

**The Effect of Antimony in the Intermediate  $\text{IrO}_2\text{-SnO}_2\text{-Sb}_2\text{O}_5$   
Oxide Layer on Titanium Substrate for Oxygen Evolution  
 $\text{Mn}_{1-x-y}\text{Mo}_x\text{Sn}_y\text{O}_{2+x}$  Anodes in Seawater Electrolysis**

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**Abstract**

*An attempt is made to find out the optimal compositions for the intermediate oxide layer of  $\text{IrO}_2\text{-SnO}_2\text{-Sb}_2\text{O}_5$  in preventing insulating titanium oxide formation on titanium substrate for the oxygen evolution  $\text{Mn}_{1-x-y}\text{Mo}_x\text{Sn}_y\text{O}_{2+x}$  anodes in electrolysis of 0.5 M NaCl of pH 1 at  $1000 \text{ A.m}^{-2}$ . Effects of antimony and iridium in the intermediate  $\text{IrO}_2\text{-SnO}_2\text{-Sb}_2\text{O}_5$  layer are discussed. The 75 % of the iridium content in the intermediate layer of the oxygen evolution anodes can be substituted by  $\text{SnO}_2$  and small amount of  $\text{Sb}_2\text{O}_5$  to increase the electronic conductivity of the intermediate layer as well as the activity of the  $\text{Mn}_{1-x-y}\text{Mo}_x\text{Sn}_y\text{O}_{2+x}/\text{IrO}_2\text{-SnO}_2\text{-Sb}_2\text{O}_5/\text{Ti}$  anodes for seawater electrolysis at pH 1. Although  $\text{Sb}^{5+}$  addition is effective in decreasing the  $\text{Ir}^{4+}$  concentration in the intermediate layer of the anodes, the  $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}$  intermediate layers with the  $\text{Sb}^{5+}/\text{Sn}^{4+}$  between 0.125–0.285 in the coating solution showed excellent performance of the oxygen evolution efficiency. All the examined manganese–molybdenum–tin triple oxides,  $\text{Mn}_{1-x-y}\text{Mo}_x\text{Sn}_y\text{O}_{2+x}$ , prepared by anodic deposition on the  $\text{IrO}_2\text{-SnO}_2\text{-Sb}_2\text{O}_5$ -coated titanium substrate showed around 99 % initial oxygen evolution efficiency at a current density of  $1000 \text{ A.m}^{-2}$  in 0.5 M NaCl of pH 1 at  $25^\circ\text{C}$ .*

**Keywords:** *global  $\text{CO}_2$  recycling, hydrogen production electrode,  $\text{IrO}_2\text{-SnO}_2\text{-Sb}_2\text{O}_5$  layer, 0.5 M NaCl, titanium substrate.*

**Introduction**

It is not meaningful to decrease only the economic activity of the world for the reduction of  $\text{CO}_2$  emissions, which induce global warming, only by efforts for energy saving and by improvements of the energy efficiency. Considering these

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facts, Hashimoto and his group of Tohoku University are proposing effective CO<sub>2</sub> recycling to prevent global warming and to supply abundant energy converted from solar energy, and hence they have tailored the necessary key materials, that is, anodes and cathodes for seawater electrolysis and catalysts for CO<sub>2</sub> methanation.<sup>1-8</sup> In this project, the reaction between the hydrogen produced from seawater electrolysis and global CO<sub>2</sub> is carried out in presence of corrosion-resistant catalysts to produce the methane gas as a source of the abundant energy.

For safety production of hydrogen in seawater electrolysis, oxygen production is prerequisite without forming chlorine. In general, seawater electrolysis is practically carried out for chlorine production. Although the equilibrium potential of oxygen evolution is lower than that of chlorine evolution, the chlorine evolution is a simpler reaction than the oxygen evolution, and hence the formation of chlorine on the anode is generally unavoidable in seawater electrolysis. Nevertheless, for large-scale seawater electrolysis for prevention of global warming, environmentally harmful chlorine release is not allowed. Therefore, one of the most difficult subjects in tailoring key materials for the global CO<sub>2</sub> recycling was the anode for seawater electrolysis because, for the abundant energy (that is, CH<sub>4</sub>) production a great quantity of chlorine emissions are not allow, and hence the anode should evolve only oxygen with very high efficiency and durability even in seawater electrolysis at very high current density.

Hashimoto and his co-workers have tailored many efficient anodes prepared by thermal<sup>9-11</sup> and anodic deposition.<sup>12-18</sup> These anodes were constructed by three layers; the outer layer is the electrocatalyst of  $\gamma$ -MnO<sub>2</sub>-type double or triple oxides, the intermediate layer is generally IrO<sub>2</sub> and the inner layer is titanium substrate. The IrO<sub>2</sub> intermediate layer on titanium substrate was generally formed using the butanolic solution containing 0.52 M Ir<sup>4+</sup>. The IrO<sub>2</sub> layer with the same rutile structure as TiO<sub>2</sub> was necessary to avoid the formation of insulating titanium oxide on the titanium substrate during anodic polarization at very high current density.

