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Anodically deposited manganese–molybdenum–tungsten oxide anodes for oxygen evolution in seawater electrolysis

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Abstract

Ternary manganese–molybdenum–tungsten oxides were anodically deposited on to IrO_2-coated titanium substrates at current densities of 60–600 A m^{-2} in 0.4 M $MnSO_4$ solutions containing 0.003 M Na_2MoO_4 and 0.003 M Na_2WO_4 at pH 0–1.5 and at 30–90 °C. The effect of anodic deposition conditions on the activity, selectivity and durability of the anodes for oxygen evolution in 0.5 M NaCl solution was investigated. Most of the oxide anodes prepared initially gave an oxygen evolution efficiency of almost 100%. When the anodic deposition was performed at temperatures lower than 90 °C, gradual oxidative dissolution occurred during the electrolysis in the NaCl solution, due to formation of poorly crystalline oxides. In contrast, the oxide deposited at 90 °C revealed no obvious dissolution during electrolysis for more than 1500 h. The oxygen evolution efficiency, however, decreased gradually with time of electrolysis because of partial detachment of the deposited oxide. The anodic deposition in electrolytes at lower pH and at higher current density resulted in the formation of oxides with better adhesion to the substrate, resulting in improved anode durability. The durability was further improved by repeated anodic deposition with the oxide surface washed during intervals.

1. Introduction

In seawater electrolysis, chlorine evolution predominates at the anode rather than oxygen evolution, despite the fact that the equilibrium potential for oxygen evolution is lower than that for chlorine. However, if oxygen-evolving anodes in seawater electrolysis are tailored, there are several important practical applications related to energy and environmental issues. One of the applications is electricity transmission in seawater. For instance, in the Scandinavian Peninsula electricity generated using abundant hydraulic power is transmitted to the European Continent by high-voltage direct current transmission (HVDC) using underwater cables in the Baltic Sea. In sea storms the transmission cables are sometimes severed, and the electricity is then transmitted through the sea using electrodes preinstalled on both coasts of the Scandinavian Peninsula and the European Continent. Because of the absence of practical oxygen-evolving anodes in seawater electrolysis, a ruthenium–titanium oxide/Ti anode, which was developed the chlor-alkali industry, is currently used and an extremely low current density (i.e., 0.75 A m^{-2}) is applied in the HVDC using extremely large anodes to reduce the chlorine evolution to 5% in terms of current efficiency, which is economically unfavourable.

Among various anode materials examined so far, only anodically deposited MnO_2 anode is promising and shows relatively high oxygen evolution efficiency [1–4], although the efficiency is still insufficient. Recently, we have succeeded in improving the oxygen evolution efficiency of the MnO_2 by addition of molybdenum or tungsten to the oxide; an oxygen evolution efficiency of more than 99.9% has been attained for the electrolysis at a current density of 1000 A m^{-2} in 0.5 M NaCl solution at 30 °C [5–7]. The addition of molybdenum is more effective than tungsten addition in improving the initial oxygen evolution efficiency; an oxygen evolution efficiency of 100% has been attained on molybdenum-containing anodes. However, the anodic activity of the tungsten-containing anodes is higher than that of the molybdenum-containing anodes [6]. In the present study, the effect of simultaneous additions of molybdenum and tungsten on the oxygen evolution efficiency, activity and durability of the anodes has been examined in order to obtain anodes with high activity and selectivity for oxygen evolution in seawater electrolysis. The effect of anodic deposition conditions on the anode performance, particularly on the durability, has also been examined.

2. Experimental details

IrO_2-coated plane and expanded titanium substrates with geometrical surface area of about 100 mm^2 were used for anodic deposition. The IrO_2 coating was performed by thermal decomposition of chloroiridic acid as described elsewhere [8]. The intermediate IrO_2 layer avoids the formation of an insulating titanium oxide layer on titanium during electrolysis.

Manganese–molybdenum–tungsten oxides were anodically deposited on the IrO_2-coated titanium substrate at constant current densities of 100–1000 A m^{-2} in about 300 cm^3 of 0.4 M $MnSO_4$ solutions containing 0.003 M Na_2MoO_4 and 0.003 M Na_2WO_4 at pH 0–1.0 and 50–90 °C for 60 min. An electrolytic cell with separation of anode and cathode compartments was used for the anodic deposition. A platinum-coated titanium plate was used as a counter electrode.

The structure of the deposits was examined by α–2θ mode X-ray diffraction ($\alpha = 0.2°$) using CuK_α radiation. The molybdenum and tungsten contents in the deposits were determined using an electron probe microanalyser (Shimadzu EPMA-C1). The surface and cross section of the deposits were observed by scanning electron microscope (Jeol JSM-5400F).

Anodic polarization curves were measured galvanostatically. A current-interrupt method was used to compensate the IR drop. The oxygen evolution efficiency was measured by electrolysis at a constant current density of 1000 A m^{-2} in 300 cm^3 of 0.5 M NaCl solution until 300 C were passed. The detailed procedure was described elsewhere [8]. Briefly, the amount of chlorine formed was measured by iodometry. Assuming that the electric charge passed was used only for oxygen and chlorine evolution, the oxygen evolution efficiency was estimated from the difference between the total charge passed and that used for chlorine evolution. The durability of the electrode was examined by electrolysis at a current density of 1000 A m^{-2} in a 0.5 M NaCl solution at 30 °C and pH 8.

