J. Nepal Chem. Soc., vol. 25, 2010

Roles of Antimony and Molybdenum Additions in Mn–Sn–W–O/IrO_2–SnO_2–Sb_2O_5/Ti Anodes for Oxygen Evolution in Seawater Electrolysis

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Abstract

An attempt was made to enhance the oxygen evolution efficiency in seawater electrolysis by additions of antimony and molybdenum to manganese–tin–tungsten oxide electrocatalyst prepared by anodic deposition on the intermediate $Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti *electrode.* $Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti *supported nanocrystalline* γ–MnO_2 *type Mn–Sn–W–X(X=Sb or/and Mo)–O electrocatalysts with grain size of about 4-8 nm were tailored by anodic deposition and these anodes showed almost 100 % oxygen evolution efficiency at current density of 1000* $A.m^{-2}$ *in 0.5 M NaCl solution of pH 1 at* 25^oC*. They guaranteed the stable anode performance of 99.60-99.85% oxygen evolution efficiency for more than 5 months at current density of 1000* $A.m^{-2}$ *in 0.5 M NaCl solution of pH 1 at* 25^oC*.*

Keywords: *Oxygen evolution anodes, electrocatalyst, CO2 recycle, XRD, SCLM.*

Introduction

The intergovernmental panel on climate change (IPCC) issued a statement on August 1990 declaring that more than 60 % of CO_2 emissions must be cut in order to retain a level of long-life greenhouse gases. It has been reported that the energy consumption by a person in developed countries in 2005 was 5.9 times as high as that by a person in developing countries and the world energy consumption on the average during 18 years since 1990 resulted in 1.0193 fold increase every year[1]. 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. 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 CO_2 recycling project to prevent global warming and to supply abundant energy converted from solar energy[1-6].

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Key materials necessary for the global CO_2 recycling project are anode and cathode for seawater electrolysis, and catalyst for CO_2 conversion into CH_4 from the reaction between CO_2 and H_2. Hashimoto and coworkers are tailoring these key materials of anode and cathode for seawater electrolysis, and catalyst for CO_2 methanation. 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 is not allowed. Therefore, one of the most difficult subjects in tailoring key materials for the global CO_2 recycling project was the anode for seawater electrolysis because, for CH_4 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 of 1000 $A.m^{-2}$.

Varieties anodes composed of γ–MnO_2 type double or triple oxides for electrocatalysts were prepared by thermal decomposition[7,8] and anodic deposition[9-14] on IrO_2/Ti electrode, 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 outer layer is electrocatalysts of γ–MnO_2 type double or triple oxides and the intermediate oxide layer preventing the formation of insulating titanium oxide 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 to manufacture the anodes for seawater electrolysis at all. Therefore, the alternative materials to IrO_2 those should have sufficient durability and conductivity at high potentials for anodic polarization, and the same rutile structure as TiO_2 are required.

The present author has been reported that the Mn–Mo–Sn–O electrocatalysts on the intermediate layer of $Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti electrode containing 7.1 % of IrO_2, 79.0 % SnO_2 with 13.9 % of Sb_2O_5 from surface analysis using x-ray photoelectron spectroscopy technique[14] showed about 99.7% oxygen evolution efficiency (OEE) after electrolysis for about 3400 h in 0.5 M NaCl of pH 1 at high current density[4,5,14,15]. Similarly, the electrodeposited Mn–W–Sn–O electrocatalyst on the intermediate layer of the $Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti electrode showed about 99.85 % oxygen evolution efficiency after electrolysis for about 3600 h in 0.5 M NaCl of pH 1 at 1000 $A.m^{-2}$ current density[16]. In this context, the present research work is focused to develop a more stable and efficient oxygen production Mn–Sn–W–X(X=Sb,Mo)–O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anodes for seawater electrolysis. Particular attention was paid to identify the roles of antimony and molybdenum additions in Mn–Sn–W–O/ $Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anodes on the oxygen evolution efficiency and carried out the durability test of the anodes in 0.5 M NaCl of pH 1.