Iridium (IV) oxide is widely used as a dimensionally stable anode (DSA) in various electro-processes because IrO<sub>2</sub> acts as the effective anode and has high corrosion resistance among electroanalytically active oxides of platinum group metals. However, in order to supply a future hydrogen demand in the world, the amount of iridium is not sufficient for seawater electrolysis. The alternative materials to IrO<sub>2</sub> for prevention of oxidation of the titanium substrate during anodic polarization should have high stability at high potentials and the same rutile structure as TiO<sub>2</sub>. On the other hand, tin oxide (SnO<sub>2</sub>) has the rutile structure and is more stable than IrO<sub>2</sub>. However, the electronic conductivity of SnO<sub>2</sub> is very low as compared to IrO<sub>2</sub>. Therefore, the electronic conductivity of the tin (IV) oxide containing intermediate layer will be improved by the addition of Sb<sub>2</sub>O<sub>5</sub>. Thus, tin and antimony were thought to be candidates of alternative elements to iridium in the intermediate oxide layer. In this context, present work is focused to study the effects

of antimony and iridium in the intermediate  $\text{IrO}_2\text{-SnO}_2\text{-Sb}_2\text{O}_5$  layer on titanium substrate for oxygen evolution  $\text{Mn}_{1-x-y}\text{Mo}_x\text{Sn}_y\text{O}_{2+x}$  anodes in seawater electrolysis.

The present study is aimed to find out the optimal compositions for the intermediate oxide layer of the  $\text{IrO}_2\text{-SnO}_2\text{-Sb}_2\text{O}_5$  in preventing insulating titanium oxide formation on titanium substrate for the oxygen evolution  $\text{Mn}_{1-x-y}\text{Mo}_x\text{Sn}_y\text{O}_{2+x}$  anodes in electrolysis of 0.5 M NaCl of pH 1 at  $1000 \text{ A.m}^{-2}$ .

## **Experimental Methods**

Punched titanium metal substrate was immersed in a 0.5 M HF solution for 5 min to remove air-formed oxide film, rinsed with de-ionized water and then subjected for surface roughening by etching in 11.5 M  $\text{H}_2\text{SO}_4$  solution at  $80^\circ\text{C}$  until hydrogen evolution was ceased due to the coverage of the surface by titanium sulfate. Titanium sulfate on the titanium surface was removed by washing under tap water for about 1 hour. Then the etched-titanium sheet was used as substrate for coating of intermediate oxide layer.

Chloroiridic acid ( $\text{H}_2\text{IrCl}_6$ ), Tin (IV) chloride and antimony (V) chloride solutions having the concentration of 0.1 M (called as 100% solution in this study) each were prepared in butanol as a stock solution. The stock solutions of Chloroiridic acid, tin (IV) chloride and antimony (V) chloride were mixed to prepare the coating solution for intermediate oxide layer having different amounts of iridium, tin and antimony. The amounts of iridium and antimony in the coating solution were ranges from 0.005 to 0.100 M (that is, 5-100 %  $\text{Ir}^{4+}$ ) and from 0.001 to 0.085 M (that is, 1-85 %  $\text{Sb}^{5+}$ ), respectively. The coating solution was used for coating on the etched-titanium substrate with a brush, dried at  $80^\circ\text{C}$  for 10 min, and then baked at  $450^\circ\text{C}$  for 10 min in air. This coating procedure was repeated for three times so as to form the intermediate oxide layers of  $\text{IrO}_2\text{-SnO}_2\text{-Sb}_2\text{O}_5$  on titanium substrate. This specimen was finally baked at  $450^\circ\text{C}$  for 1 h in air. The presence of the  $\text{IrO}_2\text{-SnO}_2\text{-Sb}_2\text{O}_5$  layer is necessary to prevent the formation of insulating titanium oxide between electrocatalytically active substances and the titanium substrate during electrodeposition and electrolysis of seawater at high current density for a long time. This  $\text{IrO}_2\text{-SnO}_2\text{-Sb}_2\text{O}_5$  -coated titanium substrate was cut into  $16 \times 75 \times 1 \text{ mm}^3$  as suitable electrode and a titanium wire was spot-welded to its edge. This is called the intermediate  $\text{IrO}_2\text{-SnO}_2\text{-Sb}_2\text{O}_5/\text{Ti}$  substrate.

The intermediate  $\text{IrO}_2\text{-SnO}_2\text{-Sb}_2\text{O}_5/\text{Ti}$  substrate specimen was cleaned by anodic polarization at the current density of  $1000 \text{ A.m}^{-2}$  for 5 min in 10 M NaOH and then electroanalytically activated at  $1000 \text{ A.m}^{-2}$  for 5 min in 1 M  $\text{H}_2\text{SO}_4$  at room temperature. The  $\text{Mn}_{1-x-y}\text{Mo}_x\text{Sn}_y\text{O}_{2+x}$  anodes were anodically deposited on the clean and activated  $\text{IrO}_2\text{-SnO}_2\text{-Sb}_2\text{O}_5/\text{Ti}$  substrate at  $600 \text{ A.m}^{-2}$  in the solution containing 0.2 M  $\text{MnSO}_4 \cdot 5\text{H}_2\text{O} + 0.003 \text{ M Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O} + 0.006 \text{ M SnCl}_4 \cdot 2\text{H}_2\text{O}$  at pH -0.1 and  $90^\circ\text{C}$  for 90 minutes (3 x 30 min). The electrodeposition of the  $\text{Mn}_{1-x-y}\text{Mo}_x\text{Sn}_y\text{O}_{2+x}$

anodes was carried out by exchanging fresh electrolyte for every 30 minutes. The pH of the electrolyte was initially adjusted to -0.1 by adding concentrated H<sub>2</sub>SO<sub>4</sub>. An anode compartment was an alumina cylindrical diaphragm and a cathode was a pair of 316 stainless steel sheets set on the outside of the diaphragm in the cell so as to put the intermediate oxide layer-coated titanium substrate in the diaphragm between the stainless steel sheets.