3. Results

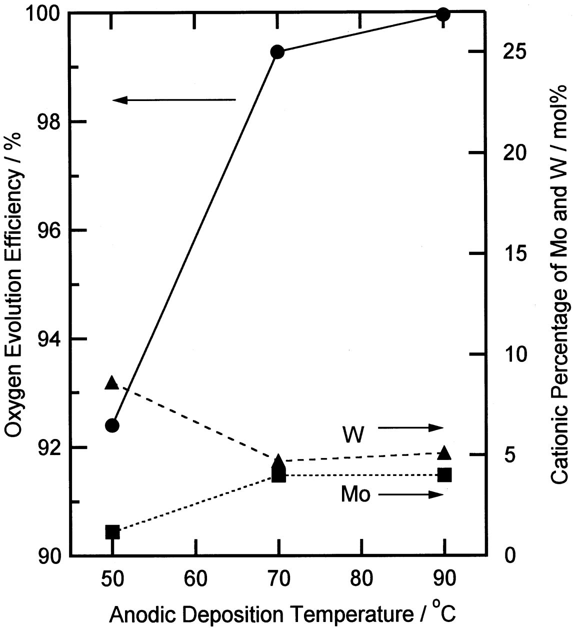

Fig. 1. Oxygen evolution efficiency of the manganese–molybdenum–tungsten oxides anodically deposited at 600 A m^{-2} in 0.4 M $MnSO_4$–0.003 M Na_2MoO_4–0.003 M Na_2WO_4 electrolyte of pH 0 as a function of deposition temperature. Change in the cationic percentages of molybdenum and tungsten in the ternary oxides with deposition temperature is also shown.

Figure 1 shows the oxygen evolution efficiency on the ternary oxide anodes anodically deposited at different temperatures. Cationic percentages of molybdenum and tungsten in the oxide deposited at each temperature are also shown. The oxygen evolution efficiency increases with deposition temperature, and an efficiency of 100% is attained at 90 °C. The cationic percentages of molybdenum and tungsten in the oxides are about 4 and 5 mol%, respectively, at deposition temperatures of both 70 and 90 °C. The oxide deposited at 50 °C has higher tungsten content (8 mol%) and lower molybdenum content (1 mol%). From our previous study [5], anodically deposited binary manganese–tungsten oxides gave high oxygen evolution efficiencies of more than 99%. Thus, the low oxygen evolution efficiency on the ternary oxide deposited at 50 °C may not be correlated with the composition of the oxide. X-ray diffraction patterns of the ternary oxides deposited at these three temperatures are shown in Figure 2. An X-ray diffrac-

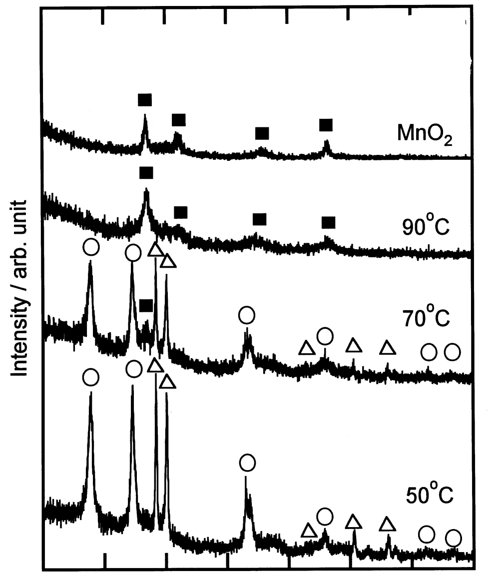

Fig. 2. X-ray diffraction patterns of the manganese–molybdenum–tungsten oxides anodically deposited at 600 A m^{-2} in 0.4 M $MnSO_4$–0.003 M Na_2MoO_4–0.003 M Na_2WO_4 electrolyte of pH 0 at 50, 70 and 90 °C. Key: (■) γ-MnO_2; (○) IrO_2; (△) Ti.

tion pattern of the MnO_2 deposited at 600 A m^{-2} in an 0.4 M $MnSO_4$ electrolyte without molybdate and tungstate ions at 90 °C is also shown for comparison. The X-ray diffraction pattern of the ternary oxide deposited at 90 °C reveals reflections corresponding to the γ-MnO_2, similarly to that of the anodically deposited MnO_2. However, at 70 and 50 °C the reflections of γ-MnO_2 are very weak and the reflections of underlying IrO_2 and titanium are relatively strong, indicating that only thin and poorly crystalline oxides have been deposited at lower temperatures. In fact it was confirmed from SEM observation that only a thin oxide layer, less than 1 μm thick, was deposited at 50 °C. In addition, when the oxides were deposited at temperatures lower than 90 °C, oxidative dissolution of manganese as permanganate ions occurred during electrolysis at 1000 A m^{-2} in 0.5 M NaCl solution. In contrast, such oxidative dissolution could not be found for the oxides deposited at 90 °C. Thus, for the preparation of the ternary anodes with high durability as well as with high oxygen evolution efficiency in seawater electrolysis, the temperature of anodic deposition must be as high as possible.