Experimental Methods

Punched titanium metal substrate was treated 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 H_2SO_4 solution at 80°C as described elsewhere in details[15-17]. The treated–titanium metal was used as substrate for coating of the intermediate Ir_{1-x-}

$_y$Sn$_x$Sb$_y$O$_{2+0.5y}$ oxide layer. The Ir$_{1-x-y}$Sn$_x$Sb$_y$O$_{2+0.5y}$ intermediate oxide layer was prepared using coating solution which was prepared by mixing of 0.024 M chloroiridic acid {$H_2IrCl_6.6H_2O$}, 0.0676 M tin chloride {$SnCl_4.5H_2O$} and 0.0084 M $SbCl_5$ butanolic solutions in which the sum of the metallic cations was kept at 0.1 M. The details about the coating procedures are described eleswhere[15-17]. It is noteworthy to mention here that iridium, tin and antimony oxides on the titanium substrate were identified as IrO_2, SnO_2 and Sb_2O_5, respectively, from XPS analysis[15] and the intermediate Ir$_{1-x-y}$Sn$_x$Sb$_y$O$_{2+0.5y}$ layer was consisted of triple oxides of a rutile structure with fine grains instead of the mixture of oxides of iridium, tin and antimony[15-17].

The Ir$_{1-x-y}$Sn$_x$Sb$_y$O$_{2+0.5y}$ intermediate oxide layer–coated titanium substrate specimen is also called as Ir$_{1-x-y}$Sn$_x$Sb$_y$O$_{2+0.5y}$/Ti electrode was degreased by anodic polarization at 1000 A.m^{-2} for 5 minutes in 10 M NaOH solution and then electro-analytically rinsed at 1000 A.m^{-2} current density for 5 minutes in 1 M H_2SO_4 solution at room temperature. The Mn–Sn–W–X(X=Sn,Mo)–O electrocatalysts for oxygen evolution were anodically deposited on the clean and activated Ir$_{1-x-y}$Sn$_x$Sb$_y$O$_{2+0.5y}$/Ti electrode at 600 A.m^{-2} in the solution containing 0.2 M $MnSO_4.5H_2O$ + 0.006M $SnCl_4.5H_2O$ + 0.0045 M $Na_2WO_4.2H_2O$ + {0.003 M $SbCl_5$ solution or 0.003 M $Na_2MoO_4.2H_2O$} at pH –0.1 and 90°C for 90 minutes. The electrodeposition of the Mn–Sn–W–X(X=Sb,Mo) oxide electrocatalysts were carried out by exchanging electrolyte for every 30 minutes.

The performance of the Mn–Sn–W–X(X=Sb,Mo)–O/Ir$_{1-x-y}$Sn$_x$Sb$_y$O$_{2+0.5y}$/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[8,13]. The amount of chlorine formed was analyzed by iodimetric titration of chlorine and hypochlorite.

Galvanostatic polarization measurement of the electrodeposited Mn–Mo–X–O(X=Zn,Sn,W) electrocatalysts on the Ir$_{1-x-y}$Sn$_x$Sb$_y$O$_{2+0.5y}$/Ti electrode was carried out in 0.5 M NaCl solution of pH 1 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 surface morphology of the anodically deposited Mn–Sn–W–X (X=Sb,Mo)–O/Ir$_{1-x-y}$Sn$_x$Sb$_y$O$_{2+0.5y}$/Ti anodes were observed using confocal scanning laser microscope (CSLM). The laser source used was He–Ne having wavelength of 633 nm. The electrodeposited Mn–Sn–W–X(X=Sb,Mo)–O/Ir$_{1-x-y}$Sn$_x$Sb$_y$O$_{2+0.5y}$/Ti anodes were characterized by X–ray diffraction (XRD) patterns using Cu K$_\alpha$ radiation and surface composition was analyzed by X–ray photoelectron spectroscopic (XPS) techniques.