The oxygen evolution efficiency was measured by electrolysis at constant current density of 1000 A.m<sup>-2</sup> in 300 mL of 0.5 M NaCl solution of pH 1 at 25°C until the amount of charges of 300 coulombs was passed. The amount of oxygen evolved was determined as the difference between the total charge passed and the charge for chlorine formation during electrolysis as described elsewhere.<sup>19,20</sup> Amount of chlorine formed was analyzed by idiomatic titration of chlorine and hypochlorite.

Galvanostatic polarization curve of the Mn<sub>1-x-y</sub>Mo<sub>x</sub>Sn<sub>y</sub>O<sub>2+x</sub>/IrO<sub>2</sub>-SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>5</sub>/Ti anodes was measured in 0.5 M NaCl solution of pH 1 at 25°C. The ohmic drop was corrected using a current interruption method. The potential written in this paper hereafter is the overpotential and relative to Ag/AgCl reference electrode with saturated KCl solution.

## Results and Discussion

Figure 1 shows the initial oxygen evolution efficiency of the electrodeposited Mn<sub>1-x-y</sub>Mo<sub>x</sub>Sn<sub>y</sub>O<sub>2+x</sub>/IrO<sub>2</sub>-SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>5</sub>/Ti anodes measured at the current density of 1000 A.m<sup>-2</sup> in 0.5 M NaCl of pH 1 at 25°C, as a function of the concentration of Sb<sup>5+</sup> in the coating solution. Amounts of iridium and antimony in the coating solution were fixed in the range of 0.005–0.100 M (that is, 5–100 % Ir<sup>4+</sup>) and of 0.001–0.085 M (that is, 1–85 %) Sb<sup>5+</sup>, respectively. The total concentrations of Sn<sup>4+</sup> and Sb<sup>5+</sup> in the coating solution were also fixed in the range of 0.095 M–0.040 M (that is, 95–40 % of tin and antimony). The initial oxygen evolution efficiency of all the examined Mn<sub>1-x-y</sub>Mo<sub>x</sub>Sn<sub>y</sub>O<sub>2+x</sub> anodes electrodeposited on the intermediate IrO<sub>2</sub>-SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>5</sub> layer containing less than 0.050 M (that is, 50 %) Sb<sup>5+</sup> is around 99 % or high. A further increase in the amount of Sb<sup>5+</sup> in the intermediate oxide layer (that is, more than 50 % Sb<sup>5+</sup>), the initial oxygen evolution efficiency of the anodes is also decreased with increasing Sb<sup>5+</sup> content in the coating solution. In general, the Mn<sub>1-x-y</sub>Mo<sub>x</sub>Sn<sub>y</sub>O<sub>2+x</sub> anodes, those were deposited on the intermediate oxide layers of IrO<sub>2</sub>-SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>5</sub> containing less than 0.020 M (that is, 20 %) Sb<sup>5+</sup> in the coating solutions, show the highest initial oxygen evolution efficiency. These results revealed that small additions of Sb<sup>5+</sup> in the intermediate IrO<sub>2</sub>-SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>5</sub> layer on titanium substrate seems to be effective for the high oxygen evolution efficiency of the Mn<sub>1-x-y</sub>Mo<sub>x</sub>Sn<sub>y</sub>O<sub>2+x</sub> anodes. However, it is necessary to study the

stability test of these electrodes for long time electrolysis that will be discussed subsequently in future studies.

