

Effects of Antimony and Tin Additions in the Intermediate $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}$ Layer of Mn–Mo–Sn–O Electrocatalyst for Hydrogen Production from Seawater Electrolysis

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Abstract

The oxygen production anode for seawater electrolysis is composed of two layers on the titanium substrate. The outermost layer is electrocatalysts of $\gamma\text{-MnO}_2$ type $\text{Mn}_{1-x-y}\text{Mo}_x\text{Sn}_y\text{O}_{2+x}$ triple oxides and the intermediate layer preventing insulating oxide formation on the titanium substrate is generally IrO_2 . Due to limited amount of iridium, alternative materials to the intermediate IrO_2 having sufficient durability and conductivity at high potentials for anodic polarization are required. In this context, decrease in the amount of IrO_2 by substitution with SnO_2 and increase in the electronic conductivity of the intermediate layer by Sb_2O_5 addition is performed in this work. The additions of SnO_2 with Sb_2O_5 to the intermediate layer of the Mn–Mo–Sn–O/ $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}$ /Ti anodes was effective to decrease the use of IrO_2 , maintaining the high electronic conductivity of the intermediate $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}$ layer and the high activity of oxygen evolution in seawater electrolysis at pH 1 for about 1550 h. The oxygen evolution efficiency of the nanocrystalline $\gamma\text{-MnO}_2$ type Mn–Mo–Sn–O/ $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}$ /Ti anodes with 0.208 M Ir^{4+} , 0.208–0.416 M Sn^{4+} and 0.104 M Sb^{5+} in the intermediate layers was about 98.5 % during electrolysis for about 1550 hours without any degradation in 0.5 M NaCl solution of pH 1 at 25°C.

Keywords: Oxygen evolution efficiency, electrocatalyst, seawater electrolysis, CO_2 recycling,

Introduction

It has been recently reported that the primary energy consumption by a person in developed countries is about 5.9 times as high as that by a person in developing countries and the world energy consumption on the average during last nineteen years since 1990 resulted in 1.0193 fold increase every year¹. This means a continuous increase in primary energy consumption results in continuous increase in CO_2 emissions. Such a huge CO_2 emissions resulting from complete exhaustion of fossil fuel reserves will induce intolerable global warming. In this context, it is meaningful for mentioning here that the intergovernmental panel on climate change (IPCC) was issued a statement on August 1990 declaring more than 60 % of CO_2 emissions must be cut in

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order to retain a level of long-life greenhouse gases¹. Considering these facts, Koji Hashimoto and his research groups of Tohoku University and Tohoku Institute of Technology in collaboration of Daiki Atka Engineering Company of Japan are proposing global CO₂ recycling project to prevent global warming and to supply abundant energy converted from solar energy¹⁻⁸.

Key materials necessary for the global CO₂ recycling project are anode and cathode for seawater electrolysis, and catalyst for CO₂ conversion into CH₄ from the reaction between CO₂ and H₂. Hashimoto and coworkers are tailoring these key materials of anode and cathode for seawater electrolysis, and catalyst for CO₂ methanation for last twenty years. Furthermore, oxygen production is prerequisite without forming environmentally harmful chlorine for safety production of hydrogen in seawater electrolysis. For large-scale seawater electrolysis to produce the hydrogen gas at cathode for prevention of global warming, environmentally harmful chlorine release at anode during the seawater electrolysis should not be allowed.

In general, seawater electrolysis is practically carried out for chlorine production in chlor-alkali industry. 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 to produce the hydrogen gas at cathode for the CO₂ recycle project, environmentally harmful chlorine release is not allowed. In this context, therefore, one of the most difficult subjects in tailoring key materials for the global CO₂ recycling project was the anode for seawater electrolysis because, for CH₄ production a large quantity of chlorine emissions are not allowed and hence the anode should evolve only oxygen with very high efficiency and durability even in seawater electrolysis at very high current density of 1000 A.m⁻².

