Fabrication of Ti/TiO₂/MO_x Electrodes Using Photoelectrodeposition Technique

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Photoelectrochemical deposition of metallic oxide (PbO₂, RuO_x, NiOOH, and CoOOH) onto a Ti substrate was studied and the electrochemical behavior of the prepared Ti/TiO₂/MO_x electrodes was examined. The photoelectrochemical deposition of MO_x occurred in the solutions containing Mⁿ⁺ ions on the Ti substrate under anodic bias. Electron holes produced on the TiO₂ film surface under illumination may contribute the MO_x formation. The prepared Ti/TiO₂/MO_x electrodes showed a tunneling current under anodic bias.

Key Words: Titanium Dioxide Film, Electrodeposition, Lead Dioxide, Ruthenium Oxide

1 Introduction

The electrochemical fabrication of functional materials, which is called the soft solution electrochemical process, will become more important in the future, because this is a low energy process under environmentally benign conditions.^{1, 2)} Many advanced thin films such as perovskite,³⁻⁷⁾ superlattice,⁸⁾ quantum dot,^{9, 10)} and nano-porous film,¹¹⁾ *etc.*, have been prepared by the soft solution electrochemical process. Moreover, the characteristic states of the films can be easily controlled by the preparation conditions such as potential, current density, temperature, pH, *etc.*, during the electrolysis. Recently, a photoelectrochemical epitaxial growth technique has been developed for the deposition of metallic oxides, where the deposition was carried out under the illumination of light with higher energies than the bandgap of the electrode substrates.¹²⁻¹⁵⁾

Anodic oxide formation on a metal surface is important process for the surface chemistry of metals including corrosion science and semiconductor technology. Many studies about anodic TiO₂ films have also been carried out. It has been found, from the analysis of electron diffraction pattern, that a thin anodic TiO₂ film (nm size) has a rutile structure and may epitaxially grow on polycrystalline Ti metal and that the film thickness can be easily controlled by the anodic potential.¹⁶⁻²¹⁾ Some functional oxide films containing Ti on a Ti metal substrate such as BaTiO₃, SrTiO₃ and Cr doped TiO₂, have also been prepared using the anodic oxidation process.^{22, 23)}

It is well known that PbO₂ and RuO₂ with metallic conductivity are very useful as inert anodes in acidic solution.²⁴⁻²⁷⁾ The Ti/PbO₂ electrodes where α - and β -PbO₂ are anodically deposited on a Ti plate in a solution containing Pb²⁺ are important in practical applications.²⁶⁾ In

this case, the TiO₂ film formed on the Ti plate must be released²⁴⁾ or some conducting mixed oxides must be coated on the Ti substrate^{25, 26)} before the PbO₂ electrodeposition, because the TiO₂ film produced on the Ti substrate (Ti/TiO₂) under anodic bias behaves as an insulator and disturbs the electrodeposition of PbO₂. The Ti/RuO_x electrode has been mainly prepared by thermal decomposition of Ru compounds on a Ti substrate.²⁷⁾ These hydrated compounds act as the electrode for electrochemical capacitor²⁸⁾ as well as the inert anode.

The TiO₂ film has a strong photoresponse as an *n*-type semiconductor in photoelectrochemistry in spite of its nanometer scale thickness.²⁹⁾ This property can be used during the photoelectrochemical fabrication of some materials. In this paper, some preparation methods of the Ti/TiO₂/MO_x electrodes (MO_x=PbO₂, RuO_x, NiOOH, CoOOH) using photoelectrochemical technique were demonstrated and their electrochemical behavior was studied.