Figure 3 shows the oxygen evolution efficiency of the manganese–molybdenum–tungsten oxide anodes as a function of pH of the deposition electrolytes. The X-ray diffraction patterns of the ternary oxides deposited between pH 0–1.0 at 90 °C consisted only of reflections corresponding to γ-MnO_2 and no reflections from underlying substrates were detected, indicating the deposition of sufficiently thick oxides. As shown in Figure 3, all the anodes show high oxygen evolution efficiencies of 99.9% or more. Cationic percentages of molybdenum and tungsten in the deposited oxides increase with pH. The slightly low oxygen evolution efficiency of the anode deposited at pH 0 in comparison with those deposited at higher pH may be related to the low molybdenum content in the oxide deposited at pH 0; manganese–molybdenum binary oxides containing 8 mol% or more molybdenum in cationic percentage showed 100% oxygen evolution efficiency [6], whereas the oxygen evolution efficiency of manganese-tungsten binary oxides did not attain 100% [5]. Figure 4 shows the anodic polarization curves of these ternary oxides deposited at different pH. The Tafel slopes are similar, being about 160 mV $(\text{decade})^{-1}$, but the anodic activity increases slightly with decrease in pH. This pH dependence of the anodic activity is possibly related to the molybdenum content in the oxides. The manganese–molybdenum binary oxides containing 8 mol% or more molybdenum showed lower anodic activity for oxygen evolution than a molybdenum-free MnO_2 anode [6], contrasting with enhancement of the anodic activity of MnO_2 by the addition of tungsten [5]. From these previous results, an increase in the molybdenum content in the ternary oxide should decrease the anodic activity.

The durability oxide anodes is also dependent on pH (Figure 5). The oxygen evolution efficiency of the ternary oxide anodes decreases gradually with time of electrolysis in 0.5 M NaCl solution, due to partial detachment of the deposited oxides from the IrO_2-coated substrate. The oxygen evolution efficiency decreases more slowly on anodes deposited at lower pH. During anodic deposition, oxygen evolution occurred simultaneously and became more vigorous with a

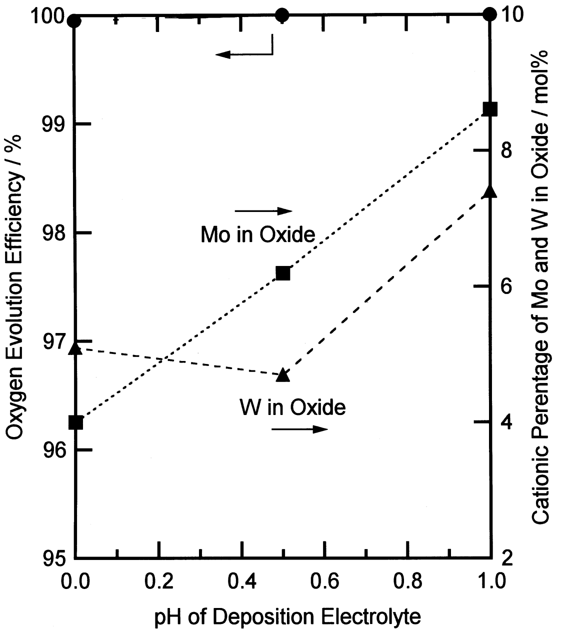

Fig. 3. Oxygen evolution efficiency of the manganese–molybdenum–tungsten oxides anodically deposited at 600 A m^{-2} in 0.4 M $MnSO_4$–0.003 M Na_2MoO_4–0.003 M Na_2WO_4 electrolyte at 90 °C as a function of pH of the deposition electrolyte. Change in the cationic percentages of molybdenum and tungsten in the ternary oxides with pH of deposition electrolyte is also shown.

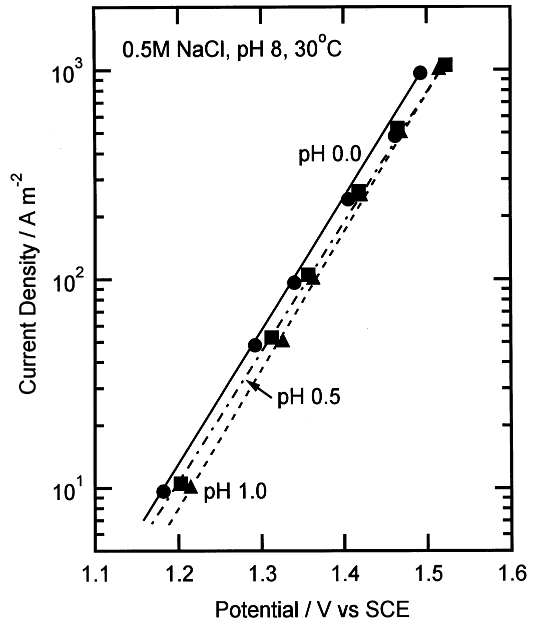

Fig. 4. Anodic polarization curves of the manganese–molybdenum–tungsten oxides anodically deposited at 600 A m^{-2} in 0.4 M $MnSO_4$–0.003 M Na_2MoO_4–0.003 M Na_2WO_4 electrolyte of pH 0, 0.5 and 1.0 at 90 °C, measured in 0.5 M NaCl solution at 30 °C.