Varieties of anodes composed of γ -MnO₂ type double, triple or quadrate oxides for electrocatalysts were prepared by thermal decomposition^{9,10} and anodic deposition¹¹⁻¹⁶ in the intermediate IrO₂ layer on the titanium metal substrate, and these anodes showed about 90-100 % initial oxygen evolution efficiency in the electrolysis of 0.5 M NaCl solution at the current density of 1000 A.m⁻². These anodes are formed by two layers; the outermost layer is electrocatalysts of γ -MnO₂ type double, triple or quadrate oxides and the intermediate oxide layer preventing the formation of insulating titanium oxide on the titanium substrate is generally IrO₂. The preparation of such traditional IrO₂ intermediate layer was performed using butanolic solution of 0.52 M chloroiridic acid (H₂IrCl₆.6H₂O). However, in order to supply a future hydrogen demand in the world, the amount of iridium is not sufficient to manufacture the anodes for seawater electrolysis at all. Therefore, the alternative materials to IrO₂ should have sufficient durability and conductivity at high potentials for anodic polarization, and the same rutile structure as TiO₂ are required. In this context, tin and antimony were thought to be candidates of alternative elements to iridium in the intermediate oxide layer of the anodes for seawater electrolysis because, tin oxide (SnO₂) has the rutile structure and is more stable than IrO₂. However, the electronic conductivity of the SnO₂ is very low as compared to IrO₂. Therefore, the electronic conductivity of the tin (IV) oxide containing intermediate layer of the oxygen evolution anodes will be improved by the addition of antimony (V) oxide.

The present author has been reported that the anodically deposited Mn-X(X=Sn,W,Mo)-O¹⁷, Mn-W-X(X=Sn,Sb,Mo)-O¹⁸, Mn-Mo-X(X=Zn,Sn,W)-O^{19,20}, Mn-Mo-Sn-O^{4-8,21-23}, Mn-Sn-W-X(X=Sb,Mo)-O²⁴ electrocatalysts on the intermediate layer of IrO₂-SnO₂-Sb₂O₅/Ti electrode

showed about 99.70-99.85% oxygen evolution efficiency (OEE) after electrolysis for about 3400–3600 h in 0.5 M NaCl of pH 1 at high current density of 1000 A.m⁻². The intermediate oxide layer of the IrO₂–SnO₂–Sb₂O₅/Ti electrode was prepared using the mixture of coating solutions (butanolic) containing 0.024 M Ir⁴⁺, 0.0676 M Sn⁴⁺ and 0.0084 M Sb⁵⁺ on titanium substrate in which the sum of the metallic cations in the intermediate oxide layer was kept at 0.1 M.

In this context, the present research work is focused to develop a more stable and efficient oxygen evolution Mn–Mo–Sn–O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti anodes containing different amounts of Ir⁴⁺, Sn⁴⁺ and Sb⁵⁺ cations (in which the sum of the metallic cations is kept at 0.52 M) in the intermediate oxide layer of the anodes for seawater electrolysis. Particular attention was focused to study the roles of iridium, tin and antimony additions in the Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti electrode for the oxygen evolution Mn–Mo–Sn–O anodes in electrolysis of 0.5 M NaCl of pH 1 at the current density of 1000 A.m⁻².

Experimental Methods

Punched titanium metal substrate was immersed in 0.5 M HF solution to remove air-formed oxide film, rinsed with de-ionized water and then subjected for surface roughening by etching in 11.5 M H₂SO₄ solution at 80°C as described elsewhere in details^{21,22}. The treated–titanium metal sheet was used as substrate for coating of the intermediate Ir_{1-x-y}Sn_xSb_yO_{2+0.5y} oxide layer.

Chloroiridic acid (H₂IrCl₆.6H₂O), tin (IV) chloride and antimony (V) chloride solutions having the concentration of 0.52 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, tin and antimony in the coating solutions were ranges from 0.052 to 0.520 M, 0.208 to 0.416 M and 0.052 to 0.104 M, respectively. The coating solution was used for coating on the etched-titanium substrate with a brush, dried at 80°C for 10 min, and then baked at 450°C for 10 minutes in air. The coating procedure was repeated for three times so as to form the intermediate oxide layers of Ir_{1-x-y}Sn_xSb_yO_{2+0.5y} on titanium substrate. This specimen was finally baked at 450°C for 1 h in air. The presence of the Ir_{1-x-y}Sn_xSb_yO_{2+0.5y} layer is necessary to prevent the formation of insulating titanium(IV) oxide between electrocatalytically active substances and the titanium substrate during anodic deposition and electrolysis of seawater at high current density of 1000 A.m⁻² for a long time. This Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}-coated titanium substrate was cut into 16 x 75 x 1 mm³ as suitable electrode and a titanium wire was spot-welded to its edge. This is called the intermediate Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti electrode.

The Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti electrode was degreased by anodic polarization at 1000 A.m⁻² for 5 minutes in 10 M NaOH solution and then electrochemically polished at 1000 A.m⁻² current density for 5 minutes in 1 M H₂SO₄ solution at room temperature. The Mn–Mo–Sn–O electrocatalyst for oxygen evolution was anodically deposited on the clean and activated Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti electrode at 600 A.m⁻² in the mixture of aqueous solution of 0.2 M MnSO₄.5H₂O, 0.003 M Na₂MoO₄.2H₂O and 0.006M SnCl₄.5H₂O at pH -0.1 and 90°C for 90 minutes. The electrodeposition of the Mn–Mo–Sn oxide electrocatalysts were carried out by exchanging electrolyte for every 30 minutes.

The characterization of the $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}/\text{Ti}$ electrodes and electrodeposited Mn-Mo-Sn-O/ $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}/\text{Ti}$ anodes was done by X-ray diffraction (XRD) patterns using Cu K_α radiation. The apparent grain size of the coated-electrodes and electrodeposited anodes was estimated from full width at half maximum (FWHM) of the most intense XRD reflection using Scherrer's formula²⁵ as given in equation (1):

$$t = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

where, t is the apparent grain size (in nm), λ is the X-ray wavelength ($= 0.15148$ nm for Cu K_α), β is the FWHN in radian and θ is the diffraction angle of the most intense peak.

The performance of the Mn-Mo-Sn-O/ $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}/\text{Ti}$ anodes was examined by oxygen evolution and galvanostatic polarization measurements. The oxygen evolution efficiency was measured by electrolysis at a constant current density of 1000 A.m^{-2} in 300 ml of 0.5 M NaCl solution of pH 1 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^{10,15}. The amount of chlorine formed was analyzed by iodimetric titration of chlorine and hypochlorite.

Galvanostatic polarization measurement of the electrodeposited Mn-Mo-Sn-O electrocatalysts on the $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}/\text{Ti}$ electrode was carried out in 0.5 M NaCl solution of pH 1 at room temperature. The pH of the 0.5 M NaCl solution was adjusted at 1 using concentrated hydrochloric acid. 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 XRD patterns of the intermediate $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}$ layers formed on the titanium substrate using different coating solution mixtures having the concentrations of $0.052 \text{ M Ir}^{4+} + 0.416 \text{ M Sn}^{4+} + 0.052 \text{ M Sb}^{5+}$ [Fig. 1(a)], $0.208 \text{ M Ir}^{4+} + 0.2086 \text{ M Sn}^{4+} + 0.104 \text{ M Sb}^{5+}$ [Fig. 1(b)] and 0.520 M Ir^{4+} only [Fig. 1(c)] containing various amounts of Ir^{4+} , Sn^{4+} and Sb^{5+} ions. Broadening of the reflection peaks of the XRD patterns of the $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}/\text{Ti}$ electrodes are clearly seen with increasing the amount of iridium content. This result revealed that iridium content in the intermediate oxide layer enhanced for the formation of nanocrystalline structures and hence the apparent grain size of the electrodes was decreased with increasing the concentration of the iridium contents. The apparent grain size of these electrodes was estimated using Scherrer's formula²⁴ and found to be in the ranges of 6–14 nm. There is no separate reflections corresponding to iridium, tin and antimony oxides in the intermediate layer formed on the titanium substrate indicating the intermediate $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}$ layer should be formed by single phase oxides, not the mixture of IrO_2 , SnO_2 and Sb_2O_5 oxides. XPS analysis revealed that iridium, tin and antimony species in the intermediate $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}$ layers were in tetravalent, tetravalent and pentavalent states, respectively (not shown here). These results revealed that the intermediate $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}$ and IrO_2 layers formed on the titanium substrate are composed of single or triple oxides of a rutile structure with fine grains instead of the mixture of IrO_2 , SnO_2 and Sb_2O_5 .

