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# Effects of antimony and tungsten additions in Mn–Mo–Sn oxide electrocatalyst for hydrogen production from electrolysis of 0.5 M NaCl solution

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## Abstract

Successfully tailored new types of nanocrystalline Mn-Mo-Sn-W-O and Mn-Mo-Sn-W-Sb-O electrocatalysts on the intermediate layer of $Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$ on titanium metal substrate for the production of hydrogen gas from electrolysis of 0.5 M NaCl solution of pH 1 at very high current density of 1000 $A.m^{-2}$ with forming less than 0.3 % of the environmentally harmful chlorine. Antimony and tungsten additions are more effective for better durability of both the electrodeposited Mn-Mo-Sn-X(X=Sb,W)-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anodes than that of Mn-Mo-Sn-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anode for long period electrolysis of acidic 0.5 M NaCl solution to produce hydrogen. The high oxygen evolution efficiency (OEE) of the quadrate or more oxides electrocatalysts (i. e., 99.7-99.9 % OEE) maintained during prolonged electrolysis and even after electrolysis for five or more months. The Mn-Mo-Sn-X(X=Sb,W)-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anodes showed about 99.7-99.9 % of oxygen evolution efficiency.

**Key words:** Global warming, $CO_2$ recycling, Electrodeposited anodes, Hydrogen production, Electrolysis.

## Introduction

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, 2011). 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 order to retain a level of long-life greenhouse gases. Furthermore, it is noteworthy to mention here that it is impossible and not meaningful to decrease only the economic activity of the world for the reduction of $CO_2$ emissions only by efforts for energy saving and by improvements of the energy efficiency. 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 (Hashimoto 1994; Hashimoto *et al.* 2001, 2009; Kato *et al.* 2008, 2009, 2011; El Moneim e*t al.* 2010).

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 for last twenty years. 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, for large-scale seawater electrolysis to produce hydrogen at cathode for the $CO_2$ recycle project, 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 development of stable and

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*Corresponding author. E-mail: bhattatai_05@yahoo.com more efficient anode for seawater electrolysis because, for $CH_4$ production a large 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 $\gamma$-$MnO_2$ type double, triple or quadrate oxides for electrocatalysts were prepared by anodic deposition on the intermediate layer of $IrO_2$-$SnO_2$-$Sb_2O_5$ layer on the titanium metal substrate. The anodic deposited Mn-Mo-X(X=Sn,W)-O (Bhattarai 2011a), Mn-W X(X=Sn, Sb, Mo)-O (Bhattarai 2010a), Mn-Mo-X(X=Zn, Sn,W)-O (Bhattarai 2010b), Mn-Mo-Sn-O (Bhattarai *et al.* 2007; Kato *et al.* 2008, 2009, 2011; Bhattarai 2008/2009, 2009c; El Moneim *et al.* 2010) and Mn-Sn-W-X(X=Sb,Mo) O (Bhattarai 2010d) electrocatalysts on the intermediate layer of $Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti electrode showed about 99.70 99.85% oxygen evolution efficiency (OEE) after electrolysis for about 3400 3600 h in 0.5 M NaCl solution of pH 1 at high current density of 1000 A.m$^{-2}$. The intermediate oxide layer of the $Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti electrode was prepared using the mixture of coating solutions (butanolic) containing 0.024 M Ir$^{4+}$ , 0.0676 M Sn$^{4+}$ and 0.0084 M Sb$^{5+}$ on titanium substrate in which the sum of the metallic cations in the intermediate oxide layer was kept at 0.1 M as described elsewhere (Bhattarai *et al.* 2007; Bhattarai 2008/2009). In this context, the present research work is focused to develop a more stable and efficient oxygen evolution Mn-Mo-Sn-X(X=Sb, W)-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anodes for hydrogen production without the evolution of environmentally harmful chlorine from electrolysis of 0.5 M NaCl solution of pH 1. Particular attention was focused to study the roles of antimony and tungsten additions in the Mn-Mo-Sn-X(X=Sb, W)-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anodes for the oxygen evolution 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 treated in 0.5 M HF solution to remove air-formed oxide film, rinsed with deionized water and then subjected for surface roughening by etching in 11.5 M $H_2SO_4$ solution at 80 °C as described elsewhere (Bhattarai 2008/2009, 2011b; Bhattarai *et al.* 2007; Kato *et al.* 2011). The treated-titanium metal was used as a 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 {$H_2IrCl_6.6H_2O$}, 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 have been described elsewhere (Bhattarai 2008/2009, 2011b; Bhattarai *et al.* 2007; Kato *et al.* 2011). 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 (Bhattarai *et al.* 2007) and the intermediate $Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$ layer was consisted of triple oxides of a rutile structure with fine grains instead of the mixture of oxides of iridium, tin and antimony (Bhattarai 2008/2009; Bhattarai *et al.* 2007).