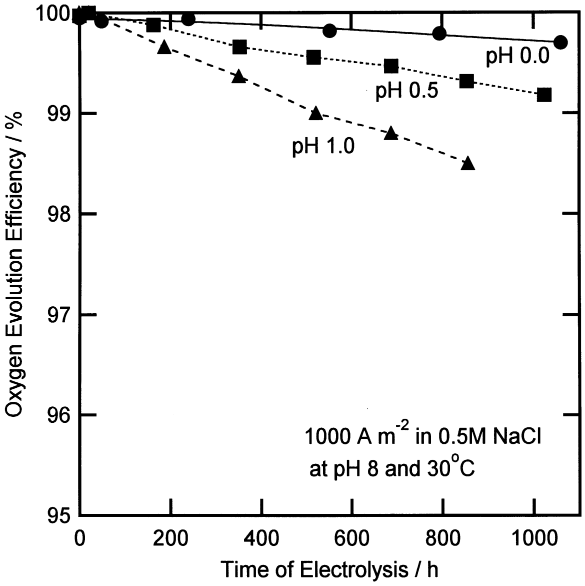

Fig. 5. Change in the oxygen evolution efficiency of the manganese–molybdenum–tungsten oxides anodically deposited at 600 A m^{-2} in 0.4 M $MnSO_4$–0.003 M Na_2MoO_4–0.003 M Na_2WO_4 electrolyte of pH 0, 0.5 and 1.0 at 90 °C with time of electrolysis at 1000 A m^{-2} in 0.5 M NaCl solution at 30 °C.

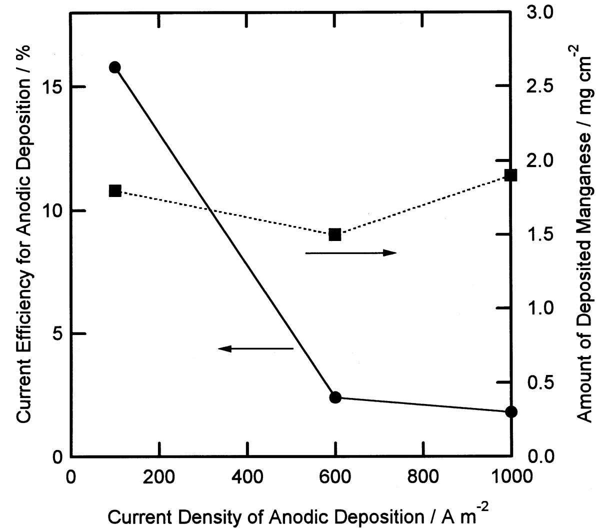

Fig. 7. Current efficiency for anodic deposition of the manganese–molybdenum–tungsten oxides anodically deposited in 0.4 M $MnSO_4$–0.003 M Na_2MoO_4–0.003 M Na_2WO_4 electrolyte of pH 0 at 90 °C for 60 min as a function of deposition current density. Change in the amount of deposited manganese in the ternary oxides with deposition current density is also shown.

decrease in pH. Under such vigorous oxygen evolution, oxides with poor adhesion to the substrate are likely to be detached during the deposition process and oxides with better adhesion can be redeposited at the detached areas. Consequently, oxides highly adherent to the substrate can be obtained at lower pH. Improvement of the adhesion by deposition at lower pH can be seen in the scanning electron micrographs shown in Figure 6. There are many cracks in all the deposited oxide layers; this is typical of anodically deposited manganese oxides with and without additive elements [7]. At pH 1.0 the cracks are wider and the areas surrounded by cracks are larger. In addition, there are several areas where deposited oxide appears to be detached during deposition, as well as those where the deposited oxides tend to be detached. Compared with this oxide deposited at pH 1.0, the oxides deposited at lower pH have higher crack density, but are apparently more adherent to the substrate.

Figure 7 shows the current efficiency for anodic deposition of the ternary oxides in the electrolyte of pH 0 at 90 °C for 60 min as well as the amount of deposited manganese ions as a function of the current density for anodic deposition. The current efficiency decreases with increase in current density, but the amount of manganese deposited does not change greatly with current density. Despite the deposition of similar amounts of manganese at current densities between 100 and 1000 A m^{-2}, the X-ray diffraction patterns of these specimens are different; the oxide deposited at 100 A m^{-2} reveals reflections from the underlying substrate, whereas such reflections are not clearly detected for the specimens deposited at 600 and 1000 A m^{-2}.

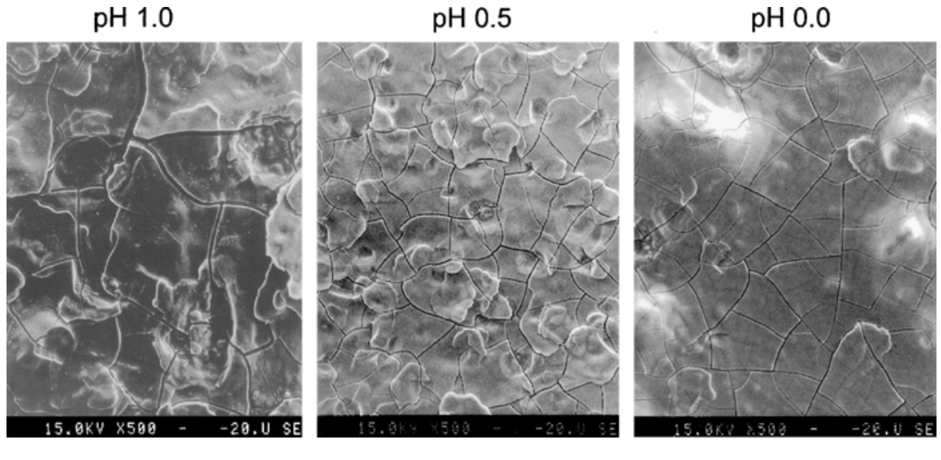
pH 1.0 pH 0.5 pH 0.0

Fig. 6. Scanning electron micrographs of surfaces of manganese–molybdenum–tungsten oxides anodically deposited at 600 A m^{-2} in 0.4 M $MnSO_4$–0.003 M Na_2MoO_4–0.003 M Na_2WO_4 electrolyte of pH 0, 0.5 and 1.0 at 90 °C.

