

Effects of Zinc and Tungsten Additions in Mn–Mo–O Electrocatalyst for Hydrogen Production from Seawater Electrolysis

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Abstract

An attempt was made to enhance the oxygen evolution efficiency in seawater electrolysis by the additions of zinc and tungsten to the Mn–Mo–O electrocatalyst anodically deposited on the intermediate $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}/\text{Ti}$ electrode to produce hydrogen gas necessary for CO_2 recycling project. The $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}/\text{Ti}$ supported nanocrystalline $\gamma\text{-MnO}_2$ type Mn–Mo–X (X=Zn, W)–O electrocatalysts with grain size of about 4–10 nm were tailored by anodic deposition and these anodes showed the almost 100 % oxygen evolution efficiency at 1000 A.m^{-2} in 0.5 M NaCl solution of pH 1 at 25 °C. They guaranteed the stable anode performance of 99.75–99.85 % oxygen evolution efficiencies for more than 5 months.

Keywords: CO_2 recycling, global warming, $\gamma\text{-MnO}_2$ electrocatalyst, oxygen evolution efficiency, hydrogen production

Introduction

The CO_2 emissions which induce global warming increase with the growth of the economic activity of the world. Since it is impossible to decrease the economic activity, it is also impossible to decrease the CO_2 emissions only by efforts for energy saving and by improvements of the energy efficiency. It is meaningful to mention here that 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 in 1990. 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 last twenty 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 carbon emissions. Such a huge carbon 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 are proposing global CO_2 recycling to prevent global warming and to supply abundant energy converted from solar energy¹⁻⁴.

Key materials necessary for the global CO_2 recycling 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 anodes and cathodes for seawater electrolysis, and catalyst for CO_2 methanation. Oxygen production is prerequisite for the CO_2 recycle project without forming environmentally harmful chlorine for safety production of hydrogen in seawater electrolysis. However, the equilibrium potential of oxygen evolution is lower than that of chlorine evolution in seawater electrolysis and the chlorine evolution is a simpler reaction than the oxygen evolution. 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 prevention of global warming, 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 was anode for seawater electrolysis because, for CH₄ 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.

A variety of γ -MnO₂ type double or triple oxides for electrocatalysts of anodes were tailored by thermal decomposition^{5,6} and anodic deposition⁷⁻¹² on the iridium dioxide (IrO₂)-coated titanium substrate. These anodes showed about 90–100 % initial oxygen evolution efficiency in electrolysis of 0.5 M NaCl solution at 1000 A.m⁻². The anodes were formed by two layers; the outer most layers is electrocatalysts of γ -MnO₂ type double or triple oxides and the intermediate oxide layer preventing the formation of insulating titanium oxide on the titanium substrate is generally IrO₂. 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. It has been reported that the γ -MnO₂ type Mn–Mo–Sn–O¹³⁻¹⁶, Mn–Sn–W–X(X=Sb,Mo)–O¹⁷ and Mn–W–X(X=Sn,Sb,Mo)–O¹⁸ anodes on the intermediate layer of Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti electrode containing about 24 % of IrO₂, 66 % of SnO₂ with 10 % of Sb₂O₅ showed almost 100 % oxygen evolution efficiency (OEE) after electrolysis for about five months or more periods in 0.5 M NaCl of pH 1 at 1000 A.m⁻². Similarly, it has been reported that the the γ -MnO₂ type Mn–Mo–Sn–O electrocatalysts on the intermediate layer of Ir_{1-x}Sn_xO₂/Ti^{19,20} and Sn_{1-x}Sb_xO_{2+0.5x}/Ti²¹ electrodes showed almost 100 % oxygen evolution efficiency (OEE) after electrolysis for about 3400 h and showed about 98 % of OEE after electrolysis for about 20 h respectively, in 0.5 M NaCl of pH 1 at 1000 A.m⁻². In this context, the present work is aimed to develop a more stable and efficient oxygen evolution Mn–Mo–X(X=Zn,W)–O/Ir_{1-x-y}Sn_x–Sb_yO_{2+y}/Ti anodes for the production of hydrogen from seawater electrolysis. Particular

attention was paid to the effect of the additions of Zn²⁺ and W⁶⁺ ions to the electrodeposited Mn–Mo–O electrocatalyst.