The $Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$ intermediate layer-coated titanium substrate specimen, is also called as $Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti electrode, was degreased by anodic polarization at 1000 A.m$^{-2}$ for 5 minutes in 10 M NaOH solution and then 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-Mo-Sn-X(X=Sb,W)-O 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 the solution containing 0.2 M $MnSO_4.5H_2O$ + 0.003 M $Na_2MoO_4.2H_2O$+ 0.006M $SnCl_4.5H_2O$+{0.003 M $SbCl_5$ solution or/and 0.0045 M $Na_2WO_4.2H_2O$} at pH -0.1 and 90°C for 90 minutes. The electrodeposition of the Mn-Mo-Sn-X(X=Sb,W) oxide electrocatalysts were carried out by exchanging electrolyte for every 30 minutes.

The performance of the three anodes, that is, Mn-Mo-Sn-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti, Mn-Mo-Sn-W-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti and Mn-Mo-Sn-W-Sb O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti were 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.* 1997; Abdel Ghany *et al.* 2002). The amount of chlorine formed was analyzed by iodimetric titration of chlorine and hypochlorite.

Galvanostatic polarization measurement of the electrodeposited Mn-Mo-Sn-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti, Mn-Mo-Sn-W-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti and Mn-Mo-Sn-W-Sb O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti 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 surface morphology of the anodically deposited Mn-Mo-Sn-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti, Mn-Mo-Sn-W-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti and Mn-Mo-Sn-W-Sb O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/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-Mo-Sn-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti, Mn-Mo-Sn-W-O/ $Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/ Ti and Mn-Mo-Sn-W-Sb O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anodes were characterized by X-ray diffraction (XRD) patterns using Cu $K_\alpha$ radiation.

## Results and Discussion

Fig. 1 shows X ray diffraction patterns of the anodically electrodeposited Mn-Mo-Sn-W-O and Mn-Mo-Sn-W-Sb-O electrocatalysts on the $Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti electrode. There are no separate peaks for manganese, molybdenum, tin, tungsten or/and antimony oxides on the anodically deposited Mn-Mo-Sn-X(X=Sb,W)-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anodes. The XRD patterns of the anodically deposited Mn-Mo-Sn-X(X=Sb,W)-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anodes show only the reflections of γ -$MnO_2$ as shown in Fig. 1.