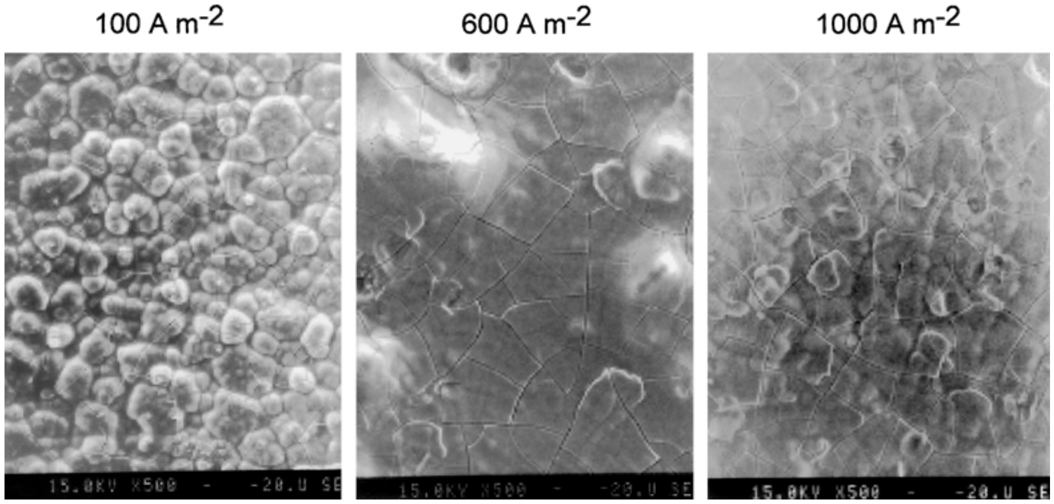

Fig. 8. Scanning electron micrographs of the surfaces of the manganese–molybdenum–tungsten oxides anodically deposited at 100, 600 and 1000 A m^{-2} in 0.4 M $MnSO_4$–0.003 M Na_2MoO_4–0.003 M Na_2WO_4 electrolyte of pH 0 at 90 °C.

The difference arises from the change in the morphology of the deposited oxides with deposition current density, as shown in the scanning electron micrographs (Figure 8). At a current density of 100 A m^{-2} surface is granular, indicating that the thickness of the oxide layer is non-uniform. The reflections from the underlying substrate in the X-ray diffraction pattern may be detected through the regions of thin oxide layer deposited. By contrast, the surface of oxides deposited at higher current densities is rather smooth, although cracks are present.

Despite the differences in surface morphology of oxides deposited at different current densities, all have high oxygen evolution efficiencies of more than 99.9% at 1000 A m^{-2} in 0.5 M NaCl solution, as shown in Figure 9. The cationic percentages of molybdenum and tungsten are about 4 and 5 mol%, respectively, in oxides deposited at 600 and 1000 A m^{-2}. At 100 A m^{-2} the tungsten concentration increases to more than 11 mol%, although the molybdenum concentration is unchanged. The high oxygen evolution efficiency of the oxides irrespective of tungsten concentration suggests that the presence of only about 5 mol% of molybdenum and tungsten is sufficient to give high oxygen evolution efficiency in the NaCl solution. Thus, all these oxides have initially high oxygen evolution efficiency. However, the oxygen evolution efficiency after prolonged electrolysis in NaCl is slightly dependent on the current density. As shown in Figure 10, the decrease in the oxygen

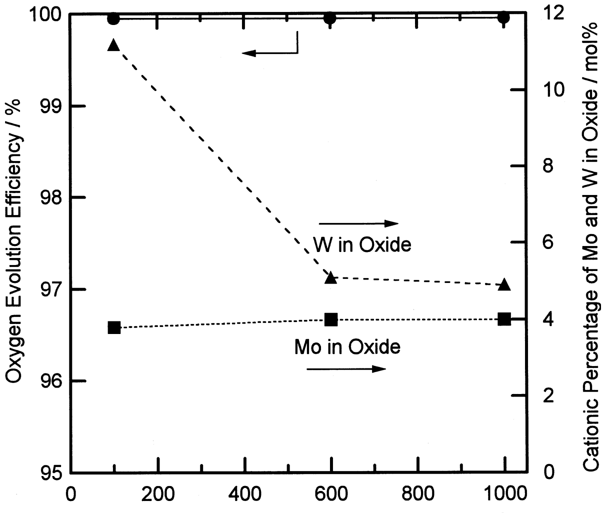

Fig. 9. Oxygen evolution efficiency of the manganese–molybdenum–tungsten oxides anodically deposited in 0.4 M $MnSO_4$–0.003 M Na_2MoO_4–0.003 M Na_2WO_4 electrolyte of pH 0 at 90 °C as a function of deposition current density. Change in the cationic percentages of molybdenum and tungsten in the ternary oxides with deposition current density is also shown.