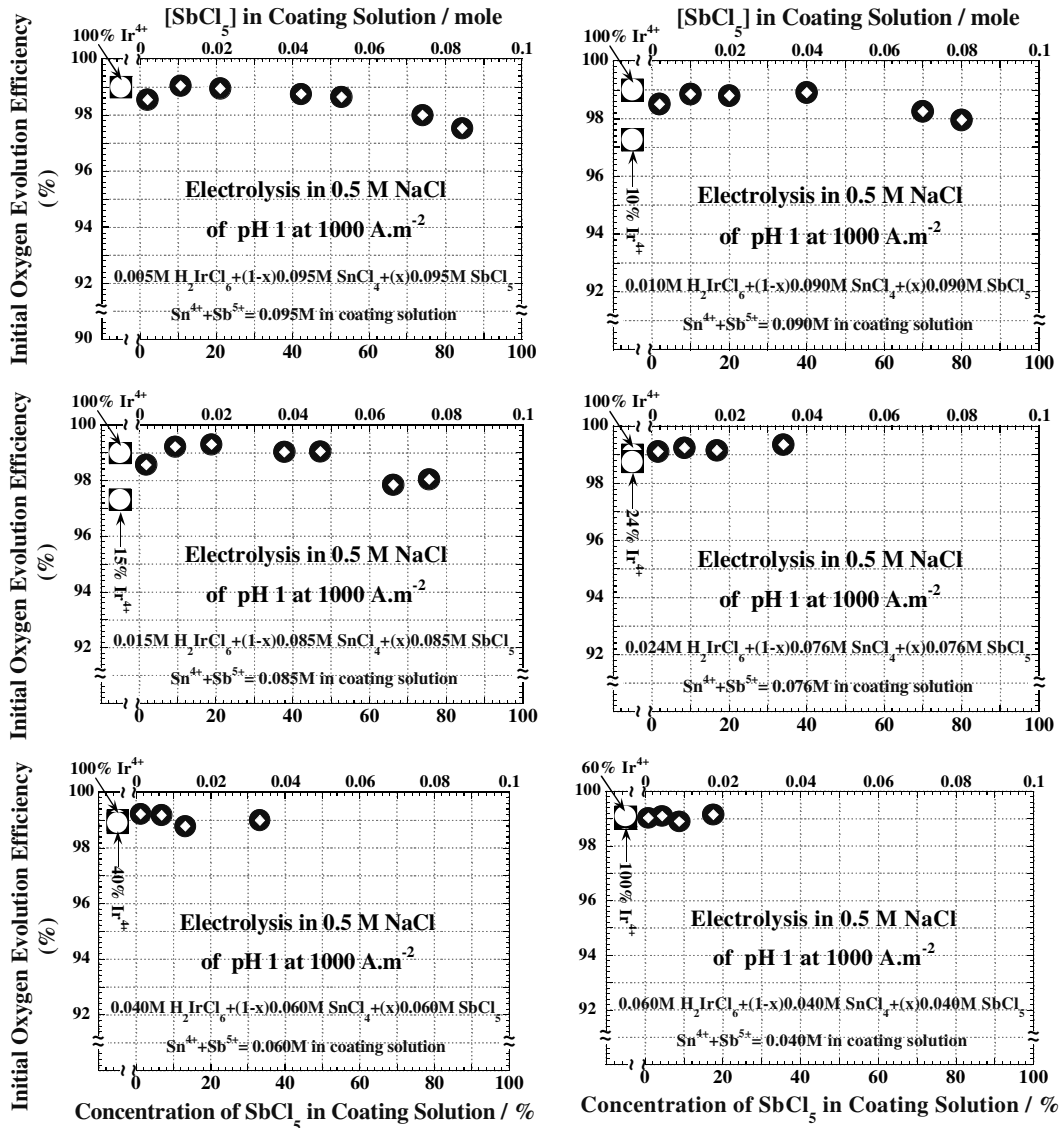


Figure 1: Changes in oxygen evolution efficiency of the electrodeposited  $Mn_{1-x-y}Mo_xSn_yO_{2+x}$  anodes on the intermediate  $IrO_2-SnO_2-Sb_2O_5$  layer containing 0.005–0.060 M (5–60 %) iridium in 0.5 M NaCl of pH 1 at the current density of  $1000 A.m^{-2}$ , as a function of antimony content in the coating solution. The oxygen evolution efficiency of the anodes containing 10, 15, 24, 40, 60 and 100%  $Ir^{4+}$  only without  $Sb^{5+}$  and  $Sn^{4+}$  in the coating solutions is also shown for comparison.

Figure 2 shows IR-corrected galvanostatic polarization curves measured in 0.5 M NaCl solution of pH 1 for the  $Mn_{1-x-y}Mo_xSn_yO_{2+x}$  anodes deposited on the  $IrO_2-SnO_2-Sb_2O_5/Ti$  substrate prepared by using the coating solution with different concentrations of antimony. The polarization curves of all the examined anodes shift upwards with a decrease in the concentrations of antimony in the intermediate layer, indicating the increase in the activity of the anodes. The change in the oxygen overpotential at  $1000 A.m^{-2}$  as a function of the concentration of  $Sb^{5+}$  in the coating solution is also shown in Fig. 3. In particular, the overpotential is clearly increased with increasing the concentration of antimony in the intermediate layer of the  $Mn_{1-x-y}Mo_xSn_yO_{2+x}/IrO_2-SnO_2-Sb_2O_5/Ti$  anodes, when the concentration of the  $Ir^{4+}$  is 0.014 M (15%) or less content in the intermediate layer of the anodes. On the other hand, the oxygen overpotentials of the anodes containing 0.024–0.060 M (24–60 %)  $Ir^{4+}$  in the intermediate layers are very close to that of the 0.100 M (100 %)  $Ir^{4+}$  only without tin and antimony contents in the coating solution, and are almost independent with the concentrations of  $Sb^{5+}$  up to about 0.040 M (40 %) of antimony. These results revealed that  $\frac{3}{4}$ <sup>th</sup> of the iridium content in the intermediate layer of the oxygen evolution anodes can be substituted by  $SnO_2$  and  $Sb_2O_5$  to increase the electronic conductivity of the intermediate layer as well as the activity of the oxygen evolution of the  $Mn_{1-x-y}Mo_xSn_yO_{2+x}/IrO_2-SnO_2-Sb_2O_5/Ti$  anodes for seawater electrolysis at pH 1 if the ratios of the  $Sb^{5+}$  and  $Sn^{4+}$  are fixed in the ranges of 0.125 to 0.285 in the intermediate  $IrO_2-SnO_2-Sb_2O_5$  layer of the anodes.