Material and Methods

Punched titanium metal substrate was immersed in a 0.5 M HF solution for 5 minutes 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 until hydrogen evolution was ceased to enhance the anchor effect of the substrate on the electrocatalysts layer. Then the treated-titanium metal was used as substrate for coating of the intermediate Ir_{1-x-y}Sn_xSb_yO_{2+0.5y} oxide layer. The Ir_{1-x-y}Sn_xSb_yO_{2+0.5y} intermediate layer was prepared using coating solution which was prepared by mixing of 0.024 M chloroiridic acid {H₂IrCl₆.6H₂O}, 0.0676 M tin chloride {SnCl₄.5H₂O} and 0.0084 M SbCl₅ butanolic solutions in which the sum of the metallic cations was kept at 0.1 M. The coating solution was used for coating on the treated-titanium substrate with a brush, dried at 80°C for 10 minutes and then baked at 450°C for 10 minutes in air. This coating procedure was repeated 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 Ir_{1-x-y}Sn_xSb_yO_{2+0.5y} intermediate layer-coated titanium substrate specimen 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 for 5 minutes in 1 M H₂SO₄ solution at room temperature. This is called the Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti electrode.

The Mn–Mo–X(X=Zn,W) oxide electrocatalysts for oxygen evolution were 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 0.2 M MnSO₄.5H₂O + 0.003 M Na₂MoO₄.2H₂O + {0.006 M Zn(NO₃)₂.6H₂O or/and 0.0045 M Na₂WO₄.2H₂O} at pH –0.1 and 90°C for 90 minutes. The electrodeposition of the Mn–Mo–X(X=Zn,W) oxide electrocatalysts were carried out by exchanging electrolyte for every 30 minutes. The

performance of the Mn–Mo–X–O (X=Zn,W)/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 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^{7,11}. The amount of chlorine formed was analyzed by iodimetric titration of chlorine and hypochlorite.

Galvanostatic polarization measurement of the electrodeposited Mn–Mo–X (X=Zn,W)–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 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 Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti electrodes and Mn–Mo–X (X=Zn,W)–O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti anodes were characterized by X–ray diffraction (XRD) patterns using CuK_α radiation.

Results and Discussion

Figure 1 shows X–ray diffraction patterns of the intermediate Ir_{1-x-y}Sn_xSb_yO_{2+0.5y} layer on titanium substrate and the electrodeposited Mn–Mo–Zn–O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti anode. There are no separate peaks for IrO₂, SnO₂ and Sb₂O₅ at the XRD patterns of the Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti electrode as shown in Fig. 1(a), indicating the formation of single–phase IrO₂–SnO₂–Sb₂O₅ layer. It is noteworthy to mention here that iridium, tin and antimony oxides on the titanium substrate were identified as IrO₂, SnO₂ and Sb₂O₅, respectively, from XPS analysis^{13,14}. These results revealed that the intermediate Ir_{1-x-y}Sn_xSb_yO_{2+0.5y} layer is consisted of triple oxides of a rutile structure with fine grains instead of the mixture of iridium, tin and antimony oxides. On the other hand, there are no separate peaks for manganese, molybdenum and zinc oxides for the anodically deposited Mn–Mo–Zn–

