

Research

Effects of Ir, Sn and Sb 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

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Abstract

An attempt is made to reduce the use of IrO_2 by the IrO_2 - SnO_2 - Sb_2O_5 intermediate layer which is necessary to avoid the growth of insulating titanium oxide on the titanium substrate for oxygen evolution $\tilde{\alpha}$ - MnO_2 type nanocrystalline Mn–Mo–Sn–O/ $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}$ /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 97.2–98.6 % 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.

Key-words: Oxygen evolution efficiency, electrocatalyst, seawater electrolysis, CO₂ recycling, XRD

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 year (Hashimoto *et al.* 2009). This means a continuous increase in primary energy consumption results in continuous increase in CO₂ emissions. Such a huge CO₂ 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 CO₂ emissions must be cut in order to retain a level of long-life greenhouse gases. Considering these facts, Koji Hashimoto and his research groups of Tohoku University and Tohoku Institute of Technology in collaboration with Daiki Atka Engineering Company of Japan are proposing global CO₂ recycling project to prevent global warming and to supply abundant energy converted from solar

energy (Hashimoto *et al.* 2001, 2009; Hashimoto 1994; Kato *et al.* 2008, 2009; El-Moneim *et al.* 2010).

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 is not 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 anodes composed of g-MnO₂ type double, triple or quadrate oxides for electrocatalysts were prepared by thermal decomposition (Izumiya *et al.* 1997a,b) and anodic deposition (Izumiya *et al.* 1998, Fujimura *et al.* 1999, 2000; Habazaki *et al.* 2001; Abdel Ghany *et al.* 2002; El-Moneim *et al.* 2006) 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 were formed by two layers; the outermost layer is electrocatalysts of g-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 those 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 anodic deposited Mn-X(X=Sn,W,Mo)-O (Bhattarai 2010a), Mn-W-X(X=Sn,Sb,Mo)-O (Bhattarai 2010b), Mn-Mo-X(X=Zn,Sn,W)-O (Bhattarai 2010c,d), Mn-Mo-Sn-O (Kato *et al.* 2008, 2009; El-Moneim *et al.* 2010; Bhattarai *et al.* 2007; Bhattarai 2008/2009), Mn-Sn-W-X(X=Sb,Mo)-O (Bhattarai 2010e) 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.

Materials and 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 (Bhattarai *et al.* 2007; Bhattarai 2008/2009). 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), 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 amounts of iridium, tin and antimony in the coating solution were 0.052 M, 0.416 M and 0.052 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. This is called the intermediate Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti electrode. Then, the Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti electrode was degraded by anodic polarization at 1000 A.m⁻² for 5 minutes in 10 M NaOH solution and then electro-analytically rinsed

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 electro-deposition of the Mn–Mo–Sn oxide electrocatalysts were carried out by exchanging electrolyte for every 30 minutes.

The characterization of the Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti electrodes and electrodeposited Mn–Mo–Sn–O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti anodes was done by X-ray diffraction (XRD) patterns using Cu K_α radiation. The apparent grain size of the electrodes and electrodeposited anodes was estimated from full width at half maximum (FWHM) of the most intense XRD reflection using Scherrer's formula (Cullity 1977) 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.

Galvanostatic polarization measurement of the electrodeposited Mn–Mo–Sn–O electrocatalysts on the Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti electrode was carried out in 0.5 M NaCl solution of pH 1 (adjusted by adding concentrated sulfuric acid) at room temperature. 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.

The performance of the Mn–Mo–Sn–O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/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 (Izumiya *et al.* 1997b; Abdel Ghany *et al.* 2002). The amount of chlorine formed was analyzed by iodimetric titration of chlorine and hypochlorite.