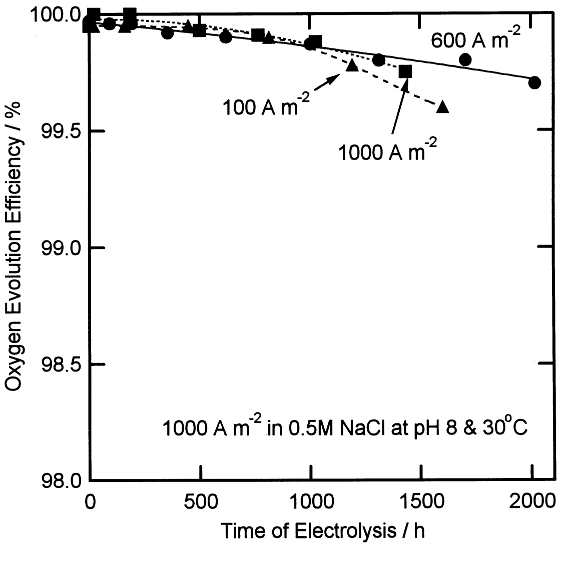

Fig. 10. Change in the oxygen evolution efficiency of the manganese–molybdenum–tungsten oxides anodically deposited at 100, 600 and 1000 A m^{-2} in 0.4 M $MnSO_4$–0.003 M Na_2MoO_4–0.003 M Na_2WO_4 electrolyte of pH 0 at 90 °C with time of electrolysis at 1000 A m^{-2} in 0.5 M NaCl solution at 30 °C.

evolution efficiency with time of electrolysis is slightly faster for the oxide anode deposited at a low current density of 100 A m^{-2}. The reason may also be due to the relatively poor adhesion of the oxide deposited at lower current densities; at higher current densities more vigorous oxygen evolution occurs during anodic deposition, resulting in the formation of an oxide layer that is not detached easily even by the high stresses due to violent gas evolution during electrolysis.

From these results, it has been found that anodically deposited manganese–molybdenum–tungsten oxide anodes show initially high oxygen evolution efficiencies of 99.9% or more at 1000 A m^{-2} in 0.5 M NaCl. Detachment of the deposited oxides from the substrate, which results in a gradual decrease in the oxygen evolution efficiency during electrolysis, is suppressed by anodic deposition at higher current density and at lower pH, under which vigorous oxygen evolution occurs simultaneously with deposition. The detachment of the deposited oxides during electrolysis, however, cannot be totally avoided even by deposition at a high current density of 600 A m^{-2} at pH 0 (Figure 11). From the micrograph and X-ray image of the underlying iridium, the deposited oxide is partly detached after electrolysis for 2000 h, and the surface of the underlying iridium oxide appears. Thus, chlorine evolution occurs on such regions, due to high efficiency for chlorine evolution on IrO_2.

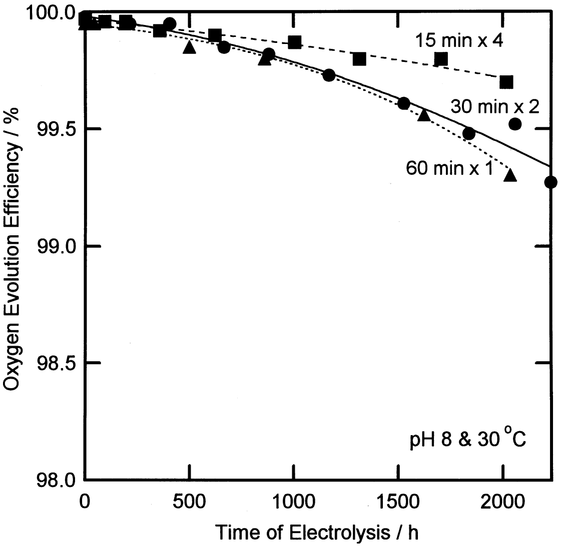

Fig. 12. Change in the oxygen evolution efficiency of the manganese–molybdenum–tungsten oxides anodically deposited at 600 A m^{-2} in 0.4 M $MnSO_4$–0.003 M Na_2MoO_4–0.003 M Na_2WO_4 electrolyte of pH 0 at 90 °C for 60 min, with time of electrolysis at 1000 A m^{-2} in 0.5 M NaCl solution at 30 °C and pH 8. Anodic deposition was carried out for 60 min with and without interruption every 15 and 30 min. Deposition electrolyte was exchanged and deposited oxide surface was washed during interruption.

To improve the durability of the ternary oxide anodes further, repeated anodic deposition was performed. In the repeated deposition, the deposition electrolyte was exchanged and the deposited oxide surface was washed in distilled water during the intervals. Since formation of too thick oxides must be avoided due to increased residual stress [8], the total deposition time was always set to be 60 min. Figure 12 shows the change in the oxygen evolution efficiency of the ternary oxide anodes deposited at different repeated times during electrolysis at 1000 A m^{-2} in 0.5 M NaCl at 30 °C. Obviously, the decrease in oxygen evolution efficiency is suppressed by repeated deposition. In particular, the four time depo-

