Novel Vermilion / Greenish Blue Electrochromism of PPTA / Iridium Oxide / Au Thin Films Prepared by Electrodeposition

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An aramid resin, poly(*p*-phenylene terephthalamide) (PPTA) was available on an ITO electrode as a stable matrix film. Electrochromic iridium oxide was electrodeposited on the electrode. In the oxidized state, original iridium oxide without PPTA film showed blue, while the PPTA / iridium oxide film showed greenish blue: the maximum absorption wavelength of the original iridium oxide film was about 650 nm, while that of the PPTA / iridium oxide film was about 600 nm. The XPS-binding energy of Ir 4f_{5/2} and Ir 4f_{7/2} electrons was shifted to about 2 eV higher energy, meaning that the color change was probably due to donating of the lone pair electrons of PPTA to the iridium. The electrodeposition of Au on the PPTA / iridium oxide film was carried out. The obtained Au-electrodeposited PPTA / iridium oxide film showed quite different electrochromic properties. New redox current peaks appeared in the CV of the film. The film was colored vermillion in the reduced state and greenish blue in the oxidized state. The XPS-binding energy of Ir 4f_{5/2} and Ir 4f_{7/2} electrons was shifted to about 2 eV lower energy, implying that the electrodeposition of Au transformed the electronic state and structure of iridium oxide, suggesting the formation of a -Au-Cl-Ir- binuclear Cl-bridged complex and/or the plasmon absorption of the Au microparticles dispersed in the PPTA film.

Key Words : Electrochromism, Iridium Oxide, Poly(*p*-phenylene terephthalamide), Electrodeposition of Au, Vermilion Color

1 Introduction

Some metal oxides show electrochromism.¹⁾ Among the metal oxides, iridium oxide is widely recognized as an excellent electrochromic display (ECD) material about which many studies have been reported. According to Gottesfeld's papers,^{2, 3)} advantages of this material over other electrochromic inorganic oxides such as WO₃ are shown to include: (1) fast response; (2) strong absorbance by the colored state throughout the visible spectral region; (3) good open-circuit memory; and (4) an operating potential range which avoids electrolyte decomposition. Iridium oxide becomes blue in the oxidized state and colorless in the reduced state. If new colors were added to the color change, the ECD applicability of iridium oxide could be expanded. However, such attempts are very limited in spite of several reports dealing with electrochromic iridium oxide.¹⁻²⁴⁾

Several preparation methods have been reported for iridium oxide film. Among the methods, electrodeposition methods give iridium oxide films with excellent ECD properties.^{4, 5)} The redox reaction is determined by the XPS-binding energies of Ir-O bond and Ir-OH bond:²⁾

Although the electrodeposited iridium oxide film exhibits excellent ECD properties, the film contains a large

amount of water, and is so soft that it is easily scratched. The water can be removed from the film with heat treatment, and the film becomes hard and resistant to scratching.⁶⁾ Unfortunately, however, the heat treatment affects the ECD properties: the reversibility of the coloring-decoloring reaction and the lifetime of color changes are much lower than those of the original film.

The scratching problem would be solved if iridium oxide was electrodeposited in a stable matrix polymer film. A free-standing ECD film could be obtained and a different color change could be achieved because of the different electronic surroundings. In addition, a new color other than that displayed by the original iridium oxide could appear with metal electrodeposition. In this study, we used an aramid resin, poly(*p*-phenylene terephthalamide) (PPTA), as the matrix polymer film, which is stable and permeable to dissolved species.²⁵⁾ To obtain a new color, we further electrodeposited Au on the PPTA / iridium oxide film. The ingress of Au into WO₃ film transforms the electronic state of WO₃, and the Au-WO₃ film shows a new color change other than the original WO₃ film.²⁶⁾ Likewise, the Au-electrodeposited PPTA / iridium oxide film showed new color electrochromism: greenish blue in the oxidized state (+0.8 V) and vermillion in the reduced state (-0.2 V).