Results and Discussion

Figure 1 shows the effects of the additional elements on the $MnO_2/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti$ anodes for initial oxygen evolution efficiency measured in 0.5 M NaCl solution of pH 1 at the current density of 1000 $A.m^{-2}$. The additions of antimony and molybdenum on the $Mn–Sn–W–O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti$ anodes showed high activity of the oxygen evolution efficiency of about 98-99 % in 0.5 M NaCl solution of pH 1 at 25°C. In particular, the initial oxygen evolution efficiency of the $Mn–Sn–W–Mo–O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti$ and $Mn–Sn–W–Sb–Mo–O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti$ anodes showed highest oxygen evolution efficiency, that is, about 99 % at the current density of 1000 $A.m^{-2}$ in 0.5 M NaCl solution of pH 1 at 25°C (Fig. 1). This result revealed that the simultaneous additions of antimony and molybdenum or molybdenum only seem to be more effective for the initial oxygen evolution efficiency than the single addition of antimony in the $Mn–Sn–W–O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti$ anode.

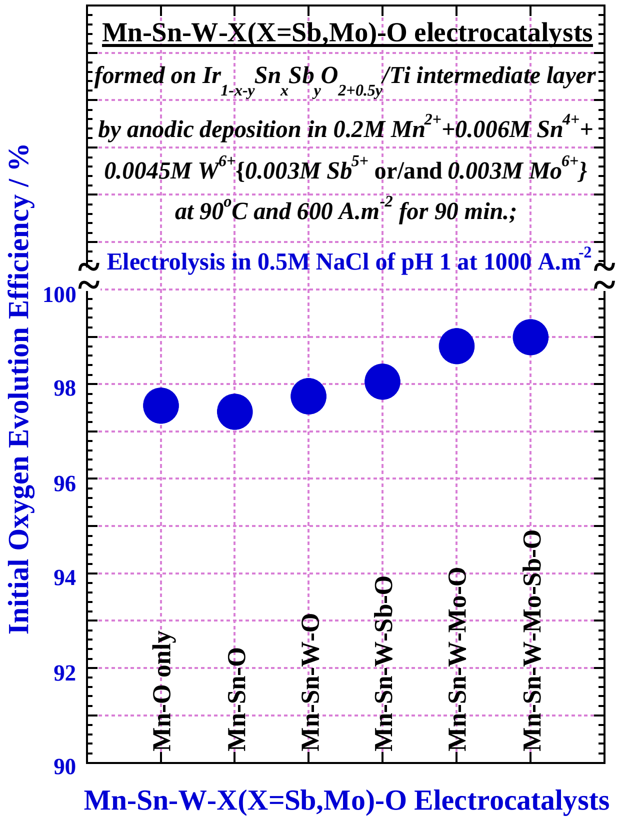

***Figure 1**: Initial oxygen evolution efficiency of the $Mn–Sn–W–X(X=Sb,Mo)–O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti$ anodes in 0.5 M NaCl of pH 1 at the current density of 1000 $A.m^{-2}$.*

Figure 2 shows the durability result on the $Mn–Sn–W–X(X=Sb,Mo)–O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti$ anodes in 0.5 M NaCl solution of pH 1 at 25°C. The initial oxygen evolution efficiency of the Mn–Sn–W–O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anode is 97.75 %, whereas those of the Mn–Sn–W–Mo–O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti and Mn–Sn–W–Sb–Mo–O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anodes are about 99 % as shown in Fig. 1. However, all the three examined anodes showed about 99.70 to 99.85 % oxygen evolution efficiency after electrolysis of 0.5 M NaCl of pH 1 at 25°C for about 500–3600 hours and the oxygen evolution efficiency of all three different anodes is independent of the electrolysis time for about 3600 hours. These results revealed that all the examined three different electrodes guaranteed the stable anode performance of about 100 % oxygen evolution efficiencies for more than five months at very high current density of 1000 $A.m^{-2}$.

