichloro-ethane before use.

The ITO, the WO_3 film, and the solid-electrolyte layers were sandwiched with the counter electrode in a pile between two bakelite plates (3 mm thick). The bakelite plate facing the glass had a window 10 mm in diameter so as to make it possible to detect the change in color through it.

The change in color was measured in the reflection mode using tungsten lamps and a photo transistor, as is shown in Fig. 2. A d.c. constant current or voltage was supplied to the ECD cell from a d.c. constant-current source (Metronix) and a function generator (Hokuto Denko HB-104). The change in the optical density, $\Delta O.D.$, is defined by the following

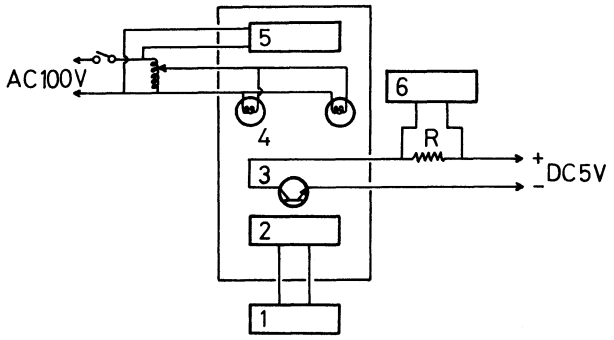

Fig. 2. Schematic diagram for measurement of the optical density changes. 1: d.c. source, 2: ECD cell, 3: photo transistor, 4: tungsten lamp, 5: fan, 6: recorder.

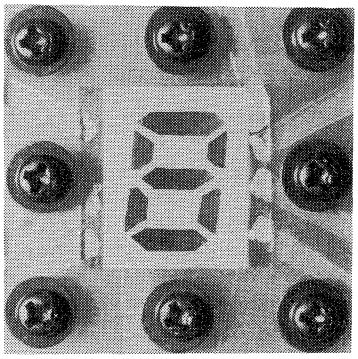

Fig. 3. Demonstration of a seven-segment numeric ECD.

equation:

$$\Delta O.D. = \log CR = \log R_0/R$$

where CR is the contrast ratio and where R_0 and R are the reflection strengths at bleaching and at coloring respectively. In this study, R_0/R was detected in the form of the ratio of the potential drop, V_0/V. V_0 (bleaching) and V (coloring) are the values at a resistor connected in series to the photo transistor. They were recorded by means of a servocoder (Graphtec SR 6341). All the measurements were carried out at room temperature.

Considering the practical ECD cell, a model of the seven-segment numeric ECD was prepared tentatively using WO_3 (EC material), an electrolyte (SPA), graphite (counter electrode), and an acryl plate (package). The appearance is shown in Fig. 3. The white color of SPA can be seen to offer an excellent contrast to the blue color of WO_3.

Results

The optical-density change ($\Delta O.D.$) versus the injected-charge curves at a constant current of 700 μA/cell are shown in Fig. 4. The change in color of the ECD is caused by the double injection of protons and electrons into the WO_3 film (to be described later). Whether or not the distribution of protons in the bulk of the WO_3 film is homogeneous can be considered in principle to influence the $\Delta O.D.$ measured in the reflection mode. In this study, the experimental duration of each run was short, and protons appeared to stay near the surface layer of the WO_3 film on the electrolyte. Therefore, the $\Delta O.D.$ values measured were regarded as not to be influenced by the distribution state of the protons.

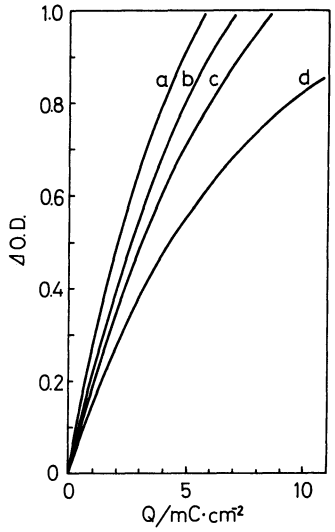

Fig. 4. Optical density changes as a function of injected charge. Counter electrodes a: Au, b: graphite, c: Pt, d: Ag.

Each cell at a certain charge should display a uniform $\Delta O.D.$ value, independent of the material used as the counter electrode. However, as may be seen from Fig. 4, the forms of the curves are different from each other. A high value of the $\Delta O.D.$ at a certain charge means a high current efficiency for coloration, since $\Delta O.D.$ is caused by the concentration change in the color based on an electrochemical reaction. In this experiment, the charge required to achieve $\Delta O.D.$=0.5 was used for the estimation of the current efficiency. The ECDs with Ni, Au, and Cu electrodes colored even in the low-charge region and needed 2.1—2.3 mC cm^{-2} to get $\Delta O.D.$=0.5. The cells with Ag and Pt electrodes indicated efficiencies slightly lower than the efficiency of the cell with graphite as the counter electrode. These data are summarized in Table 1. The three ECDs with Al, Ti, and Zr did not color enough for the $\Delta O.D.$ to be detected.