2 Experimental

All chemicals were of reagent grade and used without

further purification. A PPTA film with 12 μm thickness was prepared on the ITO electrode substrate by previously described method.²⁷⁾ The electrodeposition of iridium oxide was carried out based on Yamanaka's methods.^{6, 7)} The employed electrodeposition solution was 0.052 mol dm^{-3} IrCl_4 aqueous solution containing 30 wt % H_2O_2 and 0.04 mol dm^{-3} $(\text{COOH})_2$ and aged in the dark for two days for stabilization. The iridium oxide was electrodeposited by constant-potential electrolysis at +0.7 V until the charge passed was 0.3 C cm^{-2} . The thickness of the iridium oxide was about 2 μm . The electrodeposition solution of Au was a 0.1 M HAuCl_4 aqueous solution, and the Au was electrodeposited by constant-potential electrolysis at -0.2 V. In addition, aqueous solutions were prepared using double-distilled water.

A standard three-electrode system was employed for every electrolysis and electrochemical measurement. The working electrode on which the PPTA film was pre-coated was an ITO coated glass plate 0.8 cm wide and 5 cm long. The ITO plate was cut from a large ITO glass plate with 1-mm thickness supplied by the Nippon Sheet Glass Co. The surface electric resistance was 30 $\Omega\Box$. Prior to use, the ITO plate electrode was washed with acetone and then with water. A commercial Ag/AgCl electrode was used as the reference electrode and a Pt plate electrode as the counter electrode. The three electrodes were arranged in the optical quartz cell only when the absorption spectra were measured. The arrangement of the electrodes in the cell chamber was the same as previously described (Fig. 1).

Electrolyses were conducted using a Hokuto Denko HA-501 potentiostat/galvanostat connected with a Hokuto Denko HB-104 function generator and with a Hokuto Denko HF-201 coulometer. Cyclic voltammograms (CVs) were recorded on a Graphtec WX-2400 *x-y* recorder. The absorption spectra of the films were obtained using a

JASCO V-530 spectrophotometer.

To examine the oxidation level of iridium, the XPS spectra of the films were measured. The XPS spectra were obtained from a Perkin-Elmer ESCA PHI 5400 spectrometer using a Mg $K\alpha$ anode at a power of about 400 W. The vacuum level during the measurement was less than 10^{-9} torr. The C(1s) binding energy of 284.6 eV was used as the internal standard.

The switching time and lifetime of the color change of the films were estimated from plots of both the current and absorbance response to the applied square-wave potentials. The potentials were controlled with the potentiostat system previously described except for the recorder. The transient current response was recorded using a Rikadenki R-61 K x-t recorder with wave memory functions. The transient absorbance response at the maximum absorption wavelength was detected by amplifying the direct voltage signals from the photomultiplier of the spectrophotometer. The signals were also recorded using the same x-t recorder.

The morphologies of the obtained films were observed with a Hitachi S-2300 scanning electron microscope (SEM) and the film thickness was determined from the SEM observations. The X-ray diffraction (XRD) patterns were obtained using a Rigaku RINT 2400 V with Cu $K\alpha$ radiation.

3 Results and Discussion

3.1 Electrochromism of the PPTA / iridium oxide film

To examine how the PPTA matrix film influences the electrochromism of iridium oxide, the CVs and absorption spectra were measured. Iridium oxide was electrodeposited on an ITO electrode and the PPTA-precoated ITO electrode until the charge passed was 0.3 C cm^{-2} . The PPTA film comprises many porous layers, and it is permeable to dissolved species.²⁵⁾ Dissolved ions and molecules pass freely through the film and reach the electrode substrate. Iridium oxide can be electrodeposited on the PPTA-precoated ITO electrode even though the whole electrode surface is covered by the PPTA film. Figure 2 shows the CVs of the iridium oxide film and the PPTA / iridium oxide film in 0.1 mol dm^{-3} HClO_4 aqueous solution. The reversible redox current peaks due to the coloring-decoloring reaction (eqn. (1)) are evident at about 0.6 V. For the redox current peaks, the anodic peak potentials are the same, while the cathodic peak potentials of the PPTA / iridium oxide film is 35 mV higher than that of the iridium oxide film. All the current peaks were directly proportional to the scan rate, not to the root of the scan rate, implying that the reactions were controlled by the charge transfer process of iridium oxide on the electrode.