O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti anode. The XRD patterns of the electrodeposited Mn–Mo–Zn–O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti anode show only the reflections of γ–MnO₂ as shown in fig. 1b. The XRD patterns of the Mn–Mo–W–O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti anode had only the reflections of γ–MnO₂ which is not shown here. Furthermore, the apparent grain size of the anodically deposited Mn–Mo–X (X=Zr,W)–O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti anodes was estimated from full width at half maximum (FWHM) of the most intense XRD reflection by using the Scherrer's formula²². The estimated apparent grain size of the anodically deposited Mn–Mo–X (X=Zn,W)–O electrocatalysts was found about 7 nm. These results revealed that the anodically deposited Mn–Mo–X (X=Zr,W)–O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti anodes consisted of the nanocrystalline γ–MnO₂–type triple oxides consisting of Mn²⁺, Mo⁶⁺, W⁶⁺ or Zn²⁺ ions.

Figure 2 shows IR–corrected galvanostatic polarization curves measured in 0.5 M NaCl solution of pH 1 at 25°C for the anodically deposited Mn–M (M=Sn,Mo,W)–O electrocatalysts on the Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti electrode. The anodically deposited Mn–Mo–O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti anode shows lowest oxygen overpotential among the other two Mn–W–O/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 at high current density of 1000 A.m⁻². Consequently, it can be said that molybdenum addition is more effective for high electronic conductivity among these binary manganese–base oxide electrocatalysts.

Figure 3 shows IR–corrected galvanostatic polarization curves measured in 0.5 M NaCl solution of pH 1 at 25°C for the anodically deposited Mn–Mo–X (X=Zn,W)–O electrocatalysts on the Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti electrode to study the effect of additional elements of zinc and tungsten in the Mn–Mo–O electrocatalyst. All these examined Mn–Mo–X (X=Zn,W)–O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti anodes show almost same value of the oxygen overpotential at the current density of 1000 A.m⁻² and the oxygen overpotential of these anodes are lower than that of the MnO₂ electrocatalyst. These results revealed that

the additions of zinc and tungsten in the Mn–Mo–based oxide electrocatalysts is more effective for high electronic conductivity of the Mn–Mo–based Mn–Mo–X(X=Zn,W)–O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti anodes.

Figure 4 shows the effects of the additional elements on the Mn–Mo–X (X=Zn,W)–O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti anodes for oxygen overpotential at 1000 A.m⁻² and the initial oxygen evolution efficiency measured in 0.5 M NaCl solution of pH 1 at 25°C. The oxygen overpotential at the current density of 1000 A.m⁻² for all the examined Mn–Mo–X(X=Zn,W)–O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti anodes in this study is almost same (that is, about in 1.60 V vs Ag/AgCl) and the overpotential values of these anodes are lower than that of the MnO₂/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti anode.

It is noteworthy to mention here that the oxygen overpotential value of about 1.60 V vs Ag/AgCl at 1000 A.m⁻² observed in the present study for the anodically deposited Mn–Mo–X(X=Zn,W)–O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti anodes is almost same the oxygen overpotential values as previously reported for the anodically deposited Mn–X–Y(X=Mo,W and Y=Sn)–O/IrO₂/Ti anodes^{7,8,10,12}. 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 IrO₂/Ti electrodes. These results revealed that the addition of SnO₂ with small amount of Sb₂O₅ 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 IrO₂ 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. On the other hand, the additions of zinc and tungsten on the Mn–Mo–O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti anodes showed high activity of the oxygen evolution efficiency of about 99 % or more in seawater electrolysis. In particular, the initial oxygen evolution efficiency of the Mn–Mo–Zn–O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti anode shows highest oxygen evolution efficiency, that is, about 99.65 % in 0.5 M NaCl solution of pH 1 at 25°C (fig. 4).

Furthermore, the durability test on the Mn–Mo–based oxide electrodes was carried out. Figure 5 shows the durability result on the Mn–Mo–X (X=Zn,W)–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. Both these anodes showed about 99.75 to 99.85 % oxygen evolution efficiency in the electrolysis of 0.5 M NaCl of pH 1 at 25°C and the oxygen evolution efficiency is independent of the electrolysis time for about 3700 hours. The Mn–Mo–Zn–O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti anode shows slightly higher oxygen evolution efficiency of about 99.85% than that of the Mn–Mo–W–O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti anodes.