2 Experimental

All experiments for the electrodeposition of the metal oxides denoted as MO_x were performed in a conventional three-electrode electrochemical cell with a Pt counter electrode and a saturated Ag/AgCl reference electrode. The working electrode was a polycrystalline 99.99% pure Ti plate with a 1 cm² contact area to the electrolyte. Prior to the experiments, the Ti electrodes were etched with 3 wt% HF + 5 wt% HNO₃ solution to dissolve a TiO₂ film formed on the surface in air (pretreatment). The electrodepositions of PbO₂, RuO_x, NiOOH, and CoOOH were made under illumination in Pb(NO₃)₂, RuCl₃, Ni(CH₃COO)₂, and Co(CH₃COO)₂ solutions, respectively. A 500 W ultra-high pressure Hg lamp

was used as the light source. The deposition was carried out by a single potential sweep method with 1 mV s^{-1} or at a constant current for PbO_2 and was by a cyclic voltammetric method with 50 mV s^{-1} for the case of RuO_x , but at a constant potential for NiOOH and CoOOH . The electrochemical test of the prepared $\text{Ti/TiO}_2/\text{MO}_x$ electrodes was made in H_2SO_4 or KOH solution. $\text{Hg/Hg}_2\text{SO}_4$ and Hg/HgO were used as the references in the tests in H_2SO_4 and KOH solutions respectively, because a Cl^- free condition was necessary in the solution for this test.

The structures and the morphologies of the formed oxide films were examined by X-ray diffraction (XRD) analysis with monochromatic $\text{Cu-K}\alpha$ radiation and scanning electron microscopy (SEM) or electron-probe microanalysis (EPMA).

3 Results and Discussion

3.1 $\text{Ti/TiO}_2/\text{PbO}_2$ electrode

Figure 1 shows the model for the photoelectrochemical deposition of the PbO_2 under illumination during the anodic formation of the TiO_2 film on the Ti substrate, where the solution contains a Pb^{2+} ion. Initially, the TiO_2 film is formed on the Ti substrate under anodic bias. The photoelectrochemical deposition of PbO_2 will begin on the surface of the TiO_2 film if a hole in its valence band is produced under illumination.

Figure 2 shows SEM micrographs of the surfaces of Ti electrodes, where the electrolysis was made at $500 \mu\text{A cm}^{-2}$ in 0.1 M ($\text{M} = \text{mol dm}^{-3}$) $\text{Pb}(\text{NO}_3)_2$ under illumination (A) and in the dark (B). The surface was completely

Fig. 1 Model of the PbO_2 photoelectrodeposition onto Ti substrate during the anodic formation of TiO_2 film.

illumination

dark

Fig. 2 SEM photographs of the $\text{Ti/TiO}_2/\text{PbO}_2$ electrode surfaces. The electrodes were prepared at $500 \mu\text{A cm}^{-2}$ for 30 min under illumination (A) and in the dark (B).

covered with PbO_2 (A), but not in (B). The deposited PbO_2 consisted of β - and α - PbO_2 according to XRD analysis. The same deposition was also observed for the non-pre-treated Ti substrate if the electrolysis is carried out under illumination.

Figure 3 shows typical voltammograms of the Ti/TiO_2 (A) and the PbO_2 -coated Ti electrodes (B-D), i.e., $\text{Ti/TiO}_2/\text{PbO}_2$ electrodes, in $0.5 \text{ M H}_2\text{SO}_4$, where (A) and (D) electrodes were prepared by electrolysis of the Ti substrates at $500 \mu\text{A cm}^{-2}$ for 30 min in NaNO_3 (A) and $\text{Pb}(\text{NO}_3)_2$ (D) solutions under illumination respectively. The electrodes (B) and (C) were also prepared by the same methods as (D) after heat-treatments of the Ti substrate at 923 K (B) and 673 K (C) for 5 h in air. That is, thick TiO_2 films (thickness: about $10 \mu\text{m}$ (B) and about $2 \sim 3 \mu\text{m}$ (C)) cover the surfaces of these electrodes (B and C) before the photoelectrochemical PbO_2 deposition. The PbO_2 completely covered the TiO_2 surfaces for the electrodes (B) and (C) like the electrode (D) according to the SEM observation.