Figure 4 shows the initial oxygen evolution efficiency of the electrodeposited  $Mn_{1-x-y}Mo_xSn_yO_{2+x}/IrO_2-SnO_2-Sb_2O_5/Ti$  anodes measured at the current density of  $1000 A.m^{-2}$  in 0.5 M NaCl of pH 1 at  $25^\circ C$ , as a function of the concentration of  $Ir^{4+}$  in the coating solution. The ratios of  $Sb^{5+}$  and  $Sn^{4+}$  (that is,  $Sb^{5+}/Sn^{4+}$ ) in the coating solutions were also fixed in the ranges of 0.022–0.800 as shown in Figs 4(a)–(d). The initial oxygen evolution efficiency of all the examined  $Mn_{1-x-y}Mo_xSn_yO_{2+x}$  anodes on the intermediate layer formed from 0.015–0.060 M (that is, 15–60 %)  $Ir^{4+}$  solution is about 99 % and independent of the concentration of iridium in the intermediate layer. However, a slight decrease in the initial oxygen evolution efficiency of the anodes on the intermediate layer formed from 0.005–0.010 M (5–10 %)  $Ir^{4+}$  in the coating solution is clearly observed, particularly for those anodes deposited on the intermediate  $IrO_2-SnO_2-Sb_2O_5$  layer containing very small amount of  $Sb^{5+}$  (that is,  $Sb^{5+}/Sn^{4+} = 0.022$  as shown in Fig. 4. a) and very high amount of  $Sb^{5+}$  (that is,  $Sb^{5+}/Sn^{4+} = 0.800$  as shown in Fig. 4.d) in the coating solution. These results revealed that both very small and high amounts of antimony addition in the intermediate  $IrO_2-SnO_2-Sb_2O_5$  layer of the  $Mn_{1-x-y}Mo_xSn_yO_{2+x}/IrO_2-SnO_2-Sb_2O_5/Ti$  anodes are not effective to decrease the use of  $IrO_2$ , maintaining the high activity of oxygen evolution in seawater at pH 1. Consequently, the ratio of the  $Sb^{5+}/Sn^{4+}$  should be in between 0.125 to 0.285 in the intermediate layer for the most effective  $Mn_{1-x-y}Mo_xSn_yO_{2+x}/IrO_2-SnO_2-Sb_2O_5/Ti$  anodes for seawater electrolysis.