The current efficiencies shown in Fig. 4 were compared, for reference, with those in the few papers which have described ECDs with a solid-proton conductor. The ECD with antimony (V) oxide as a solid electrolyte and Fe_3O_4 as a counter electrode was reported to require 5 mC cm^{-2} to achieve a $\Delta O.D.$ of 0.5.[18] Similarly, the cell containing *p*-toluenesulfonic acid (TsOH)/urea-glycerol and Pt black was said to need 5 mC cm^{-2}.[9] It can be said from these data that the current efficiencies of ECDs with such counter electrodes as Au and Ag are comparable with, or even higher than, the data previously reported.

In order to examine the coloring-bleaching response to step voltage, the square-wave voltage was applied to

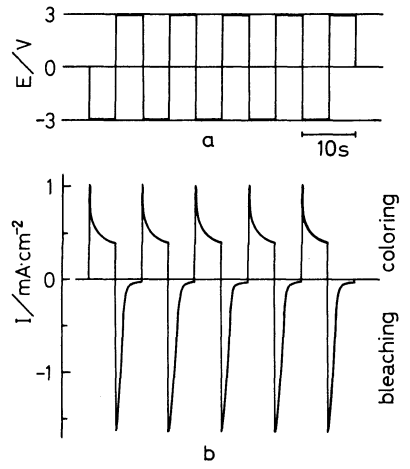

Fig. 5. Current wave form of ECD cell with graphite by applying square-wave voltage (±3 V) to a cell at 0.1 Hz. a: voltage wave form, b: current wave form.

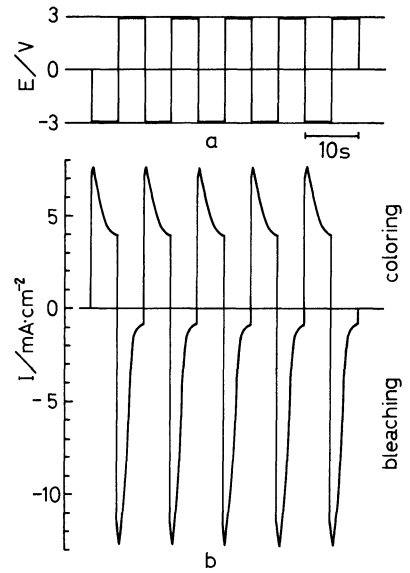

Fig. 6. Current wave form of ECD cell with Ag by applying square-wave voltage (±3 V) to a cell at 0.1 Hz. a: voltage wave form, b: current wave form.

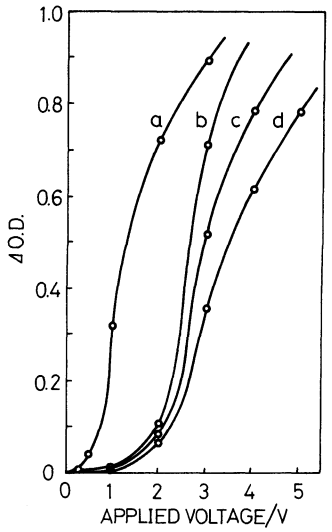

Fig. 7. Optical density changes at various applied voltages. Counter electrodes a: Ag, b: Au, c: graphite, d: Pt.

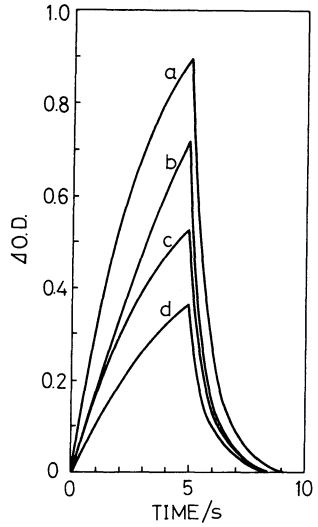

Fig. 8. Response time under an applied voltage of ±3 V. Counter electrodes a: Ag, b: Au, c: graphite, d: Pt.

the ECD and the voltage corresponding to the current was recorded. The current wave form at 0.1 Hz is shown in Fig. 5 on the cell with a graphite electrode, while the current-wave form obtained on the cell with Ag is shown in Fig. 6. In the former case, the current-wave forms differ in their coloring and bleaching processes. The current limit on the coloring process was observed below 1 s. In the latter case, the current was about ten times larger than that in the cell with graphite, and differences in shape in the current-wave forms were observed between the coloring and bleaching processes. The current limit on the coloring process was also observed, but it was slightly more moderate than the current limit shown in Fig. 5.