In spite of almost the same CV behavior, the color in the oxidized state differed slightly from each other. In the oxidized state, the original iridium oxide film became dark blue, while the PPTA-iridium oxide film was greenish blue. The absorption spectra are shown in Fig. 3. The maximum absorption wavelength is about 650 nm for the iridium oxide film and about 600 nm for the PPTA-

Fig. 1 Schematic drawing of the arrangement of the working electrode (ITO electrode) and the Ag/AgCl electrode in the spectrophotometer cell chamber.

Fig. 2 CVs at 10 mV s^{-1} of the iridium oxide film (-----) and the PPTA / iridium oxide film (—) in $0.1 \text{ mol dm}^{-3} \text{ HClO}_4$ aqueous solution.

Fig. 3 Visible and near-infrared absorption spectra of the iridium oxide film (-----) and the PPTA / iridium oxide film (—) at $+0.8$ and 0 V in $0.1 \text{ mol dm}^{-3} \text{ HClO}_4$ aqueous solution.

iridium oxide film. The difference in the color is probably due to the oxidation level of the iridium. Figure 4 illustrates the XPS spectra of Ir $4f_{5/2}$ and Ir $4f_{7/2}$ electrons of the films. The XPS-binding energies of Ir $4f_{5/2}$ and Ir $4f_{7/2}$ electrons of the iridium oxide film are in fair agreement with those reported previously,^{9–11)} indicating that the average valence of the iridium in the colored iridium oxide film is very near 4.0. The XPS-binding energies of the PPTA / iridium oxide film is about 2 eV higher than that of the iridium oxide film, suggesting a higher oxidation level of the iridium in the PPTA / iridium oxide film. A probable speculation for the cause is the donating of the lone pair electrons of PPTA to the iridium. There are many lone pair electrons on the oxygen and nitrogen atoms in the PPTA polymeric backbone (Fig. 5), which are available for donating. The donating may enhance the oxidation level of the iridium in the PPTA / iridium oxide film.

Fig. 4 XPS spectra of Ir $4f_{5/2}$ and Ir $4f_{7/2}$ electrons of the iridium oxide film (-----) and the PPTA / iridium oxide film (—).

Fig. 5 Unit molecular structure of PPTA.

3. 2 Electrochromism of Au-electrodeposited PPTA / iridium oxide film

In order to obtain a different color other than that of the original inorganic ECD films, other metal oxides and noble metals have been introduced into the original films. For WO_3 film which shows blue-colorless electrochromism, red color tones were obtained for Au- WO_3 film, although the mechanisms are not yet well-understood.⁷⁾ In this study, Au was electrodeposited on the original iridium oxide film and on the PPTA / iridium oxide film. Unfortunately, however, the Au / iridium oxide film had almost the same electrochromism as the original iridium oxide film, regardless of the electrodeposited amount of Au. On the other hand, the PPTA / iridium oxide / Au film showed quite different electrochromism from that of the original iridium oxide. The film became greenish blue in the oxidized state and vermilion in the reduced state. This color change was first obtained for the iridium oxide system. Figure 6 shows the absorption spectra of the reduced and oxidized film. The absorption spectra of the PPTA / iridium oxide film are also shown for comparison. It is interesting to find the new absorption peak at around 550 nm with a relatively large absorption intensity from 400 to 500 nm. It is noteworthy that the absorption peak hardly vanishes in the reduced state at -0.2 V . That makes the film vermilion in the reduced state.