4. Conclusion

An attempt was made to enhance the oxygen evolution efficiency in seawater electrolysis by the additions of zinc and tungsten to the electrodeposited Mn–Mo–O electrocatalyst on the intermediate Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti electrode. The following conclusions are drawn from the examination of the manganese–based oxide electrocatalysts for oxygen evolution efficiency in 0.5 M NaCl of pH 1 at 25°C.

Successfully tailored new types of anodically deposited nanocrystalline Mn–Mo–Zn–O and Mn–Mo–W–O electrocatalysts on the intermediate layer of the Ir_{1-x-y}Sn_xSb_yO_{2+0.5y} on titanium substrate for the production of hydrogen gas from seawater electrolysis with forming less than 0.25 % of the environmentally harmful chlorine gas at the anodes of a simple electrolyzer. The high oxygen evolution efficiency of these ternary oxide electrocatalysts maintained during prolonged electrolysis and even after the electrolysis for five or more months. The Mn–Mo–X(X=Zn,W)–O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti anodes electrocatalysts showed an oxygen evolution efficiency of about 99.75–99.85 %.

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References

1. Hashimoto K., Kato Z., Kumagai N. and Izumiya K., Materials and technology for supply of renewable energy and prevention of global warming, *J. Physics: Conference Series*, **144**, 1 (2009)
2. Hashimoto K., Metastable metal for green materials for global atmosphere conservation and abundant energy supply, *Mater Sci Eng.*, **A179/A180**, 27 (1994)
3. Hashimoto K., Habazaki H., Yamasaki M., Meguro S., Sasaki T., Katagiri H., Matsui T., Fujimura K., Izumiya K., Kumagai N. and Akiyama E., Advanced materials for global carbon dioxide recycling, *Mater. Sci. Eng.*, **A304-306**, 88 (2001)
4. Hashimoto K., Yamasaki M., Meguro S., Sasaki T., Katagiri H., Izumiya K., Kumagai N., Habazaki H., Akiyama E. and Asami K., *Corros. Sci.*, **44**, 371 (2002)
5. Izumiya K., Akiyama E., Habazaki H., Kawashima A., Asami K. and Hashimoto K., Surface activation of manganese oxide electrode for oxygen evolution from seawater, *J. Appl. Electrochem.*, **27**, 1362 (1997)
6. Izumiya K., Akiyama E., Habazaki H., Kumagai N., Kawashima A. and Hashimoto K., Effects of a additional elements on electrocatalytic properties of thermally decomposed manganese oxide electrodes for oxygen evolution from seawater, *Mater. Trans. JIM*, **38**, 899 (1997)
7. Izumiya K., Akiyama E., Habazaki H., Kumagai N., Kawashima A. and Hashimoto K., Anodically deposited manganese oxide and manganese–tungsten oxide electrodes for oxygen evolution from seawater, *Electrochim. Acta*, **43**, 3303 (1998)
8. Fujimura K., Izumiya K., Kawashima A., Akiyama E., Habazaki H., Kumagai N., Kawashima A. and Hashimoto K., Anodically deposited manganese–molybdenum oxide anodes with high selectivity for evolving oxygen in electrolysis of seawater, *J. Appl. Electrochem.*, **29**, 765 (1999)
9. Fujimura K., Matsui T., Habazaki H., Kawashima A., Kumagai N. and Hashimoto K., The durability of manganese–molybdenum oxide anodes for oxygen evolution in seawater electrolysis, *Electrochim. Acta*, **45**, 2297 (2000)
10. Habazaki H., Matsui T., Kawashima A., Kumagai N. and Hashimoto K., Nanocrystalline manganese–molybdenum–tungsten oxide anodes for oxygen evolution in seawater electrolysis, *Scripta Mater.*, **44**, 1659 (2001)
11. Abdel Ghany N. A., Kumagai N., Meguro S., Asami K. and Hashimoto K., Oxygen evolution anodes composed of anodically deposited Mn–Mo–Fe oxides for seawater electrolysis, *Electrochim. Acta*, **48**, 21 (2002)
12. El–Moneim A.A., Kumagai N., Asami K. and Hashimoto K., New nanocrystalline manganese–molybdenum–tin oxide anodes for oxygen evolution in seawater electrolysis. in *Corrosion and Electrochemistry of Advanced Materials in Honor of Koji Hashimoto* (Eds S. Fujimoto, H. Habazaki, E. Akiyama and B. MacDougall), *ECS Transactions*, The Electrochemical Society, Pennington, NJ. **1(4)**, 491 (2006)
13. Bhattarai J., Shinomiya H., Kato Z., Izumiya K., Kumagai N. and Hashimoto K., Improvement of the intermediate layer in preventing insulating oxide formation in titanium substrate for oxygen evolution anodes in seawater electrolysis, in *Proc. 54th Japan Conf. Materials & Environments*, Japan Society of Corrosion Engineers (JSCE), Hiroshima, Japan, **C–207**, 345 (2007)
14. Bhattarai J., 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 MN_{1-x} .