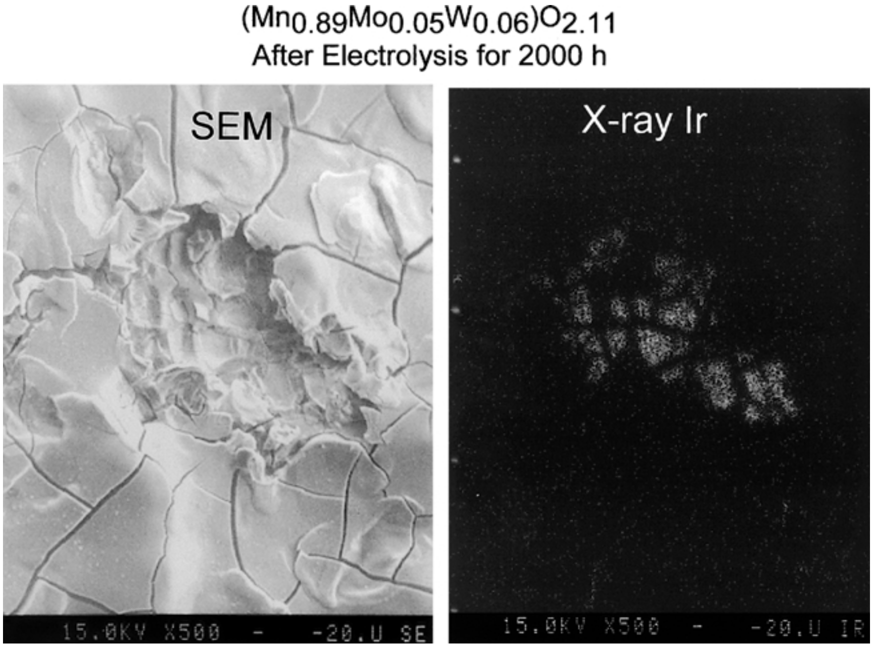

Fig. 11. A scanning electron micrograph and an X-ray image of iridium for the surface of the manganese–molybdenum–tungsten oxide anodically deposited at 600 A m^{-2} in 0.4 M $MnSO_4$–0.003 M Na_2MoO_4–0.003 M Na_2WO_4 electrolyte of pH 0 at 90 °C after electrolysis at 1000 A m^{-2} in 0.5 M NaCl solution at 30 °C for 2000 h.

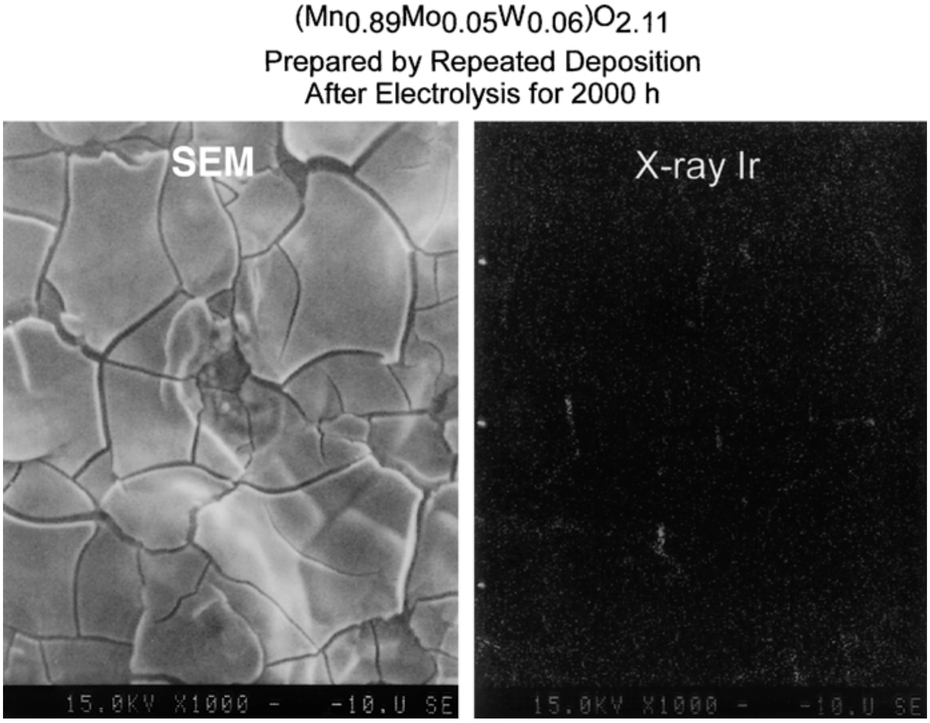

Fig. 13. A scanning electron micrograph and an X-ray image of iridium for the surface of the manganese–molybdenum–tungsten oxide anodically deposited at 600 A m^{-2} in 0.4 M $MnSO_4$–0.003 M Na_2MoO_4–0.003 M Na_2WO_4 electrolyte of pH 0 at 90 °C for 60 min, with interruption every 15 min after electrolysis at 1000 A m^{-2} in 0.5 M NaCl solution at 30 °C for 2000 h.

sition is effective, and an oxygen evolution efficiency of 99.7% is attained even after electrolysis for 2000 h. From surface observation using scanning electron microscopy and EPMA analysis (Figure 13), the severe detachment of the four times deposited oxide was not observed. Although, there are apparently detached regions, even in these regions underlying iridium was not clearly detected, suggesting detachment of only the outer part of the deposited oxide layer. This is probably due to formation of multilayers in the deposited oxide as a consequence of repeated deposition. Thus, exposure of the underlying IrO_2 surface to electrolyte during electrolysis is suppressed effectively, resulting in high oxygen evolution efficiencies even after prolonged electrolysis.