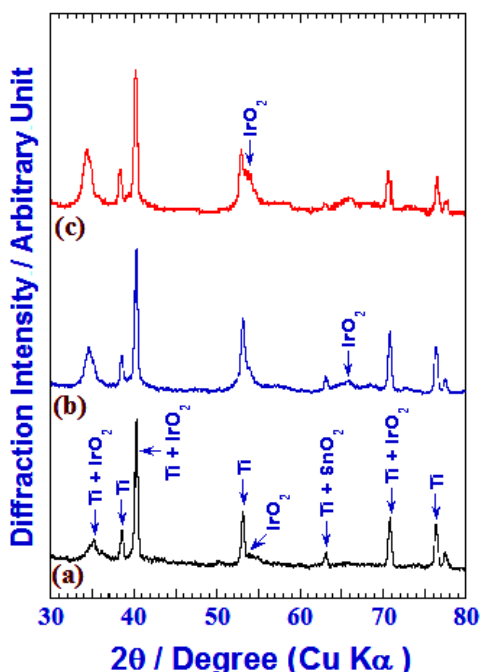


Figure 1: X-ray diffraction patterns of the $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}/\text{Ti}$ electrodes prepared using coating solutions of the mixture of (a) $0.052\text{ M Ir}^{4+} + 0.416\text{ M Sn}^{4+} + 0.052\text{ M Sb}^{5+}$, (b) $0.208\text{ M Ir}^{4+} + 0.208\text{ M Sn}^{4+} + 0.104\text{ M Sb}^{5+}$ and (c) 0.52 M Ir^{4+} only

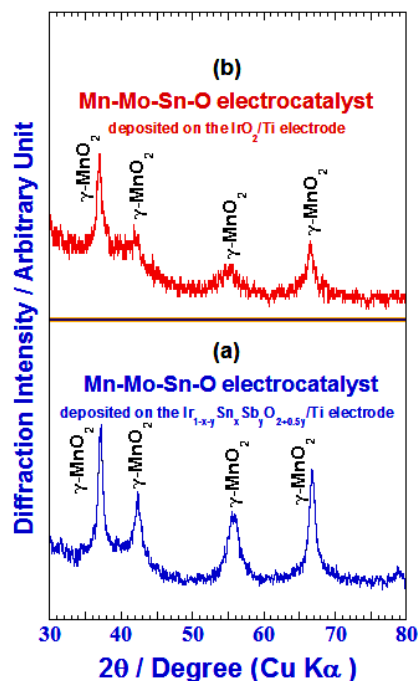


Figure 2: X-ray diffraction patterns of the electrodeposited (a) $\text{Mn-Mo-Sn-O}/\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}/\text{Ti}$ and (b) $\text{Mn-Mo-Sn-O}/\text{IrO}_2/\text{Ti}$ anodes. The electrodeposition of these anodes were carried out on the surface of the intermediate oxide layers prepared using (a) $0.208\text{ M Ir}^{4+} + 0.208\text{ M Sn}^{4+} + 0.104\text{ M Sb}^{5+}$ and (b) 0.52 M Ir^{4+} only containing coating solutions

Furthermore, the XRD patterns of the electrodeposited $\text{Mn-Mo-Sn-O}/\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}/\text{Ti}$ and $\text{Mn-Mo-Sn-O}/\text{IrO}_2/\text{Ti}$ anodes are shown in Figs 2(a) and 2(b), respectively. These XRD patterns clarified that both the electrodeposited Mn-Mo-Sn-O electrocatalysts deposited on the $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}/\text{Ti}$ and IrO_2/Ti electrodes consisted of $\gamma\text{-MnO}_2$ type triple oxide only with no sign of separate oxide phase of molybdenum and tin. The estimated apparent grain size of all the electrodeposited $\text{Mn-Mo-Sn-O}/\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}/\text{Ti}$ anodes was found in the ranges of 3-8 nm. It is meaningful to mention here that the apparent grain size of the electrodeposited $\text{Mn-Mo-Sn-O}/\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}/\text{Ti}$ anodes is decreased with increasing the amounts of iridium in the intermediate layer of the anodes. These results revealed that the electrodeposited $\text{Mn-Mo-Sn-O}/\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}/\text{Ti}$ anodes are composed by a nanocrystalline $\gamma\text{-MnO}_2$ type triple oxides consisting of Mn^{2+} , Mo^{6+} and Sn^{4+} ions.