Results and Discussion

Figures 1 (a) and (b) show the XRD patterns of the intermediate Ir_{1-x-y}Sn_xSb_yO_{2+0.5y} layers formed on the titanium substrate using different coating solution mixtures having the concentrations of 0.052 M Ir⁴⁺ + 0.416 M Sn⁴⁺ + 0.052 M Sb⁵⁺ and 0.520 M Ir⁴⁺ only, respectively, containing various amounts of Ir⁴⁺, Sn⁴⁺ and Sb⁵⁺ ions. Broadening of the reflection peaks of the XRD patterns of the Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/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. There is no separate reflections corresponding to iridium, tin and antimony oxides in the intermediate layer formed on the titanium substrate indicating the intermediate Ir_{1-x-y}Sn_xSb_yO_{2+0.5y} layer should be formed by single phase oxides, not the mixture of IrO₂, SnO₂ and Sb₂O₅ oxides. The apparent grain size of these electrodes was estimated using Scherrer's formula (Cullity 1977) and found to be in the ranges of 6–14 nm. The apparent grain size of the electrodes was decreased with increasing the concentration of the iridium contents. It is meaningful to mention here that the x-ray photoelectron spectroscopic analysis revealed that iridium, tin and antimony species in the intermediate Ir_{1-x-y}Sn_xSb_yO_{2+0.5y} layers were in tetravalent, tetravalent and pentavalent states, respectively (not shown here). These results revealed that the intermediate Ir_{1-x-y}Sn_xSb_yO_{2+0.5y} and IrO₂ 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 IrO₂, SnO₂ and Sb₂O₅.

Figures 2 (a) and (b) show the XRD patterns of the electrodeposited Mn–Mo–Sn–O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti and Mn–Mo–Sn–O/IrO₂/Ti anodes, respectively. The XRD patterns clarified that both the electrodeposited Mn–Mo–Sn–O electrocatalysts deposited on the Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti and IrO₂/Ti electrodes consisted of α-MnO₂ type triple oxide only with no sign of separate oxide phase of molybdenum and tin. The estimated apparent grain size of all the electrodeposited Mn–Mo–Sn–O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti anodes was found in the ranges of 3-8 nm. These results revealed that the electrodeposited Mn–Mo–Sn–O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti anodes are composed by a nanocrystalline α-MnO₂ type triple oxides consisting of Mn²⁺, Mo⁶⁺ and Sn⁴⁺ ions.

Figure 3 shows IR-corrected galvanostatic polarization curves for the electrodeposited Mn–Mo–Sn–O electrocatalyst

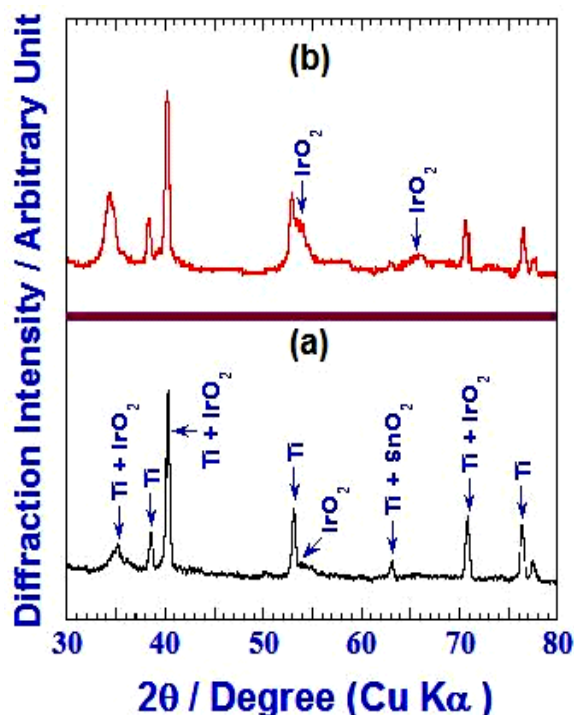


Figure 1: X-ray diffraction patterns of the $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}/\text{Ti}$ electrodes prepared using coating solutions containing of (a) 0.052 M Ir^{4+} + 0.416 M Sn^{4+} + 0.052 M Sb^{5+} and (b) 0.52 M Ir^{4+} only.