Different behavior was observed for the CV data and the XPS-binding energies of Ir $4f_{5/2}$ and Ir $4f_{7/2}$ electrons of the PPTA / iridium oxide / Au film, compared with those of the PPTA / iridium oxide film. Figure 7 compares the CVs of the PPTA / iridium oxide / Au film and the PPTA / iridium oxide film. Besides the redox current peaks originating from the reaction of eqn. (1), a new redox current is evident at around 0 V in the CV of the

Fig. 6 Visible and near-infrared absorption spectra of the PPTA / iridium oxide film (-----) and the PPTA / iridium oxide / Au film (——) at +0.8 and -0.2 V in 0.1 mol dm⁻³ HClO₄ aqueous solution.

Fig. 7 CVs at 10 mV s⁻¹ of the PPTA / iridium oxide film (-----) and the PPTA / iridium oxide / Au film (——) in 0.1 mol dm⁻³ HClO₄ aqueous solution.

PPTA / iridium oxide / Au film. There is no doubt that the new color, vermilion, is related to the new redox current. The XPS-binding energies of Ir 4f_{5/2} and Ir 4f_{7/2} electrons of the PPTA / iridium oxide / Au film were about 2 eV lower than those of the PPTA / iridium oxide film (Fig. 8). This shift is probably due to the disappearance of the donating of PPTA by the Au electrodeposition. The donating of the lone pair electrons of PPTA to the iridium disappears, and the XPS spectral pattern is almost the same as that of the iridium oxide without the PPTA film (see the dashed line in Fig. 3).

The obtained results can be explained mainly by -Au-Cl-Ir- binuclear Cl-bridged complex formation. The electrodeposition of Au occurs through the electroreduction of AuCl₄⁻. When the electroreduction takes place on the PPTA / iridium oxide film, the binuclear Cl-bridged complex is probably formed, at least in part. Once the binuclear Cl-bridged complex is formed, it scarcely decomposes during electrooxidation, as can be seen in the

Fig. 8 XPS spectra of Ir 4f_{5/2} and Ir 4f_{7/2} electrons of the PPTA / iridium oxide film (-----) and the PPTA / iridium oxide / Au film (——).

CV and absorption spectral data. In Fig. 7, the irreversible redox peak current at around 0 V is probably due to the redox reaction of the binuclear Cl-bridged complex partially formed in the PPTA / iridium oxide film. The current is much smaller than the redox current of the coloring-decoloring reaction (eqn. (1)), and little color change of the binuclear Cl-bridged complex occurs. Therefore, the color change of the film originates in the overlap of the coloring-decoloring reaction (eqn. (1)) and the vermilion color of the complex.

The binuclear Cl-bridged complex could not be formed if there was no Cl source. To make sure this, two Au-deposited PPTA / iridium oxide films were prepared: (A) PPTA / iridium oxide film covered with vapor-deposited gold film and (B) PPTA / iridium oxide film electrodeposited by gold using a different electrodeposition solution, which was a Na₃PO₄ (15 g dm⁻³)/Na₂HPO₄ (20 g dm⁻³) buffer solution containing 0.014 mol dm⁻³ KAu(CN)₂. Both the voltammetric behavior and absorption spectra at different potentials were almost the same as those of the PPTA / iridium oxide film (Figs. 2 and 3). For the films (A) and (B), the deposited gold barely influenced the electrochromic properties of the PPTA / iridium oxide film. This fact strongly supports that the new color change is due to the formation of the binuclear Cl-bridged complex.

There is still another reason why the PPTA / iridium oxide / Au film shows the vermilion color. The film contains not only the binuclear Cl-bridged complex but also the microparticles of metallic gold. The absorption band from 520 to 660 nm in the reduced PPTA / iridium oxide / Au film may be assigned to the plasmon absorption of the microparticles of metallic gold dispersed in the film.