Figure 3 shows IR-corrected galvanostatic polarization curves for the electrodeposited Mn-Mo-Sn-O electrocatalyst on the $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}/\text{Ti}$ electrodes in 0.5 M NaCl solution of pH 1 at 25°C study the effects of iridium, tin and antimony additions in the intermediate oxide layer formed on the titanium substrate. The electrodeposited $\text{Mn-Mo-Sn-O}/\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}/\text{Ti}$ and

Mn-Mo-Sn-O/IrO₂/Ti anodes in which the intermediate oxide layer was formed using the coating solution mixture having 0.208 M Ir⁴⁺-0.208 M Sn⁴⁺-0.104 M Sb⁵⁺, and 0.52 M Ir⁴⁺ only show lowest oxygen overpotential at current density of 1000 A.m⁻² than that of the Mn-Mo-Sn-O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti anode in which the intermediate oxide layer was formed using the coating solution mixture having 0.052 M Ir⁴⁺-0.416 M Sn⁴⁺-0.052 M Sb⁵⁺. In particular, the oxygen overpotential at the current density of 1000 A.m⁻² of the Mn-Mo-Sn-O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti anodes is slightly shifted to lower potential value with increasing the amounts of Ir⁴⁺ as well as Sb⁵⁺ in the intermediate layer of the anodes as shown in Fig.3. Furthermore, it is meaningful to mention here that the simultaneous additions of the 0.208 M Ir⁴⁺, 0.208 M Sn⁴⁺ and 0.104 M Sb⁵⁺ in the intermediate layer has almost same oxygen overpotential value as that contained only 0.52 M Ir⁴⁺. Consequently, it can be said that simultaneous additions of Ir⁴⁺, Sn⁴⁺ and Sb⁵⁺ in the intermediate layer to Mn-Mo-Sn-O electrocatalyst is more effective for showing high electronic conductivity of the electrocatalyst than the additions of iridium, tin or antimony to the Mn-Mo-Sn-O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti anode in 0.5 M NaCl of pH 1 at the current density of 1000 A.m⁻².

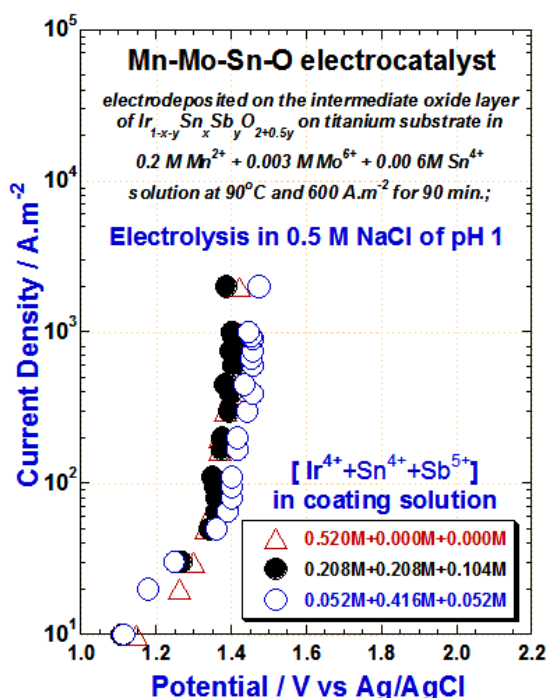


Figure 3: Galvanostatic polarization curves measured in 0.5 M NaCl solution at pH 1 for Mn-Mo-Sn-O electrocatalyst prepared by electrodeposition on the intermediate Ir_{1-x-y}Sn_xSb_yO_{2+0.5y} layers with different concentrations of Ir⁴⁺, Sn⁴⁺ and Sb⁵⁺ ions