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 to study the effects of iridium, tin and antimony additions in the intermediate oxide layer formed on the titanium substrate. The electrodeposited 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/ IrO_2/Ti anodes in which the intermediate oxide layer was formed using the coating solution mixture having 0.052 M Ir^{4+} -0.416 M Sn^{4+} -0.052 M Sb^{5+} , and 0.52 M Ir^{4+} only show all most same oxygen overpotential particularly at current density of 1000 $\text{A}\cdot\text{m}^{-2}$. Consequently, it can be said that simultaneous additions of Ir^{4+} , Sn^{4+} and Sb^{5+} in the intermediate layer to Mn–Mo–Sn–O electrocatalyst is also effective as that of the Mn–Mo–Sn–O/ IrO_2/Ti anode for showing high electronic conductivity of the electrocatalyst in 0.5 M NaCl of pH 1 at the current density of 1000 $\text{A}\cdot\text{m}^{-2}$.

Figure 4 shows the durability result on the Mn–Mo–Sn–O/ $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}/\text{Ti}$ anodes in 0.5 M NaCl solution of pH 1 at 25°C. The initial oxygen evolution efficiency of the Mn–Mo–Sn–O/ IrO_2/Ti anode which was electrodeposited on the intermediate IrO_2 layer formed from

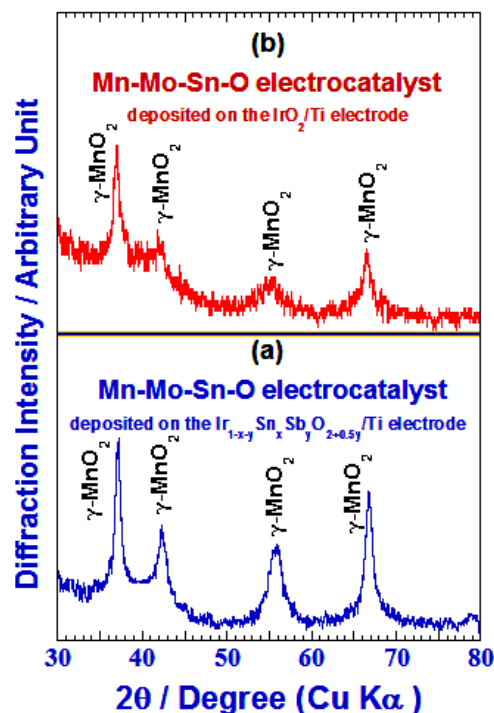


Figure 2: X-ray diffraction patterns of the electrodeposited (a) Mn–Mo–Sn–O/ $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}/\text{Ti}$ and (b) Mn–Mo–Sn–O/ IrO_2/Ti anodes. The electrodeposition of these anodes were carried out on the surface of the intermediate oxide layers prepared using (a) 0.052 M Ir^{4+} + 0.416 M Sn^{4+} + 0.052 M Sb^{5+} and (b) 0.52 M Ir^{4+} only containing coating solution.

the 0.52 M Ir^{4+} , was about 99.3 %, whereas that of the Mn–Mo–Sn–O/ $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}/\text{Ti}$ anode was about 97.2% as shown in Fig. 4. However, the oxygen evolution efficiencies of both the electrodeposited Mn–Mo–Sn–O/ $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}/\text{Ti}$ anodes containing 0.52 M Ir^{4+} only and 0.052 M Ir^{4+} -0.416 M Sn^{4+} -0.052 M Sb^{5+} 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/ IrO_2/Ti anode in which the intermediate layer was formed using the coating solution containing 0.100 M Ir^{4+} only (Bhattarai *et al.* 2007; Bhattarai 2008/2009) (data is not shown here). These results revealed that the simultaneous additions of iridium, tin and antimony in the intermediate oxide layer 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 seems to be more effective than the single addition of 0.10 M Ir^{4+} in the intermediate oxide layer of the Mn–Mo–Sn–O/ IrO_2/Ti anode, and guaranteed the stable anode performance of about 98.6 % oxygen evolution efficiency for more than two months for production of hydrogen from the seawater electrolysis.