3.3 Morphology of the PPTA-iridium oxide film

We have already shown several properties of the PPTA film:^{6, 8, 12)} (i) it is obtainable on the electrode substrate as a stable film by electrodeposition; (ii) dissolved species are permeable through the PPTA film because of its porosity; (iii) the PPTA film-coated electrode is so electroactive that electrolysis can be carried out using the electrode; (iv) the PPTA film has a layer-stacking structure. The SEM observations were performed with-

out covering with vapor-deposited gold film. No SEM image of the PPTA film without iridium oxide was obtained because PPTA is an electronic insulator. On the other hand, the electronic conductivity of iridium oxide made a sharp SEM image. The SEM image of the PPTA / iridium oxide film is shown in Fig. 9(a). The fact that the layer-stacking structure of the PPTA film is evident implies that iridium oxide is electrodeposited inside the whole PPTA film. The SEM image of the PPTA / iridium oxide / Au film shows that the metal gloss of gold covers over the film (Fig. 9(b)).

3.4 Switching time and lifetime in the electrochromism

To examine the switching time and lifetime of the iridium oxide, PPTA / iridium oxide and PPTA / iridium oxide / Au films, the absorbance responses of the films on the ITO electrode were measured versus the square-wave potential pulse at the initial stage. The absorbance was monitored at 650 nm for the iridium oxide film, at 600 nm for the PPTA / iridium oxide film and at 550 nm for the PPTA / iridium oxide / Au film. The absorbance responses are indicated in Fig. 10. The switching time of the PPTA / iridium oxide film is almost the same as that of the iridium oxide film and is found to be about 10 s. It is interesting to find that the PPTA / iridium oxide / Au film has the shortest switching time of about 5 s.

As can readily be seen in Fig. 9(b), gold covers over

the film surface. This means that gold is electrodeposited inside the film as well because the PPTA film is an electronic insulator. Probably the gold inside the film promotes the electronic connection between the iridium oxide and the electrode substrate. This reflected the CV behavior of the PPTA / iridium oxide / Au films with the same amount of iridium oxide and different amount of electrodeposited gold (Fig. 11). The redox current peak originated from the redox reaction of iridium oxide increases with the amount of the electrodeposited gold.

The lifetime of the films did not differ much from each

Fig. 10 Absorbance response of the iridium oxide film (a), the PPTA / iridium oxide film (b) and the PPTA / iridium oxide / Au film (c) in $0.1 \text{ mol dm}^{-3} \text{ HClO}_4$ aqueous solution. The square-wave potential-time profile is shown by the lower curve of each figure: $E_c = +0.8$ (a), $+1.0$ (b) and $+1.0 \text{ V}$ (c).

(a) PPTA-iridium oxide film

(b) Au-electrodeposited PPTA-iridium oxide film

Fig. 9 SEM photographs of the PPTA / iridium oxide film (a) and the PPTA / iridium oxide / Au film (b).

Fig. 11 CVs at 10 mV s^{-1} of the PPTA / iridium oxide film with different Au-electrodeposited amount in $0.1 \text{ mol dm}^{-3} \text{ HClO}_4$ aqueous solution. The charge passed during the Au-electrodeposition is 10 (·····), 20 (-----) and 30 mC (—).

other. Each color change was observable after at least 2×10^3 repetitions. Unfortunately, however, no color change was seen when the number of the repetitions exceeded 10^4 , all the films remained permanently black blue. We are trying to improve the lifetime to the practical level.

4 Conclusions

Iridium oxide can be electrodeposited on a PPTA film-coated ITO electrode, and a free-standing PPTA / iridium oxide film is easily prepared. In the oxidized state, the PPTA / iridium oxide film shows greenish blue: the maximum absorption wavelength of the PPTA / iridium oxide film was about 600 nm. By comparing the XPS-binding energy of Ir 4f_{5/2} and Ir 4f_{7/2} electrons, the greenish blue color is due to donating of the lone pair electrons of PPTA to the iridium.

The electrodeposition of gold on the PPTA / iridium oxide film can be carried out. The obtained PPTA / iridium oxide / Au film shows quite different electrochromic properties. New redox current peaks appear in the CV of the film and the film is colored vermilion in the reduced state and greenish blue in the oxidized state. The vermilion color is probably originated from the formation of a -Au-Cl-Ir- binuclear Cl-bridged complex and/or the plasmon absorption of the Au microparticles dispersed in the PPTA film. The vermilion-greenish blue electrochromism is expected to expand the practical ECD applicability of iridium oxide. In addition, for the color change, the switching time is less than 5 s and the lifetime is more than 10^3 repetitions.