$y\text{Mo}_x\text{Sn}_y\text{O}_{2+x}$ anodes in seawater electrolysis, *J. Nepal Chem. Soc.*, **23**, 21 (2008/2009)

15. Kato Z., Bhattarai J., Izumiya K., Kumagai N and Hashimoto K., The improvement of the intermediate layer by substitution of iridium with tin in Mn–Mo–Sn triple oxide/ IrO_2 /Ti anodes for oxygen evolution in seawater electrolysis, in *Abstract book of 214th Electrochemical Society Meeting*, Abstract No. 1632, The Electrochemical Society, Pennington, NJ (2008)

16. El-Moneim A.A., Bhattarai J., Kato Z., Izumiya K., Kumagai N. and Hashimoto K., Mn–Mo–Sn oxide anodes for oxygen evolution in seawater electrolysis for hydrogen production, in *Oxide Films* (Eds P Marcus, S Fujimoto and H Terryn), *ECS Transactions*, The Electrochemical Society, Pennington, NJ, **25(40)**, 127 (2010)

17. Bhattarai J., 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, *J. Nepal Chem. Soc.*, **25**, 9 (2010)

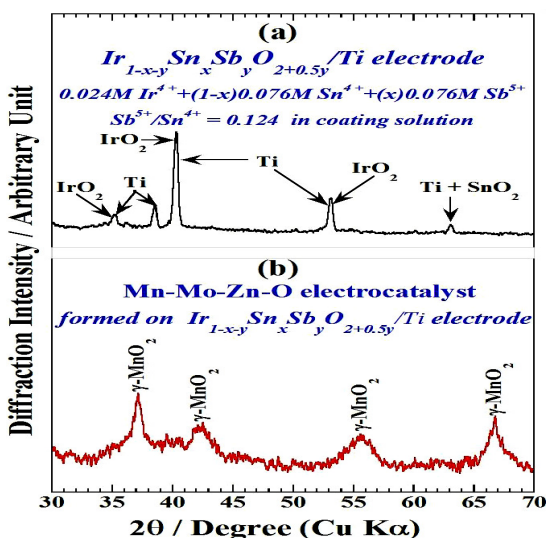


Figure-1: XRD patterns of (a) $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}/\text{Ti}$ electrode and (b) anodically deposited Mn-Mo-Zn-O electrocatalyst deposited on the $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}/\text{Ti}$ electrode

18. Bhattarai J., Effects of tin, antimony and molybdenum in Mn–W–O/ $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}/\text{Ti}$ anodes for oxygen evolution in seawater electrolysis, *Scientific World*, **8**, 39 (2010)