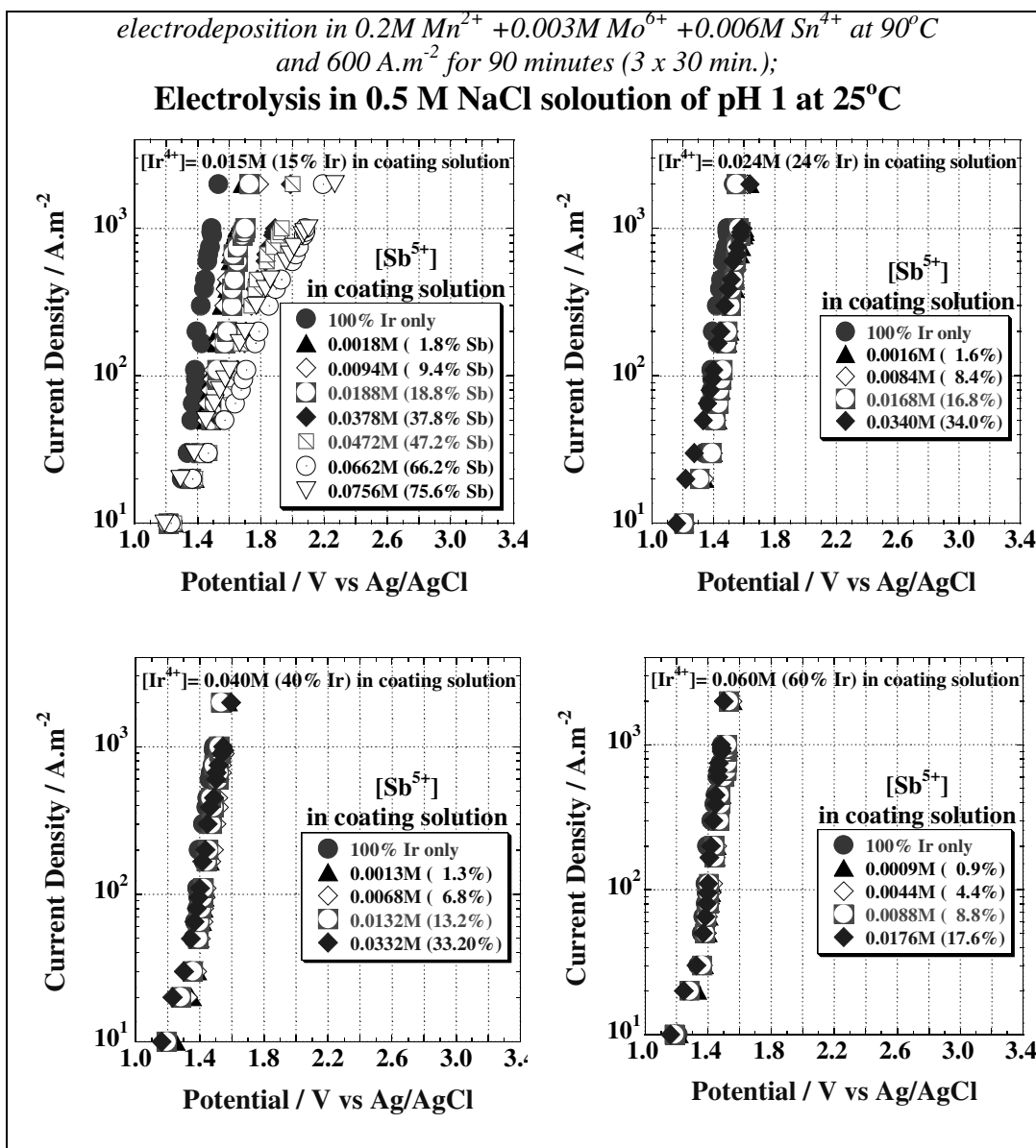


Figure 2: Galvanostatic polarization curves measured in 0.5 M NaCl of pH 1 for Mn<sub>1-x-y</sub>Mo<sub>x</sub>Sn<sub>y</sub>O<sub>2+x</sub> electrodes prepared by anodic deposition on the intermediate IrO<sub>2</sub>-SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>5</sub> layer with different amounts of IrO<sub>2</sub>, SnO<sub>2</sub> and Sb<sub>2</sub>O<sub>5</sub>.

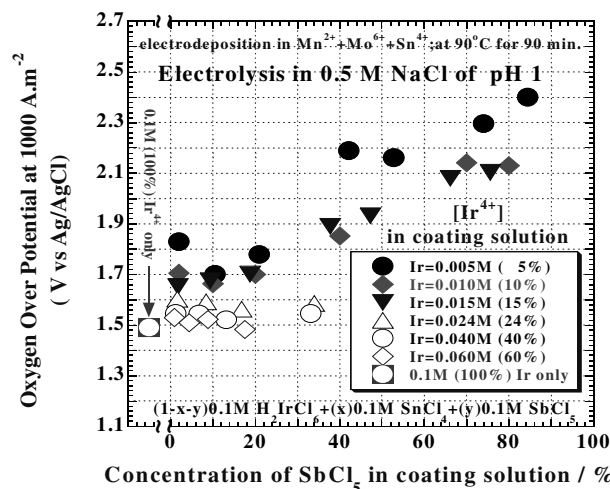


Figure 3: Changes in oxygen overpotential at the current density of  $1000 \text{ A.m}^{-2}$  in  $0.5 \text{ M NaCl}$  solution of pH 1 for the  $\text{Mn}_{1-x-y}\text{Mo}_x\text{Sn}_y\text{O}_{2+x}$  anodes prepared by anodic deposition on the intermediate  $\text{IrO}_2\text{-SnO}_2\text{-Sb}_2\text{O}_5$  layers with different amounts of  $\text{Ir}^{4+}$  and  $\text{Sn}^{4+}$ , as a function of antimony in the coating solution.

Figure 5 shows IR-corrected galvanostatic polarization curves measured in  $0.5 \text{ M NaCl}$  solution of pH 1 at  $25^\circ\text{C}$  for the electrodeposited  $\text{Mn}_{1-x-y}\text{Mo}_x\text{Sn}_y\text{O}_{2+x}$  anodes on the  $\text{IrO}_2\text{-SnO}_2\text{-Sb}_2\text{O}_5/\text{Ti}$  substrate prepared by using the coating solution with different concentrations of iridium (that is, 5-100%  $\text{Ir}^{4+}$ ). In the same time, effects of the  $\text{Sb}^{5+}/\text{Sn}^{4+}$  ratios in the intermediate layer are also studied. The polarization curves of those anodes deposited on the intermediate layer containing very low and high amounts of antimony (that is,  $\text{Sb}^{5+}/\text{Sn}^{4+} = 0.022$  and  $\text{Sb}^{5+}/\text{Sn}^{4+} = 0.800$ ) shift upwards with increasing the concentration of iridium in the intermediate layer, indicating the increase in the activity of the anodes with increasing the iridium content in the intermediate layer of these oxygen evolution anodes. However, there is no clear shift of the polarization curves, with iridium content, of those anodes which are electrodeposited on the intermediate layers containing the  $\text{Sb}^{5+}/\text{Sn}^{4+}$  ratios between 0.125–0.285. The change in the oxygen overpotential at  $1000 \text{ A.m}^{-2}$  as a function of the concentration of  $\text{Ir}^{4+}$  in the coating solution is also shown in Fig. 6. There is almost no change of the oxygen overpotential with decreasing the concentration of iridium upto  $0.024 \text{ M}$  (24 % Ir) and is almost same as that of  $0.100 \text{ M}$  (100 %)  $\text{Ir}^{4+}$  without tin and antimony in the coating solution. On the other hand, the increase of the oxygen overpotential is clearly observed if the concentration of iridium in the intermediate layer is less than  $0.015 \text{ M}$  (15 %) as shown in Fig. 6. In particular, the increase of the overpotential is more significantly observed for those anodes deposited on the  $\text{IrO}_2\text{-SnO}_2\text{-Sb}_2\text{O}_5/\text{Ti}$  layer containing very high and very low amounts of antimony. These results revealed that about  $\frac{3}{4}$ th of the iridium can be substituted by  $\text{SnO}_2$  and addition of



antimony should not be too high and low to maintain the high electronic conductivity of the intermediate oxide layer of  $Mn_{1-x-y}Mo_xSn_yO_{2+x}/SnO_2-Sb_2O_5/Ti$  anodes for seawater electrolysis at high current density.