Figure 7 shows some $\Delta O.D.$ curves obtained at various voltages for a 5-s duration. The cell with Ag colored in the considerably low-voltage region of 1—2 V, while the cell with a graphite electrode did not color so much, even at a voltage higher than 3 V. The ECD with Au exhibited a higher $\Delta O.D.$ value compared with the cell containing graphite. In several papers,[9,19,20] the Pt electrode was used, but in this study the cell set up with Pt did not show so high performance as had been expected.

The minimum voltage at which distinct coloration can be observed is regarded as the threshold voltage for coloration. According to Fig. 7, the threshold voltage can be obtained by a procedure similar to the process of estimating a decomposition voltage on a certain current-voltage curve in an electrolysis. That is, the threshold voltage is found from the point of intersection of two straight lines which are drawn on a $\Delta O.D.$-

Table 1. Characteristic Values of ECDs with Various Electrode Materials. Work Functions of the Materials are Shown for Reference

Material	$Q/\Delta O.D.$ of 0.5	Threshold voltage/V	$\Delta O.D.$ 1 s after start	Work function
	$mC \cdot cm^{-2}$			eV
Ni	2.2	1.7	0.09	4.96
Au	2.1	1.8	0.17	4.83
Graphite	2.6	1.9	0.16	4.83
Cu	2.3	2.0	0.15	4.61
Pt	3.0	2.1	0.09	4.52
Fe	2.7	2.3	0.04	4.40
Sn	4.2	3.5	0.01	4.38
Ag	4.2	0.5	0.28	4.35
Zn	4.4	>5	0.01	4.31
Al	—	—	—	4.25
Zr	—	—	—	4.21
Ti	—	—	—	4.14

voltage curve in a lower $\Delta O.D.$ region ($0 \leqq \Delta O.D. < 0.05$) and in a higher $\Delta O.D.$ region ($0.1 < \Delta O.D. < 0.5$). Most of the cells in this study had the threshold voltage of 1.7—3.5 V. However, the ECD with an Ag electrode had the extremely low value of 0.5 V, as is shown in Table 1.

Figure 8 shows the coloration speed of the ECDs containing four cells with Pt, graphite, Au, and Ag electrodes. Most of the other cells, with various metal electrodes, did not reveal any coloration speed higher than that of the ECD with graphite. The $\Delta O.D.$ values 1 s after the beginning of coloration were 0.28, 0.17, and 0.16 for the Ag, Au, and graphite electrodes respectively. The response speed of the ECD with Ag was proved to be about twice as fast as that of the ECD with graphite. In the same way, the $\Delta O.D.$ values after 5 s were 0.89, 0.72, and 0.53 for Ag, Au, and graphite respectively.

The ECD consisting of Li_2WO_4 and the Au electrode has been reported to take 50 m s to achieve $\Delta O.D.=0.3$ when 3.0 V is applied and the ECD with antimony (V) oxide has been shown to need 500 m s when 1.3 V is applied.[18] In addition, the response speed of the cell of the TsOH/urea-glycerol system was $\Delta O.D.$ of 0.35/s at the applied voltage of 1.5 V.[9] Compared with these values, the coloration speed obtained in this work was not so high.

Discussion

In the ITO/WO_3/SPA/M system (M=metal), the electrochromic reaction on coloration can be written as follows:

$$WO_3 + xH^+ + xe^- \longrightarrow H_xWO_3 \quad (1)$$

where the H^+ ions come to WO_3 from proton-conductive SPA and where, at the same time, the H^+ ions formed at the SPA/M interface move into SPA. The H^+ ions may be formed by the dissociation and/or oxidation of the adsorbed-water at the interface:

$$H_2O \longrightarrow H^+ + OH^- \quad (2)$$

$$H_2O \longrightarrow 2H^+ + 1/2O_2 + 2e^- \quad (3)$$

The $\Delta O.D.$ vs. Q curves obtained at a constant-current operation were not always on a uniform curve, although the deviation was not remarkable; i.e., the charges needed to achieve $\Delta O.D.=0.5$ ranged from 2.1 to 4.4 $mC\,cm^{-2}$, as may be seen in Table 1. Such a difference in Q may be caused by the difference in the voltage applied to the cell to flow the constant current. This was supported by the current behavior obtained at a constant-voltage operation (Figs. 5 and 6).

The voltage applied to the cell during the coloring process will drop first at the SPA/M interface to produce H^+ ions and to make them move into SPA (1st stage), secondly at the SPA layer (2nd stage), and thirdly at the WO_3/SPA interface (3rd stage). In this experiment, the voltage drops at the 2nd and 3rd stages scarcely depend on the material of the counter electrode. Therefore, the 1st stage will dominate the total process. However, the variation in the applied voltage will also have an influence on the behavior of the H^+ ions at the SPA layer and at the WO_3/SPA interface.