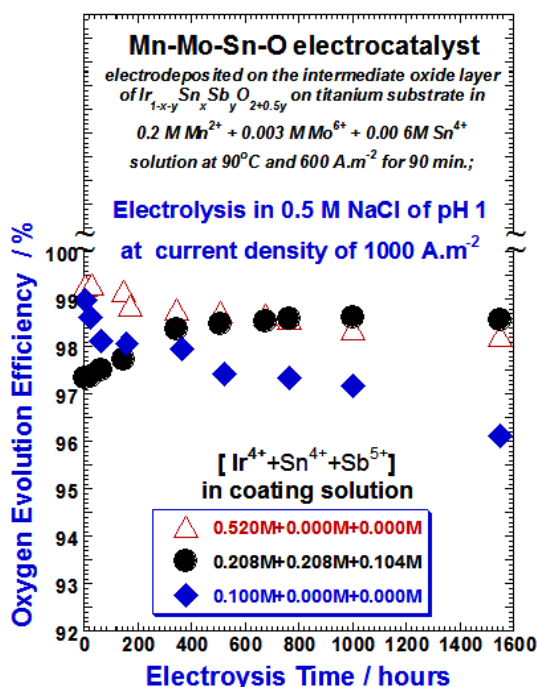


Figure 4: Changes in the oxygen evolution efficiency of the Mn-Mo-Sn-O electrocatalyst electrodeposited on the intermediate Ir_{1-x-y}Sn_xSb_yO_{2+0.5y} layers with different concentrations of Ir⁴⁺, Sn⁴⁺ and Sb⁵⁺ ions in 0.5 M NaCl of pH 1 at the current density of 1000 A.m⁻², as a function of electrolysis time

Figure 4 shows the durability result on the Mn-Mo-Sn-O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti anodes in 0.5 M NaCl solution of pH 1 at 25°C. The initial oxygen evolution efficiency of the Mn-Mo-Sn-O/IrO₂/Ti anodes which were electrodeposited on the intermediate IrO₂ layer formed from the 0.52 M and 0.10 M Ir⁴⁺, was about 99%, whereas that of the Mn-Mo-Sn-O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti anode was about 97.3% as shown in Fig. 4. However, the oxygen evolution efficiencies of both the electrodeposited Mn-Mo-Sn-O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti anodes containing 0.52 M Ir⁴⁺ only and 0.208 M Ir⁴⁺-0.208 M Sn⁴⁺-0.104 M Sb⁵⁺ contents on the intermediate layer are reached almost same value of about 98.6% after electrolysis for about 350 to 1550 hours and this OEE is significantly higher than that of the Mn-Mo-Sn-O/IrO₂/Ti anode in which the intermediate layer was formed using the coating solution containing 0.10 M Ir⁴⁺ only. These results revealed that the simultaneous additions of iridium, tin and antimony in the intermediate oxide layer of the Mn-Mo-Sn-O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti anodes seems to be more effective than the single addition of 0.10 M Ir⁴⁺ in the intermediate oxide layer of the Mn-Mo-Sn-O/IrO₂/Ti anode, and guaranteed the stable anode performance of about 98.5 % oxygen evolution efficiency for more than two months for production of hydrogen from the seawater electrolysis.

Conclusions

An attempt has been made to reduce the use of IrO₂ by the IrO₂-SnO₂-Sb₂O₅ intermediate layer which is necessary to avoid the growth of insulating titanium oxide on the titanium substrate for oxygen evolution γ -MnO₂ type nanocrystalline Mn-Mo-Sn-O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti anodes in 0.5 M NaCl solution of pH 1 at 25°C. These electrodeposited Mn-Mo-Sn-based triple oxide anodes showed about 96.0-98.5% oxygen evolution efficiency at high current density of 1000 A.m⁻² in 0.5 M NaCl solution of pH 1 at 25°C. The high oxygen evolution efficiency of these triple oxide electrocatalysts maintained during prolonged electrolysis and even after the electrolysis for about two months.

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