The Ti/TiO_2 electrode (A) acts as an n-type semiconductor electrode, where no anodic current flows because of formation of a Schottky barrier under anodic bias. It

Fig. 3 Voltammograms (sweep rate = 20 mV s^{-1}) of the Ti/TiO_2 (A) and PbO_2 -coated Ti electrodes ($\text{Ti/TiO}_2/\text{PbO}_2$) (B-D) in $0.5 \text{ M H}_2\text{SO}_4$. The PbO_2 was deposited at $500 \mu\text{A cm}^{-2}$ for 30 min under illumination for the electrodes B-D. The electrodes B and C were heated at 923 and 673 K before photoelectrodeposition of PbO_2 , but not for the electrode D.

should be noted that anodic currents for the oxygen evolution reaction flow for the electrodes (B)-(D), and that the current is the highest for the electrode (D). It is judged from the comparison with the electrode (A), that the anodic currents at the electrodes (B)-(D) are based on electron tunneling through the formed Schottky barrier.¹⁵⁾ Reduction currents from PbO_2 to PbSO_4 were also observed for these electrodes at a potential more negative than the $\text{PbO}_2/\text{PbSO}_4$ equilibrium potential (about 1.0 V). Thus, the electrodes (B)-(D) act as metallic electrodes. Fermi-level pinning will occur at the $\text{PbO}_2/\text{TiO}_2$ interface due to the presence of a large amount of surface states produced by the photoelectrodeposition process for the $\text{Ti}/\text{TiO}_2/\text{PbO}_2$ electrodes.¹⁵⁾

The degree of the anodic currents for the $\text{Ti}/\text{TiO}_2/\text{PbO}_2$ electrodes depends on the TiO_2 film thickness as shown in Fig. 3, because the TiO_2 film acts as a resistance. Consequently, the highest anodic current flows for the electrode (D) whose TiO_2 film will be about a few nm in thickness.^{29, 30)}

The $\text{Ti}/\text{TiO}_2/\text{PbO}_2$ electrode with a thin TiO_2 film was stable in a long-term test as an anode in 0.5 M H_2SO_4 solution. For example, $\text{Ti}/\text{TiO}_2/\text{PbO}_2$ electrode (In this case, the electrode was prepared by a single sweep of the Ti substrate from 0 V to 3.0 V as the final potential.) showed about 1.2 V as the overvoltage for oxygen evolution reaction under 30 mA cm^{-2} and the potential was constant for 120 h during the electrolysis. This electrode, therefore, may be used as an inert anode in acidic solution in the electrolysis industry.

3. 2 $\text{Ti}/\text{TiO}_2/\text{RuO}_x \cdot n\text{H}_2\text{O}$ electrode

Figure 4 shows cyclic voltammograms of the Ti electrode in 10^{-4} M RuCl_3 solution (containing 10^{-2} M HCl and 10^{-1} M KCl). The large voltammetric currents were observed after a few hundred cycles under illumination (A) in analogy with the $\text{Ti}/\text{RuO}_x \cdot n\text{H}_2\text{O}$ electrode,^{27, 31)} but not in the dark (B). Similar phenomena to Fig. 4 in the current differences between (A) and (B) were also observed for the Ti/TiO_2 polycrystalline electrodes (prepared by heat-treatment of Ti at 773 K for 5 h in air (thickness: about $5 \mu\text{m}$)) as shown in Fig. 5. Ru metal will deposit on the surface under cathodic bias and then will be oxidized to RuO_x (Ru(III) , Ru(IV) and Ru(VI)) under anodic bias. Finally, hydrous RuO_x film will be formed on the Ti substrate by the repeated redox reactions in the present cyclic voltammetric technique. Anyhow, both oxidation and reduction processes are important for the RuO_x deposition. The oxidation process must be relatively difficult for the Ti substrate in the dark when a relatively thick TiO_2 film covers the Ti surface because of the rectification effect of the TiO_2 film. However, the oxidation will easily proceed under illumination, because hole produced in the valence band of the TiO_2 film can oxidize Ru metal and/or RuO_x (porous films) deposited on the surface. Consequently, $\text{Ti}/\text{TiO}_2/\text{RuO}_x \cdot n\text{H}_2\text{O}$ can be fabricated by the photoelectrochemical technique.