### Conclusions

An attempt is made to reduce the use of  $IrO_2$  by the  $IrO_2-SnO_2-Sb_2O_5$  intermediate layer and to find out the optimal compositions for the intermediate oxide layer which is necessary to avoid the growth of insulating titanium oxide on the titanium substrate for oxygen evolution  $\gamma-MnO_2$  type  $Mn_{1-x-y}Mo_xSn_yO_{2+x}$  anodes in 0.5 M NaCl of pH 5 at 25°C. The following conclusions are drawn from the present study:

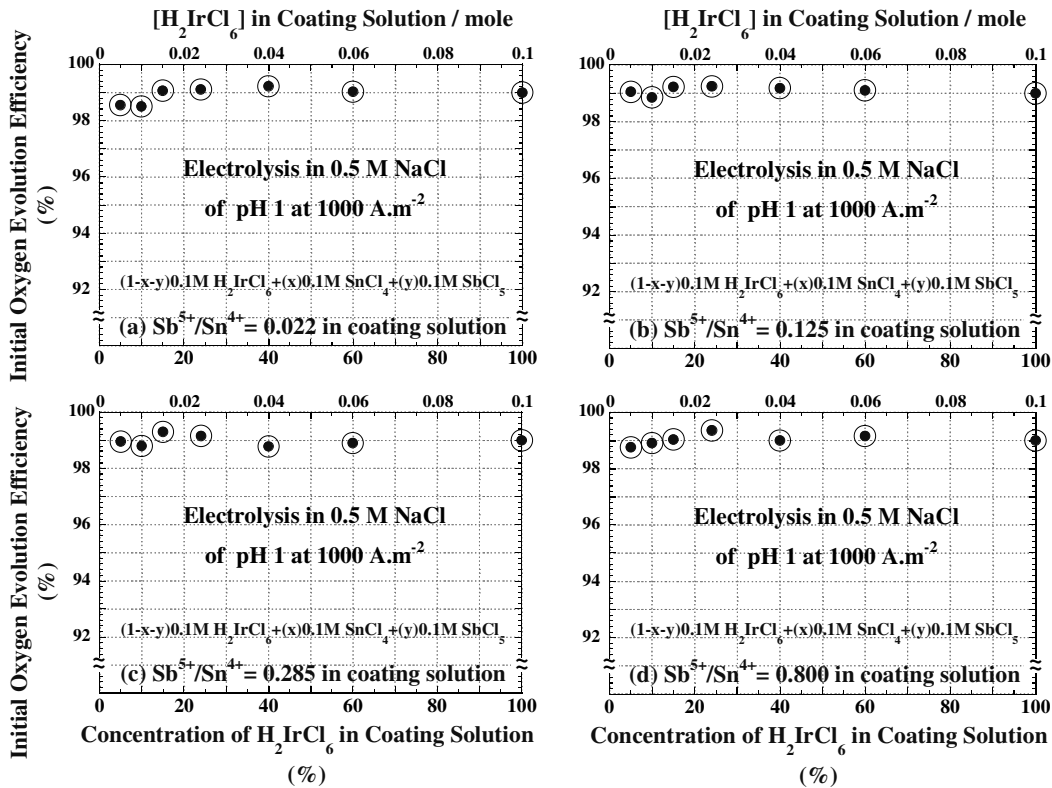


Figure 4: Changes in oxygen evolution efficiency of the  $Mn_{1-x-y}Mo_xSn_yO_{2+x}$  electrodes prepared by anodic deposition on the intermediate  $IrO_2-SnO_2-Sb_2O_5$  layer (with the  $Sb^{5+}/Sn^{4+} = 0.022-0.800$ ) in 0.5 M NaCl of pH 1 at the current density of  $1000 A.m^{-2}$ , as a function of iridium content in coating solution.