19. Kato Z., Bhattarai J., Izumiya K., Kumagai N. and Hashimoto K., Improvement of intermediate layer by formation of tin–iridium dioxide in oxygen evolution anodes for seawater electrolysis, in *Abstract book of 216th Electrochemical Society Meeting*, Abstract No. 1942, The Electrochemical Society, Pennington, NJ (2009)

20. Kato Z., Bhattarai J., Izumiya K., Kumagai N. and Hashimoto K., Durability enhancement and degradation of oxygen evolution anodes in seawater electrolysis for hydrogen production, *Appl. Surf. Sci.*, in press (2011)

21. Bhattarai J., The development of the intermediate SnO_2 – Sb_2O_5 layer on titanium substrate for oxygen evolution anodes in seawater electrolysis, *J. Nepal Chem. Soc.*, **23**, 54 (2008/2009)

22. Cullity B. D., Elements of X-ray Diffraction, 2nd edition, Addison–Wesley Publ. Co, Inc., 101 (1977)

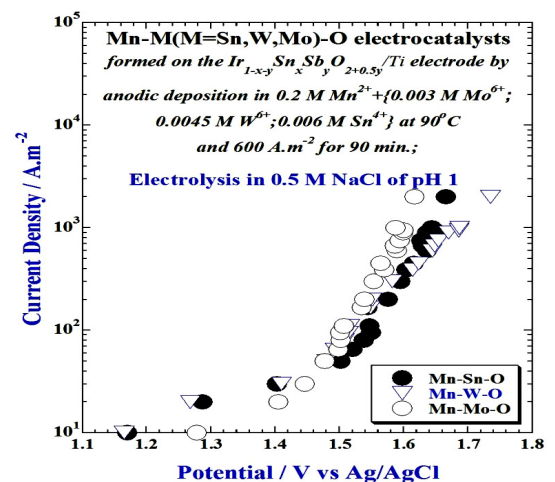


Figure-2: Galvanostatic polarization curves for Mn–M(M=Sn,W,Mo)–O/ $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}/\text{Ti}$ anodes measured in 0.5 M NaCl solution of pH 1 at 25°C

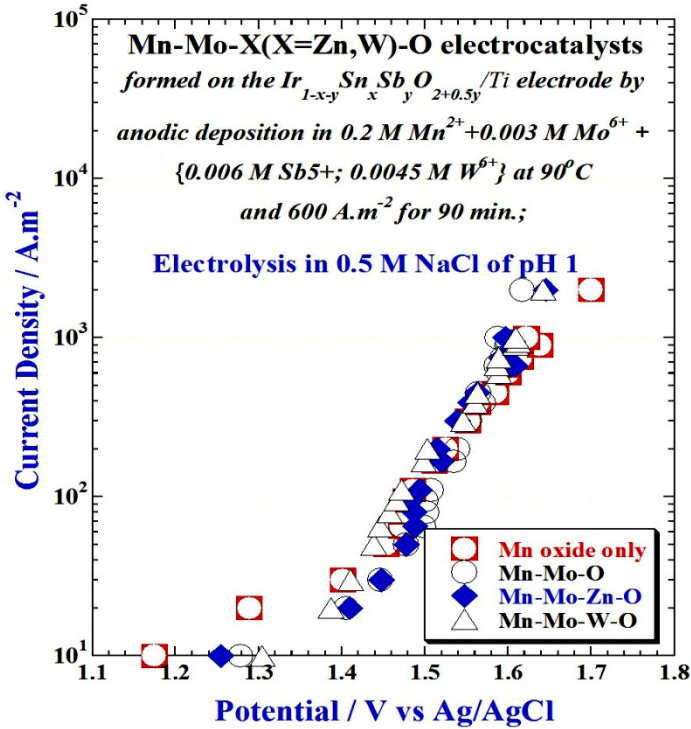


Figure-3: Galvanostatic polarization curves for the Mn-Mo-X(X=Zn,W)-O/ $Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti$ anodes in 0.5 M NaCl solution of pH 1 at 25°C.