Figure 6 (A) and (B) show SEM micrographs of the surface of the electrode prepared under illumination. The hydrous RuO_x covered the surface of the electrode pre-

Fig. 4 Voltammograms of Ti electrode in a solution of 10^{-4} M RuCl_3 , 10^{-2} M HCl , and 10^{-1} M KCl . The tests were made under illumination (A) and in the dark (B). The cyclic numbers are described in the figure.

Fig. 5 Voltammograms of Ti/TiO_2 electrode which was prepared by heat-treatment at 773 K, in a solution of 10^{-2} M RuCl_3 , 10^{-2} M HCl , and 10^{-1} M KCl . The tests were made under illumination (A) and in the dark (B).

pared under illumination (which corresponds to the electrode (A) in Fig. 4), but not for the case in the dark (which corresponds to the electrode (B) in Fig. 4). The

Fig. 6 SEM photographs of the surface of the Ti/TiO₂/RuO_x electrode which corresponds to the electrode (A) in Fig. 4. (B) is the magnified photograph of (A).

Fig. 7 Voltammograms (sweep rate = 20 mV s⁻¹) of the Ti/TiO₂/NiOOH (A) and Ti/TiO₂/CoOOH (B) electrodes prepared at 1.0 V vs. Ag/AgCl for 30 min under illumination (a) and in the dark (b). The test electrolyte is 1 M KOH.

grain sizes of RuO_x were smaller than about 0.3 μm according to the analysis of the micrograph in Fig. 6 (B).

A tunneling current was also observed under anodic bias for the prepared Ti/TiO₂/RuO_x electrode (A) in H₂SO₄ solution. However, the electrode was not so stable, because dissolution of the deposited RuO_x occurred under the anodic bias.

3.3 Ti/TiO₂/MOOH electrodes

The voltammograms of the Ti/TiO₂/NiOOH and Ti/TiO₂/CoOOH electrodes in 1 M KOH solution are shown in Fig. 7 (A) and (B) respectively. NiOOH and CoOOH were deposited under illumination at a constant potential of 1.0 V vs. Ag/AgCl for 30 min in 0.1 M Ni(CH₃COO)₂ and Co(CH₃COO)₂ solutions respectively. The amounts

of NiOOH deposits were 1.9×10^{-6} and 0.3×10^{-6} mol cm⁻² under illumination (a) and in the dark (b) respectively, while those of CoOOH were 9.0×10^{-6} and 2.7×10^{-6} mol cm⁻² respectively. Thus, the amounts of the oxides deposited under illumination are much larger than those in the dark, indicating that the photoelectrochemical deposition process is also dominant for the depositions of NiOOH and CoOOH. The large anodic tunneling currents were also observed for the Ti/TiO₂/NiOOH and Ti/TiO₂/CoOOH electrodes prepared under illumination as shown in Fig. 7. Probably, Fermi-level pinning will also occur for these electrodes in analogy with the Ti/TiO₂/PbO₂ and Ti/TiO₂/RuO_x electrodes.

4 Conclusion

Some metallic oxides such as PbO₂, RuO_x, NiOOH and CoOOH were photoelectrochemically deposited on a Ti substrate under illumination during the anodic TiO₂ formation. The Ti/TiO₂/MO_x electrodes prepared under illumination acted as metal electrodes, where anodic tunneling current for the oxygen evolution reaction was observed. This will be occurred by Fermi-level pinning at the TiO₂/MO_x interfaces.

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