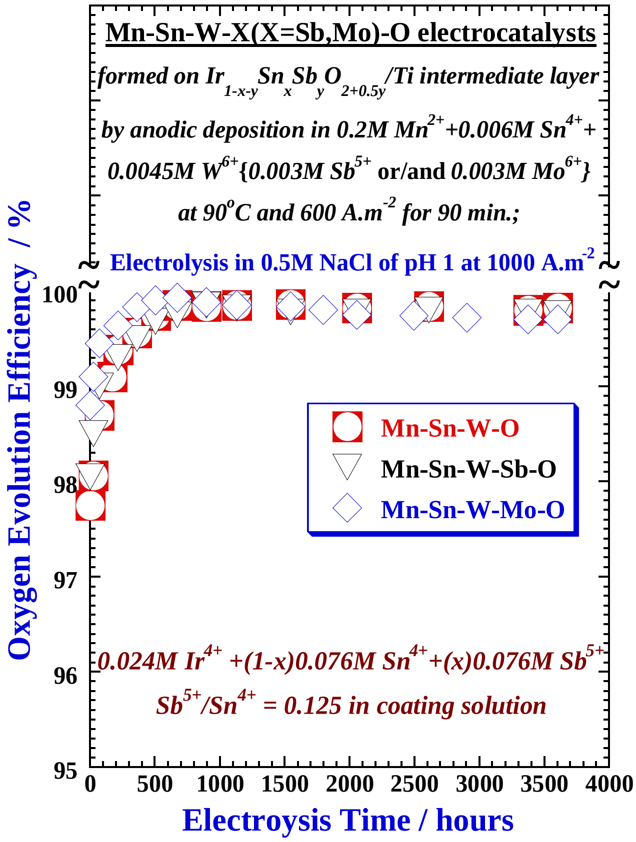

***Figure 2**: Changes in the oxygen evolution efficiency of the Mn–Sn–W–X(X=Sb,Mo)–O electrocatalysts electrodeposited in the $Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$ inter-mediate layer on the titanium substrate in 0.5 M NaCl of pH 1 at the current density of 1000 $A.m^{-2}$, as a function of electrolysis time.*

Figures 3 and 4 show the changes of the surface morphologies of the Mn–Sn–W–Sb–O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti and Mn–Sn–W–Mo–O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anodes, respectively, before and after electrolysis in 0.5 M NaCl solution of pH 1 at the current density of 1000 $A.m^{-2}$ for about 3600 hours. In both anodes, numbers of cracks and pores on the surface of the anodically deposited anodes were decreased to form a smooth surface after electrolysis for about 3600 hours in 0.5 M NaCl solution. This revealed that the filling of the cracks by the beneficial ions (Mn^{2+}, Sn^{4+}, W^{6+}, Mo^{6+}, Sn^{4+} or Sb^{5+}) presence in the electrocatalysts was clearly observed after electrolysis of the anodes for about hundreds of hours. In accordance of the changes in the surface morphologies, the durability of the oxygen evolution efficiency of these two anodes increased with increasing the electrolysis times and became steady state after electrolysis for about 500 hours as shown in Fig. 2.