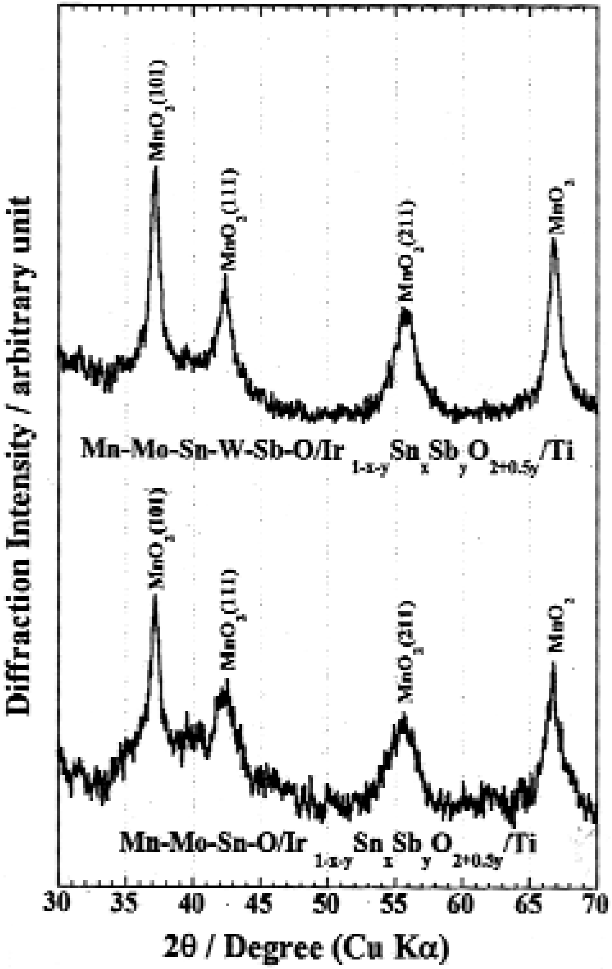


**Fig. 1:** **XRD patterns of the anodically deposited Mn-Mo-Sn-X(X=Sb,W)-O electrocatalysts on the $Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti electrode**

Furthermore, the apparent grain size of the anodically deposited Mn-Mo-Sn-X(X=Sb,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 equation (Bhattarai 2011b, Cullity 1977). The estimated apparent grain size of the electrodeposited Mn-Mo-Sn-X(X=Sb,W)-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anodes was found to be in the ranges of 5-10 nm. These results revealed that both the anodically deposited Mn-Mo-Sn-W-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti and Mn-Mo-Sn-W Sb-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anodes consisted of a nanocrystalline γ-$MnO_2$-type quadrate or more oxides consisting of $Mn^{3+}$, $Mo^{6+}$, $Sn^{4+}$, $W^{6+}$ or/and $Sb^{5+}$ ions.

Fig. 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-Mo-Sn-X(X=Sb,W)-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anodes to study the effect of antimony or/and tungsten oxides in the Mn-Mo-Sn-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anode. The galvanostatic polarization curves for the anodically deposited Mn-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti, Mn-Mo-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti and Mn-

Mo-Sn-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anodes are also shown for comparison. All the examined double, triple, quadrate or more oxide electrocatalysts deposited in the $Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti electrode show almost same and lower oxygen overpotential (that is, about 1.6 V vs Ag/AgCl) than that of Mn-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anode in 0.5 M NaCl solution of pH 1 at the current density of 1000 $A.m^{-2}$. Furthermore, the Mn-W-Sn-Sb-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti, Mn-W-Mo-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti, Mn-W-Mo-Sn-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti and Mn-W-Mo-Sn-Sb-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 $MnO_2$/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$ anode. These results revealed that the simultaneous additions of molybdenum, tin, antimony and tungsten in the Mn-based oxide electrocatalyst are more effective for high electronic conductivity of the $MnO_2$/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anodes.

Fig. 3 shows the effects of the additional elements on the Mn-Mo-Sn-X (X=Sb,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 overpotentials at the current density of 1000 $A.m^{-2}$ for the Mn-Mo-Sn-W-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti, Mn-Mo-Sn-W-Sb-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti, Mn-Mo-Sn-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti and Mn-Mo-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anodes are 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 $MnO_2$/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anode. It is noteworthy for mentioning here that the observed oxygen overpotential value of 1.60 V vs Ag/AgCl at the current density of 1000 $A.m^{-2}$ in the present study is almost same as that reported for the anodically