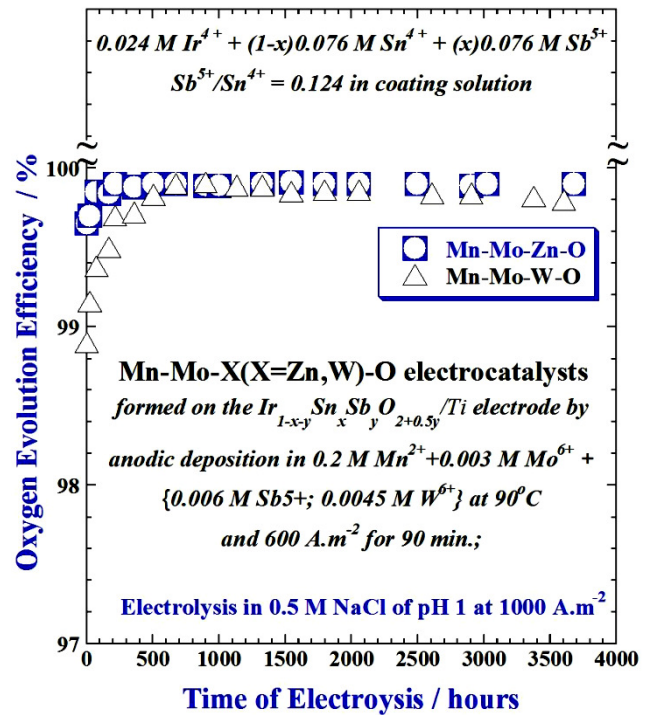


Figure-5: Changes in the oxygen evolution efficiency of the Mn-Mo-X(X=Zn,W)-O electrocatalysts deposited on the $Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti$ electrode in 0.5 M NaCl solution of pH 1 at the current density of $1000 A.m^{-2}$, as a function of electrolysis time.

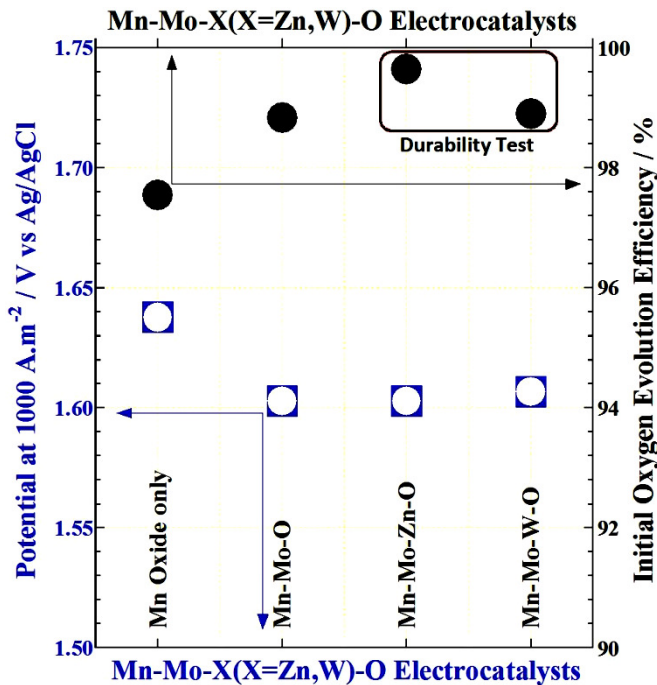


Figure-4: Changes in the oxygen overpotential and the initial oxygen evolution efficiency of the Mn-Mo-X(X=Zn,W)-O/ $Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti$ anodes in 0.5 M NaCl solution of pH 1 at the current density of $1000 A.m^{-2}$.