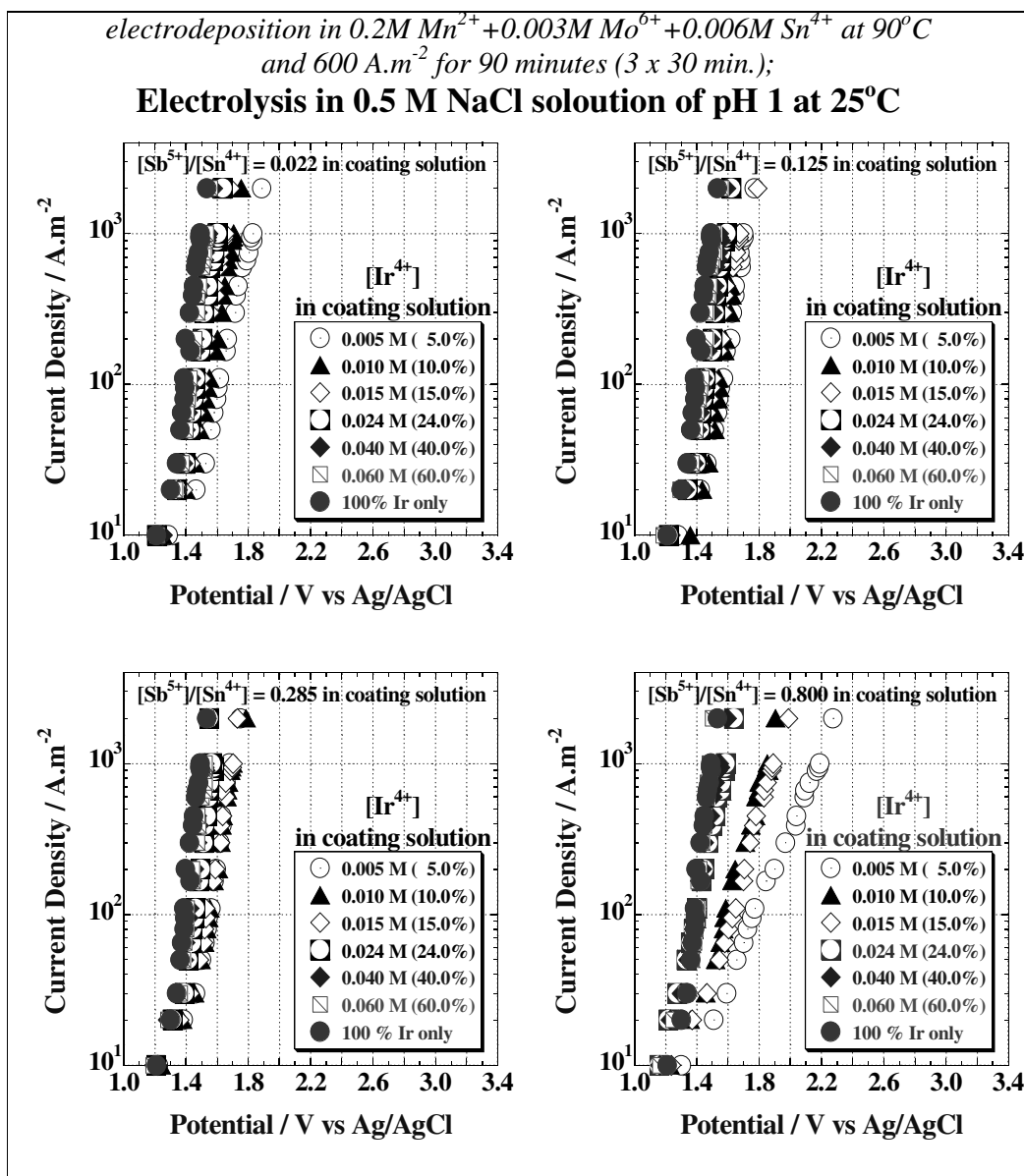


Figure 5: Galvanostatic polarization curves measured in 0.5 M NaCl of pH 1 for  $Mn_{1-x-y}Mo_xSn_yO_{2+x}$  electrodes prepared by anodic deposition on the intermediate  $IrO_2-SnO_2-Sb_2O_5$  layer with different amounts of  $IrO_2$ ,  $SnO_2$  and  $Sb_2O_5$ .

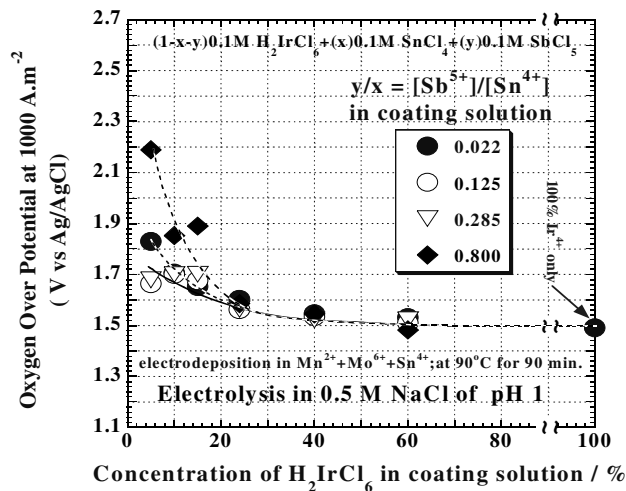


Figure 6: Changes in oxygen overpotential at the current density of  $1000 \text{ A.m}^{-2}$  in  $0.5 \text{ M NaCl}$  of pH 1 for  $\text{Mn}_{1-x-y}\text{Mo}_x\text{Sn}_y\text{O}_{2+x}$  anodes prepared by anodic deposition on the intermediate  $\text{IrO}_2\text{-SnO}_2\text{-Sb}_2\text{O}_5$  layers with different amounts of  $\text{Sn}^{4+}$  and  $\text{Sb}^{5+}$ , as a function of the iridium content in coating solution. The oxygen overpotential of the anode containing 100%  $\text{Ir}^{4+}$  only without tin and antimony in the intermediate layer is also shown for comparison.

1. The addition of  $\text{SnO}_2$  with some amounts of  $\text{Sb}_2\text{O}_5$  to the intermediate layer is effective to decrease the use of  $\text{IrO}_2$  to about 1/4, maintaining the high electronic conductivity of the intermediate layer and the high activity of oxygen evolution of the anodes for seawater electrolysis at pH 1.
2. Although  $\text{Sb}^{5+}$  addition is effective in decreasing the  $\text{Ir}^{4+}$  concentration in the intermediate layer of the  $\text{Mn}_{1-x-y}\text{Mo}_x\text{Sn}_y\text{O}_{2+x}/\text{SnO}_2\text{-Sb}_2\text{O}_5/\text{Ti}$  anodes, the  $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}$  intermediate layers with the  $\text{Sb}^{5+}/\text{Sn}^{4+}$  between 0.125–0.285 in the coating solution showed excellent performance of the oxygen evolution efficiency.

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