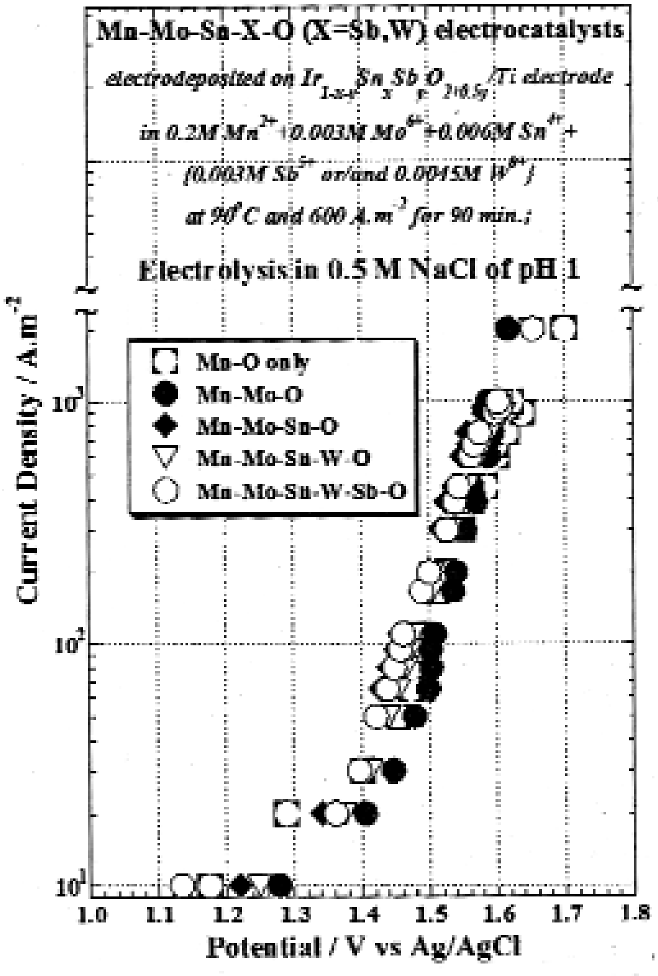


**Fig. 2: Galvanostatic polarization curves measured for the anodically deposited Mn-Mo-Sn-X(X=Sb, W)-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anodes after electrolysis in 0.5 M NaCl solution of pH 1 at 25 °C**

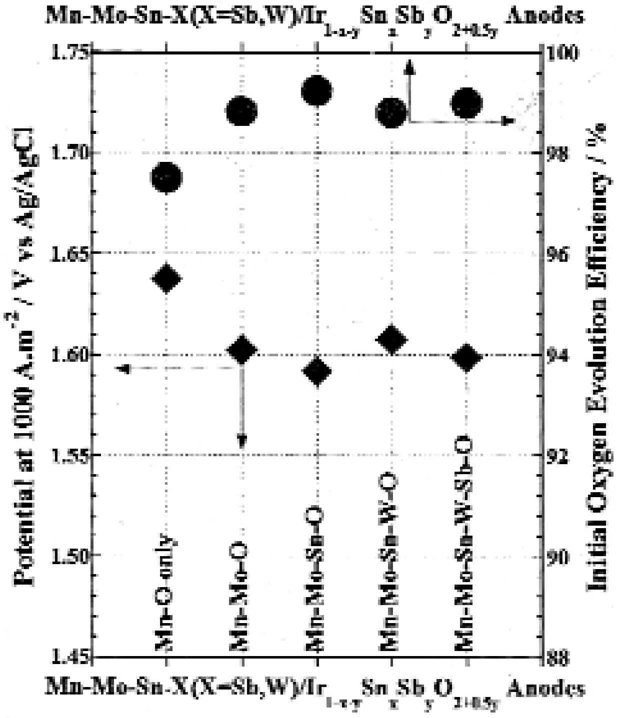


**Fig. 3: Changes in the oxygen overpotential and initial oxygen evolution efficiency of the Mn-Mo-Sn-X(X=Sb,W)-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anodes in 0.5 M NaCl of pH 1 at the current density of 1000 $A.m^{-2}$**

deposited Mn-Mo-X(X=W,Sn)-O/$IrO_2$/Ti anodes (Izumiya *et al.* 1998; Fujimura *et al.* 1999, 2000; Habazaki *et al.* 2001; El Moneim *et al.* 2006). However, the amount of iridium content in the $Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti electrode is only about 1/22 of the $IrO_2$/Ti electrode. These results revealed that the addition of $SnO_2$ with small amount of $Sb_2O_5$ to the intermediate layer of the Mn-Mo-Sn-X(X=Sb,W)-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/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. On the other hand, the additions of antimony and tungsten on the Mn-Mo-Sn-X(X=Sb,W)-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anodes show high activity of the initial oxygen evolution efficiency of about 98.85-99.25 %, while it is only about 97.50 % in 0.5 M NaCl solution of pH 1 at 25°C (Fig. 3). Furthermore, the durability test on the Mn-Mo-Sn-based oxide electrodes was carried out.