4. Discussion

The manganese–molybdenum–tungsten ternary oxides anodically deposited are solid solution oxides with γ-MnO_2 structure, similar to binary manganese–molybdenum and manganese–tungsten oxides prepared by anodic deposition. Molybdenum and tungsten are both in the hexavalent state, as confirmed by X-ray photoelectron spectroscopy [9]. Additions of molybdenum [6] and tungsten [5] into anodically deposited MnO_2 increase the oxygen evolution efficiency. The addition of molybdenum is particularly effective in enhancing the efficiency, resulting in 100% oxygen evolution efficiency [6]. From the polarization curves for oxygen and chlorine evolution, the enhancement of the oxygen evolution efficiency has been found to result from a significant increase in the overpotential for chlorine evolution by molybdenum addition, not due to enhancement of the activity for oxygen evolution [7], although the reason is still unclear. On the other hand, the addition of tungsten enhances the activity for oxygen evolution [5]. The activity for chlorine evolution is also suppressed by the addition of tungsten, but molybdenum addition reduces the activity for chlorine evolution more effectively than tungsten addition. The present ternary oxides containing both molybdenum and tungsten have shown oxygen evolution efficiencies of almost 100%, being similar to the manganese–molybdenum oxides. Thus, the addition of tungsten is not detrimental to sustaining the extremely high overpotential for chlorine evolution of the manganese–molybdenum oxides.

As shown in Figure 4, the activity for oxygen evolution increases with decrease in pH. This tendency may be correlated with a decrease in molybdenum content in oxides with decrease in pH, since manganese–molybdenum binary oxide anodes have lower activity for oxygen evolution than MnO_2 anodes. However, the ternary oxide deposited at pH 0 shows slightly higher activity for oxygen evolution than the manganese–molybdenum binary oxide anode. Thus, the simultaneous addition of small amounts of molybdenum and tungsten enhances the anodic activity without reducing the high oxygen evolution efficiency.

When the anodic deposition of the ternary oxides is carried out at below 70 °C, oxidative dissolution of manganese occurs during electrolysis, since the potential of the oxide anodes during electrolysis is higher than the equilibrium potential of the oxidation of MnO_2 to permanganate. Similarly to the present ternary oxides, oxidative dissolution has been found for manganese–molybdenum oxides anodically deposited at and below 70 °C [8]. However, both the binary and ternary oxides anodically deposited at 90 °C reveal no detectable oxidative dissolution. Oxidative dissolution also occurs for the MnO_2 oxide without molybdenum and tungsten even when anodic deposition is carried out at 90 °C [8]. Thus, additions of molybdenum and tungsten to the manganese oxide deposited at 90 °C suppress such dissolution in addition to chlorine evolution during electrolysis even at potentials far higher than the equilibrium potential for the oxidation of MnO_2 to permanganate. In other words, the additions of small amounts of molybdenum and tungsten form apparently new materials that have significantly different electrochemical characteristics from MnO_2, although almost no structural change occurs.

Although, oxidative dissolution can be avoided by anodic deposition of manganese oxides containing molybdenum and tungsten at 90 °C, the oxygen evolution efficiency still decreases gradually during electrolysis, due to partial detachment of the deposited oxides from the IrO_2-coated substrate. Detachment is related to the stress in the oxide layer, generated by gas evolution during electrolysis. Gas evolution also occurs during anodic deposition of the manganese–molybdenum–tungsten oxides. Thus, it is expected that anodic deposition under more vigorous gas evolution results in the formation of an oxide layer more adherent to the substrate. In fact, the deposition of ternary oxides at higher current density and at lower pH improves the durability of the oxide anode for oxygen evolution in NaCl solution. Many cracks are present in the oxide layers and most of the cracks appear to penetrate to the substrate. In order to avoid the penetration of cracks into the substrate, repeated anodic deposition was carried out in the present study. It has been found that the repeated deposition enhances the durability of the ternary oxide anode. After electrolysis for 2000 h, regions with a detached oxide layer were absent. As shown in Figure 13 it was found occasionally that only the outer part of the oxide layer was detached. The detachment of only the outer part of the oxide layer may be associated with the multilayered structure of the deposited oxide. In this manner, the manganese–molybdenum–tungsten oxide anodes with high oxygen evolution efficiency and high durability have been obtained by modifying the deposition conditions.

5. Conclusions

Manganese–molybdenum–tungsten ternary oxides prepared on IrO_2-coated titanium substrates by anodic deposition in 0.4 M $MnSO_4$–0.003 M Na_2MoO_4–0.003 M Na_2WO_4 electrolyte had γ-MnO_2 structure. Anodic deposition at and below 70 °C resulted in oxidative dissolution of manganese as permanganate ions during electrolysis at 1000 A m^{-2} in 0.5 M NaCl solution. Such dissolution was, however, avoided by anodic deposition at 90 °C. This temperature dependence of the oxidative dissolution was related to the crystallinity of the deposited oxides; the oxides deposited at and below 70 °C were poorly crystalline, and revealed oxidative dissolution during electrolysis. The ternary oxides deposited at 90 °C gave high oxygen evolution efficiency of 99.9% or more at 1000 A m^{-2} in 0.5 M NaCl solution. The high oxygen evolution efficiency was sustained when the anodic deposition was performed under vigorous oxygen evolution, that is, high current density and lower pH, due to improvement of the adhesion of the deposited oxides. Repeated anodic deposition with the oxide surface washed and the deposition electrolyte exchanged improved the durability of the oxide anode for oxygen evolution further, as a consequence of the formation of multilayered deposits, which effectively suppressed the exposure of the underlying substrate to the electrolyte by detachment. The ternary oxides sustained the high oxygen evolution efficiency of manganese–molybdenum binary oxides and also had slightly higher activity for oxygen evolution.

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