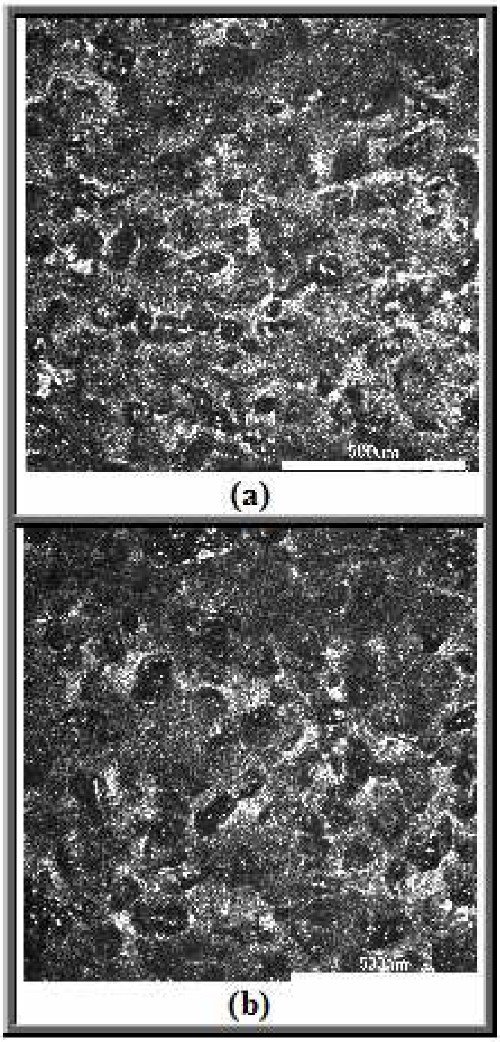

***Figure 3**: Changes in the surface morphology of the Mn–Sn–W–Sb–$O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti$ anode (a) before and (b) after electrolysis for about 3600 hours in 0.5 M NaCl of pH 1 at 1000 $A.m^{-2}$.*

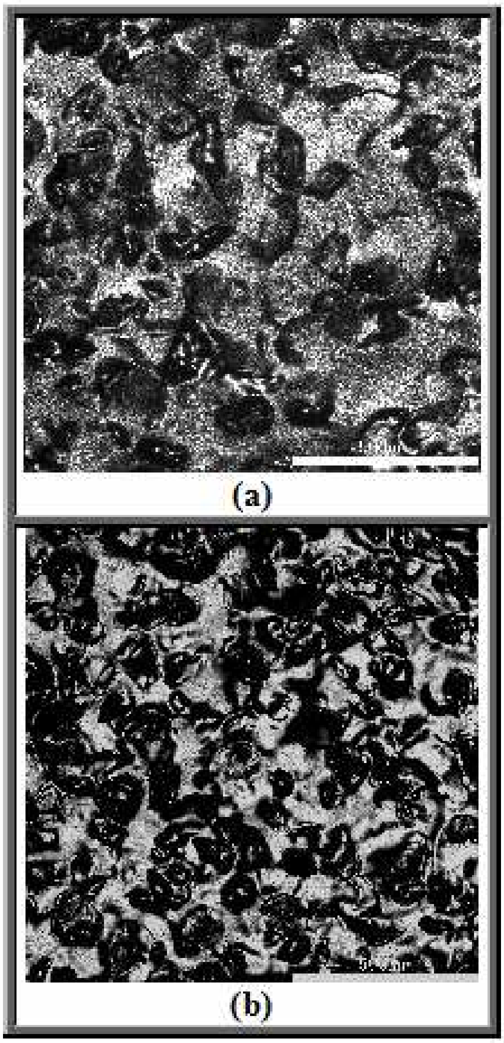

***Figure 4**: Changes in the surface morphology of the Mn–Sn–W–Mo–$O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti$ anode (a) before and (b) after electrolysis for about 3600 hours in 0.5 M NaCl of pH 1 at 1000 $A.m^{-2}$.*