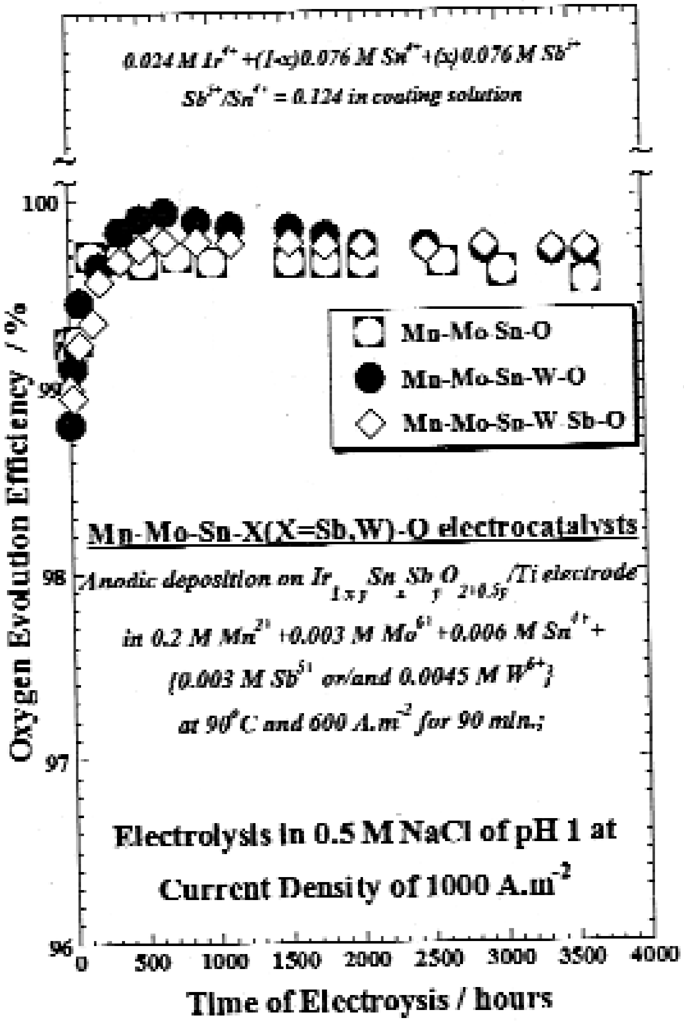
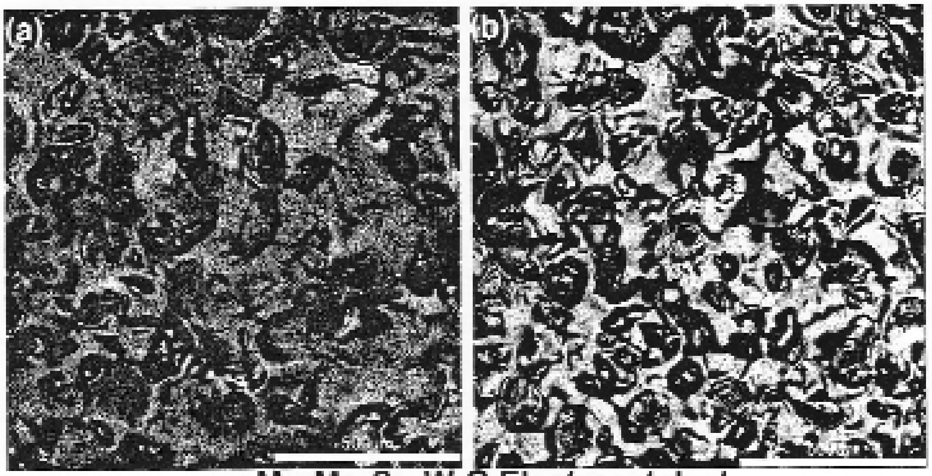