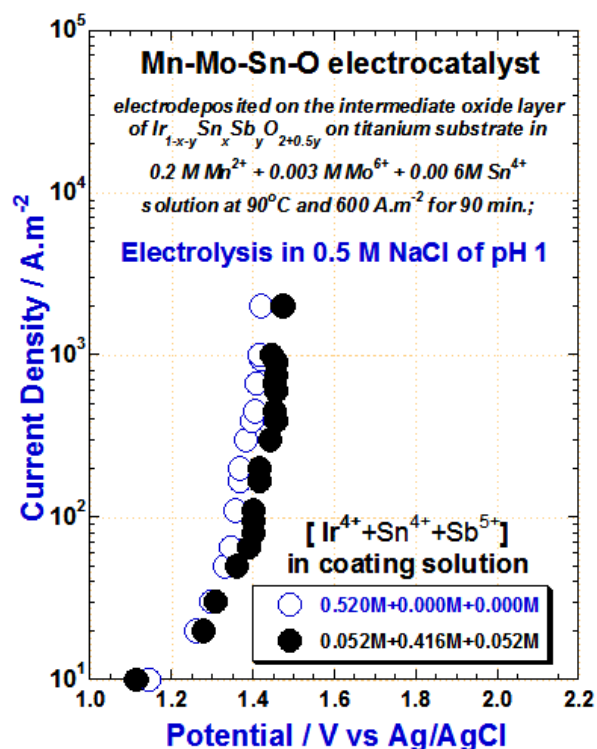


Figure 3: Galvanostatic polarization curves measured in 0.5 M NaCl solution at pH 1 for Mn–Mo–Sn–O electrocatalyst prepared by electrodeposition on the intermediate $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}$ layers with different concentrations of Ir^{4+} , Sn^{4+} and Sb^{5+} ions.

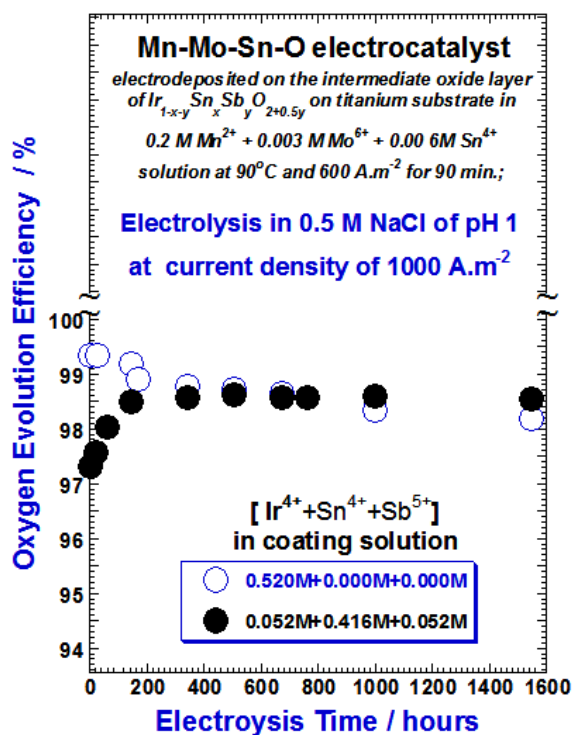


Figure 4: Changes in the oxygen evolution efficiency of the Mn–Mo–Sn–O electrocatalyst electrodeposited on the intermediate $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}$ layers with different concentrations of Ir^{4+} , Sn^{4+} and Sb^{5+} ions in 0.5 M NaCl of pH 1 at the current density of 1000 A.m^{-2} , as a function of electrolysis time.

Conclusions

For safety production of hydrogen in seawater electrolysis, oxygen production is prerequisite without forming environmentally harmful chlorine. The oxygen production anode for seawater electrolysis is composed of two layers on the titanium substrate. The outer most layer is electrocatalysts of $\alpha\text{-MnO}_2$ 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 . However, in order to supply a future hydrogen demand in the world, the amount of iridium is not sufficient for seawater electrolysis at all. Therefore, the alternative materials to the intermediate IrO_2 those should have 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 was performed in this works. 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 long times. The oxygen evolution efficiency of the nanocrystalline $\alpha\text{-MnO}_2$ type Mn–Mo–Sn–O/ $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}$ /Ti anodes with 0.052 M Ir^{4+} , 0.416 M Sn^{4+} and 0.052 M Sb^{5+} in the intermediate layers was about 98.6 % during electrolysis for about 1550 hours without any degradation in 0.5 M NaCl of pH 1 at 25°C.

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