Figure 5 shows IR-corrected galvanostatic polarization curves for electrodeposited Mn–Sn–W–X(X=Sb,Mo)–O electrocatalysts on the $Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti electrode in 0.5 M NaCl solution of pH 1 at 25°C. The anodically deposited Mn–Sn–W–O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anode shows lowest oxygen overpotential among the other Mn–Sn–W–X(X=Sb,Mo)–O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti, Mn–Sn–O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti and MnO_2/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anodes at current density of 1000 $A.m^{-2}$ as shown in Fig. 6. In particular, the oxygen overpotential at the current density of 1000 $A.m^{-2}$ of the Mn–Sn–W–O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anode is significantly shifted to lower potential value than that of the Mn–Sn–O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anode and this over potential value is even lower than those of Mn–Sn–W–Sb–O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti, Mn–Sn–W–Mo–O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti and Mn–Sn–W–Sb–Mo–O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anodes (Fig. 6). Consequently, it can be said that tungsten addition to Mn–Sn–O electrocatalyst is more effective for showing high electronic conductivity of the electrocatalyst than the additions of antimony or/and molybdenum to the Mn–Sn–W–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 $A.m^{-2}$.

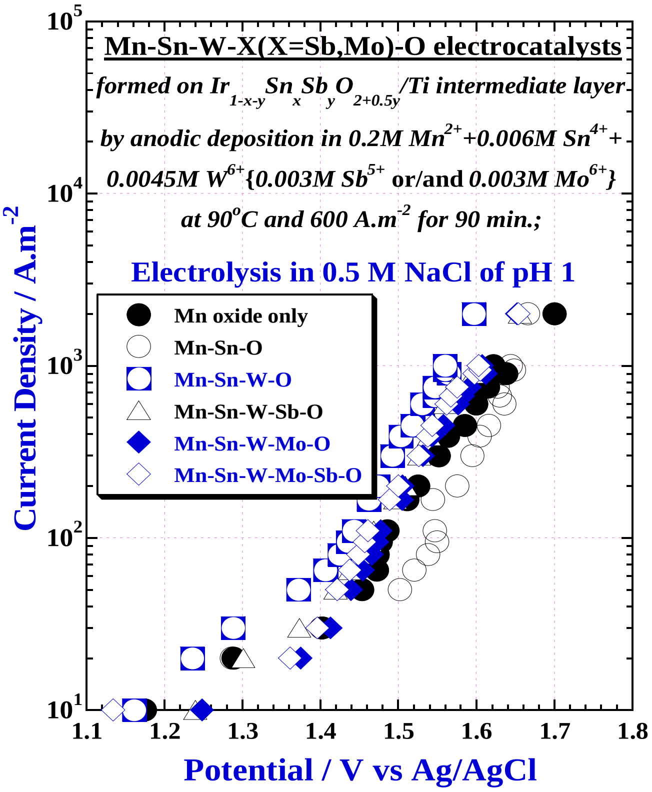

Figure 5: *Galvanostatic polarization curves measured in 0.5 M NaCl of pH 1 at 25°C for the electrodeposited Mn–Sn–W–X(X=Sb,Mo)–O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anodes.*

The oxygen overpotential at the current density of 1000 $A.m^{-2}$ for three Mn–Sn–W–Sb–O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti, Mn–Sn–W–Mo–O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti and Mn–Sn–W–Sb–

Mo–O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anodes is almost same value (that is, about in 1.60 V vs Ag/AgCl) and this overpotential value of these three different anodes is lower than that of the MnO_2/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti and Mn–Sn–O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anodes. Furthermore, it is noteworthy to mention here that the oxygen overpotential value of 1.60 V vs Ag/AgCl at current density of 1000 A.m^{-2} observed in the present study is almost same value as reported for the anodically deposited Mn–X–Y–O(X=Mo,W &Y=Sn)/IrO_2/Ti anodes [9,10,12-14]. However, the amount of iridium content in the intermediate oxide layer of the $Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti electrode is only about 1/22 of the IrO_2/Ti electrodes. These results revealed that the addition of SnO_2 with small amount of Sb_2O_5 to the intermediate layer of the Mn–X–Y–O(X=Mo,W&Y=Sn)/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anodes is effective to decrease the use of IrO_2 to about 1/22, maintaining high electronic conductivity of the intermediate $Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$ layer on titanium substrate. The result revealed that the simultaneous additions of tungsten, antimony and molybdenum in the electrodeposited binary Mn–Sn oxide electrocatalysts is more effective for high electronic conductivity of the Mn–Sn–based Mn–Sn–X–Y(X=W;Y=Sb or/and Mo)–O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anodes.