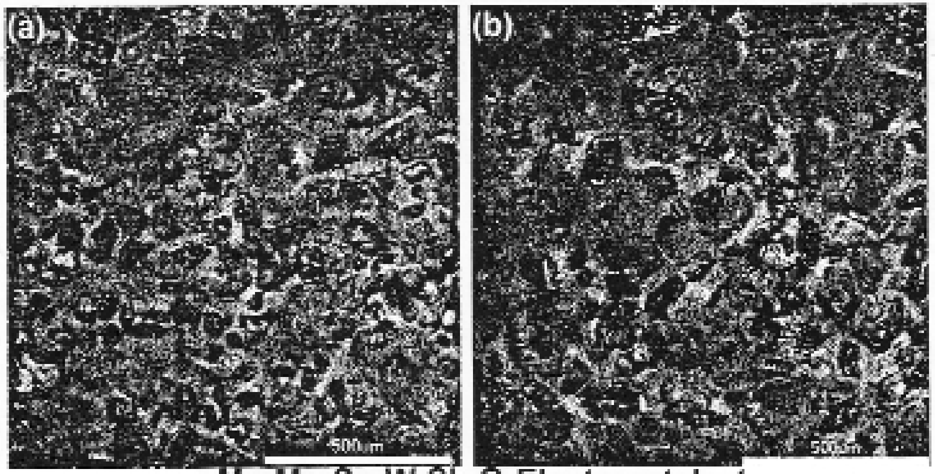
**Fig. 4: Changes in the oxygen evolution efficiency of the Mn-Mo-Sn-X(X=Sb,W)-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti in 0.5 M NaCl of pH 1 at the current density of 1000 $A.m^{-2}$, as a function of electrolysis time**

Fig. 4 shows the durability result on the Mn-Mo-Sn-X(X=Sb,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. The durability result on the electrodeposited Mn-Mo-Sn-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anode was also shown for comparison. An initial oxygen evolution efficiency of the Mn-Mo-Sn-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anode was about 99.25 %, whereas those of the Mn-Mo-Sn-W-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti and Mn-Mo-Sn-W-Sb-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anodes were about 98.8 and 99.0 %, respectively. However, both the anodically deposited Mn-Mo-Sn-W-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti and Mn-Mo-Sn-W-Sb-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anodes showed about 99.7 to 99.9 % oxygen evolution efficiency which is slightly higher OEE than that of the Mn-Mo-Sn-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anode after electrolysis between 500 3650 hours in 0.5 M NaCl of pH 1 at 25 °C. Furthermore, the oxygen evolution efficiency of the Mn-Mo-Sn-X(X=Sb,W)-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/ Ti anodes is independent of the electrolysis time for about 3650 hours. Consequently, the additions of antimony and tungsten are more effective for better durability of both the electrodeposited Mn-Mo-Sn-X(X=Sb,W) O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/ Ti anodes than that of Mn-Mo-Sn-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anode for long period electrolysis of 0.5 M NaCl of pH 1 to produce hydrogen.

Fig. 5(a) and 5(b) shows the changes of the surface morphology of the electrodeposited Mn-Mo-Sn-X(X=Sb,W)-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anodes before and after electrolysis in 0.5 M NaCl solution of pH 1 at the current density of 1000 $A.m^{-2}$ for about 1545 hours, respectively. 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 1545 hours in 0.5 M NaCl solution. This revealed that the filling of the cracks and pores by the beneficial ions ($Mn^{2+}$, $Mo^{6+}$, $Sn^{4+}$, $W^{6+}$ or $Sb^{5+}$) presence in the electrocatalysts was clearly observed after electrolysis for about one week periods or more. 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 or more as shown in Fig. 4.



Mn-Mo-Sn-W-O Electrocatalyst



Mn-Mo-Sn-W-Sb-O Electrocatalyst

**Fig. 5: Changes in the surface morphology of the Mn-Mo-Sn-W-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti and Mn-Mo-Sn-W-Sb-O/$Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}$/Ti anodes (a) before and (b) after electrolysis at the current density of 1000 A.m$^{-2}$ for 1545 h in 0.5 M NaCl solution of pH 1 at 25 °C**

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