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References

- 1) C. G. Granqvist, *Handbook of Inorganic Electrochromic Materials*, Elsevier, Amsterdam (1995).
- 2) S. Gottesfeld, J. D. E. McIntyre, G. Beni, and J. L. Shay, *Appl. Phys. Lett.*, **33**, 208 (1978).
- 3) S. Gottesfeld and J. D. E. McIntyre, *J. Electrochem. Soc.*, **126**, 742 (1979).
- 4) T. Yoshino, N. Baba, and K. Arai, *Jpn. J. Appl. Phys.*, **26**, 1547 (1987).
- 5) T. Yoshino, K. Arai, and N. Baba, *Hyomen Gijutu*, **41**, 676 (1990).
- 6) K. Yamanaka, *Jpn. J. Appl. Phys.*, **30**, 1285 (1991).
- 7) K. Yamanaka, *Jpn. J. Appl. Phys.*, **28**, 632 (1989).
- 8) R. Kötz, H. Neff, and S. Stucki, *J. Electrochem. Soc.*, **131**, 72 (1984).
- 9) G. K. Wertheim and H. J. Guggenheim, *Phys. Rev.*, **22**, 4680 (1980).
- 10) Y. Y. Kleperis, A. N. Rodionov, and A. R. Lusi, *Elektrokhimiya*, **28**, 1450 (1992).
- 11) R. D. Rauh and S. F. Cogan, *J. Electrochem. Soc.*, **140**, 378 (1993).
- 12) N. Bestaoui, E. Prouzet, P. Deniard, and R. Brec, *Thin Solid Films*, **235**, 35 (1993).
- 13) M. Collomb-Dunand-Sauthier, S. Langlois, and E. Genies, *J. Appl. Electrochem.*, **24**, 72 (1994).
- 14) M. A. Petit and V. Plichon, *J. Electroanal. Chem.*, **379**, 165 (1994).
- 15) L. Servant, M. Hernandez, J. Grondin, and J. Lassegues, *Ionics*, **1**, 351 (1995).
- 16) T. Yoshino, M. Satoh, T. Ohmori, H. Masuda, and N. Baba, *Hyomen Gijutu*, **47**, 985 (1996).
- 17) T. Yoshino, *Hyomen Gijutsu*, **49**, 20 (1998).
- 18) M. A. Petit and V. Plichon, *J. Electroanal. Chem.*, **444**, 247 (1998).
- 19) S. Taunier, C. Guery, and J. Tarascon, *Electrochim. Acta*, **44**, 3219 (1999).
- 20) C. Barbero, R. Kötz, and O. Haas, *Synth. Met.*, **101**, 170 (1999).
- 21) K. Nishio, Y. Watanabe, and T. Tsuchiya, *Thin Solid Films*, **350**, 96 (1999).
- 22) T. Pauporte and R. Durand, *J. Appl. Electrochem.*, **30**, 35 (2000).
- 23) A. Azens and C. G. Granqvist, *Appl. Phys. Lett.*, **81**, 928 (2002).
- 24) L. Sziraki and L. Bobics, *Electrochim. Acta*, **47**, 2189 (2002).
- 25) M. Takayanagi and T. Katayose, *J. Polym. Sci., Polym. Chem.*, **19**, 1133 (1981).
- 26) E. K. Sichel, J. I. Gittelman, and J. Zelez, *Appl. Phys. Lett.*, **31**, 109 (1977).
- 27) K. Koga, S. Yamasaki, K. Narimatsu, and M. Takayanagi, *Polym. J.*, **21**, 733 (1989).
- 28) T. Hirayama, J. Yano, H. Ohura, and S. Yamasaki, *Hyomen Gijutsu*, **52**, 762 (2001).