Under the application of a d.c. voltage in the coloring process, the density of the H^+ ions in the SPA will vary so as to bring about a concentration gradient which is high at the WO_3/SPA interface and low at the SPA/M interface. When a number of H^+ ions are accumulated at the WO_3/SPA interface under a high voltage, some of them diffuse back to the solid electrolyte and do not always take part in the formation of H_xWO_3.[21] On the other hand, as the voltage increases, the probability of the direct reaction of the H^+ ions with electrons may increase at the WO_3/SPA interface. Such H^+ ions cannot contribute to the formation of H_xWO_3 or in turn, to the coloration of the ECD.

The work functions of the materials[22] used as counter electrodes in this study are summarized for reference in Table 1, together with some numerical values indicating the performances of ECDs. The ECD with electrode material of a large work function seems to have a certain tendency to show a lower threshold

value and a shorter response time on coloration. However, it is not reasonable to analyze the ECD characteristics using only the work function, since there is no distinct difference among the work functions listed in Table 1.

As has been stated above, the current-wave forms (Figs. 5 and 6), threshold voltages, and response times (Table 1) vary with the electrode materials. This suggests that the characteristics of the ECDs in this study are mainly related to the anode reactions. The OH^- ions produced according to Eq. 2 are oxidized to form oxygen gas[5] or metal hydroxide at the counter electrode (anode).

$$2OH^- \longrightarrow H_2O + 1/2O_2 + 2e^- \quad (4)$$

$$M + xOH^- \longrightarrow M(OH)_x + xe^- \quad (5)$$

It may be supposed that materials which bring about the oxidation of OH^- ions at a lower voltage produce H^+ ions with more ease. Furthermore, some materials oxidizing the adsorbed-water at a lower voltage may be supposed to accelerate the production of H^+ ions according to Eq. 3. It is desirable for the oxygen gas produced in Eqs. 3 and 4 to be accommodated by the counter electrode. The surfaces of metals with a strong chemical affinity to oxygen gas, such as Al, will lose their ability as counter electrodes. ECDs using such metals did not show coloration under the present experimental conditions.

The ECD with an Ag electrode showed the lowest threshold voltage and the highest response speed in the coloring process. The reactivity of Ag with the OH^- ion and oxygen gas has to be examined. The OH^- ions produced according to Eq. 2 will react with Ag to form silver (I) hydroxide and silver (I) oxide:[23]

$$2OH^- + 2Ag \longrightarrow 2AgOH + 2e^- \quad (6)$$

$$2AgOH \longrightarrow Ag_2O + H_2O \quad (7)$$

Such redox reactions among Ag, silver (I) oxide, and hydroxide proceed easily. Moreover, Ag can physically take in oxygen gas in the form of lattice oxygen and/or adsorbed oxygen. These reactions will reduce the energy to dissociate the adsorbed-water. According to the equilibrium reactions (2) and (3), the elimination of OH^- ions and oxygen gas leads to the production of H^+ ions. Therefore, the electrochromic reaction in the cell with the Ag electrode may take place at a low-threshold voltage, and the applied voltage may be used effectively to increase the coloration speed.

Besides this explanation, the possibility of the dissolution of Ag into the electrolyte could be considered. If the Ag dissolves to give Ag^+ ions, the Ag^+ ions as well as the H^+ ions will move from the SPA/Ag interface to the electrolyte. In bleaching, some of the Ag^+ ions go back to the SPA/Ag interface with difficulty, since in the coloring process the Ag^+ ions will intercalate in SPA more rigidly than the H^+ ions.[13] However, both the current-wave forms (Fig. 6) and the response feature (Fig. 8) show that the reaction takes place more easily in the bleaching process than in the coloring process. This fact is inconsistent with the assumption mentioned above. Therefore, the possibility of the dissolution of Ag into SPA can be rejected.

Conclusion

All solid-state ECDs, ITO/WO_3/$Sn(HPO_4)_2 \cdot H_2O$ (SPA)/metal or graphite, were examined in the search for good material as counter electrodes. The $\Delta O.D.$-Q curves must be independent of the materials used for the counter electrodes. However, at Q=5 mC cm^{-2} the ECD cells with Au, graphite, Pt, and Ag showed $\Delta O.D.$ values of 0.56—0.93 higher than the cells with other metals. The reason for this phenomenon could not be determined. Asymmetric current-wave forms were, however, observed between the coloring and bleaching processes corresponding to the square-wave voltage (±3 V). The ECD cell with Ag indicated a high $\Delta O.D.$ (0.33), even at 1.0 V, and a high response speed ($\Delta O.D.$=0.28 1 s after the start under 3 V). Such characteristics were discussed with respect to the production of H^+ ions by means of the dissociation and/or oxidation of the adsorbed-water at the SPA/metal interface and the accommodation of OH^- ions and oxygen gas. These anode reactions on coloration will be discussed in a subsequent paper.

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