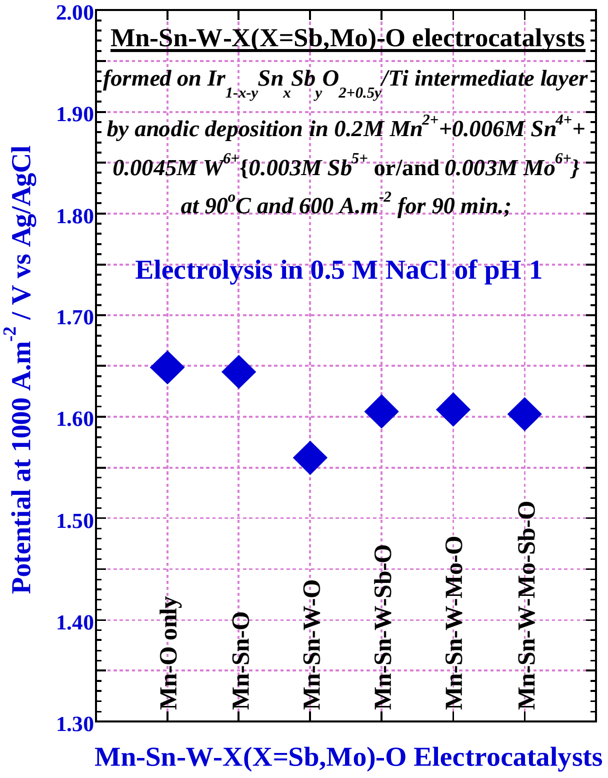

***Figure 6**: Oxygen overpotentials of the Mn–Sn–W–X(X=Sb,Mo)–O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anodes at the current density of 1000 A.m^{-2} in 0.5 M NaCl of pH 1 at 25°C. The oxygen overpotentials of the MnO2/Ir1–x–ySnxSbyO2+0.5y/Ti and Mn–Sn–O/Ir1–x–ySnxSbyO2+0.5y/Ti anodes are also shown for comparison.*

The XRD patterns of all the examined Mn–Sn–W–X(X=Sb,Mo)–O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anodes in this study had shown only the reflection of γ–MnO2 and the apparent grain size of these anodically deposited anodes was estimated using Schereer formula and found to be in the ranges of 4–8 nm. No separate reflections corresponding to tin, tungsten, antimony and molybdenum oxides were detected, indicating that the deposits were single phase oxides. XPS analysis revealed that tin, tungsten, antimony and molybdenum species were in the tetravalent, hexavalent, pentavalent and hexavalent states, respectively. These results revealed that the anodically deposited Mn–Sn–W–X(X=Sb,Mo)–O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anodes were composed of single-phase nanocrystalline γ–MnO_2 type triplet/quadrate oxides consisting of Mn^{2+}, Sn^{4+}, W^{6+}, Sb^{5+} or Mo^{6+} ions.

Conclusions

Successfully tailored new types of nanocrystalline Mn–Sn–W–X(X=Sb,Mo)–O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anodes. These electrodeposited Mn–Sn–W–based triple or quadruple oxide anodes showed about 99.70–99.85 % 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 or quadruple oxide electrocatalysts maintained during prolonged electrolysis and even after the electrolysis for five or more months.

Acknowledgements

The author would like to express his sincere gratitude to Emeritus Professor Dr. Koji Hashimoto and Dr. Zenta Kato of Tohoku Institute of Technology, Sendai, Japan for providing the research facilities of coating and an opportunity to visit Tohoku Institute of Technology, Japan as a Research Fellow.

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