INTRODUCTION

The CO₂ 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 CO₂ emissions only by efforts for energy saving and by improvements of the energy efficiency. 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 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, Professor Koji Hashimoto and his research groups at Tohoku University and Tohoku Institute of Technology have been proposed global CO₂ recycling project to prevent global warming and to supply abundant energy converted from solar energy²⁻⁵.

Key materials necessary for the global CO₂ recycling project are anodes and cathodes for seawater electrolysis, and catalysts for CO₂ conversion into CH₄ from the reaction between CO₂ and H₂. Hashimoto and his co–workers are tailoring these key materials of anodes and cathodes for seawater electrolysis, and catalyst for CO₂ methanation. 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 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 the anode for seawater electrolysis because, for CH₄ production a great 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.

A variety of γ–MnO₂ type double or triple oxides for electrocatalysts of anodes were tailored by thermal decomposition⁶⁻⁷ and anodic deposition⁸⁻¹⁵ on the iridium dioxide (IrO₂)–coated titanium substrate, and these anodes showed about 90–100 % initial oxygen evolution efficiency at 1000 A.m⁻². These anodes were formed by two layers; the outer most layer 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 triple oxide anodes on the intermediate layer of Ir₁₋ₓ₋ₓSnₓSbxO₂⁺₀.₅y/Ti electrode containing about 24% of IrO₂ with 10% of Sb₂O₅
showed about 99.7% oxygen evolution efficiency (OEE) after
electrolysis for about 3400 h in 0.5 M NaCl of pH 1 at 1000
A.m^2. In this context, the present research work is focused
to develop a more stable and efficient oxygen production
Mn–W–X(X=Sn,Mo,Mo)–O anodes for seawater electrolysis.
Particular attention was paid to the effect of the addition of
Sn^{4+}, Sb^{5+} and Mo^{6+} ions to Mn–W–O/Ir_{1–x}–Sn_{x}–Sb_{y}O_{2.5}/Ti anodes on the oxygen evolution efficiency.

MATERIALS 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 H_{2}SO_{4} solution at 80°C until
hydrogen evolution was ceased to enhance the anchor effect
of the substrate on the electrocatalysts layer. Titanium sulfate
on the titanium surface was removed by washing under tape
water for about one hour. Then the treated–titanium metal
was used as substrate for coating of the intermediate Ir_{1–x}–Sn_{x}–Sb_{y}O_{2.5} layer. The Ir_{1–x}–Sn_{x}–Sb_{y}O_{2.5} intermediate layer
was prepared using coating solution which was prepared by
mixing of 0.0240 M chloroic acid [H_{2}IrCl_{6}, 0.0676 M tin
chloride {SnCl_{4}.5H_{2}O}, 0.0084 M SbCl_{5} butanic solutions
in which the sum of the metallic cations was kept at
0.1. 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}–Sn_{x}–Sb_{y}O_{2.5} on titanium
substrate. This specimen was finally baked at 450°C for 1 hour
in air. The presence of the Ir_{1–x}–Sn_{x}–Sb_{y}O_{2.5} layer is necessary
to prevent the formation of insulating titanium oxide between
electrocatalytically active substances and the titanium
substrate during electrodeposition and electrolysis of
seawater at high current density for a long time. This Ir_{1–x}–Sn_{x}–Sb_{y}O_{2.5} coated titanium substrate was cut into 16 x 7.5
x 1 mm^3 as a suitable electrode, and a titanium wire was spot–
welded to its edge. This is called the Ir_{1–x}–Sn_{x}–Sb_{y}O_{2.5}/Ti electrode.

The Ir_{1–x}–Sn_{x}–Sb_{y}O_{2.5}/Ti electrode was degraded by anodic
polarization at 1000 A.m^2 for 5 minutes in 10 M NaOH solution
and then electroanalytically activated at 1000 A.m^2 for
5 minutes in 1 M H_{2}SO_{4} solution at room temperature. The Mn–
Mo–Mo–(X=Zn,Sn,W) oxide electrocatalysts for oxygen
evolution were anodically deposited on the degraded and
activated Ir_{1–x}–Sn_{x}–Sb_{y}O_{2.5}/Ti electrode at 600 A.m^2 in the
solution containing 0.2 M MnSO_{4}.5H_{2}O + 0.0045 M
Na_{2}WO_{4}.2H_{2}O + 0.0068 M SnCl_{4}, 0.003 M SbCl_{5} or/
and 0.003 M Na_{2}MoO_{4}.2H_{2}O at pH = 0.1 and 90°C for 90
minutes. The electrodeposition of the Mn–W–X(X=Sn,Mo,Mo) oxide electrocatalysts were carried out by
exchanging electrolyte for every 30 minutes.

The performance of the Mn–W–X(X=Sn,Mo,Mo)–O/Ir_{1–x}–
Sn_{x}–Sb_{y}O_{2.5}/Ti anodes was examined by oxygen evolution efficiency 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 (adjusted by adding concentrated
hydrochloric acid) 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. The amount of chlorine formed was
analyzed by iodimetric titration of chlorine and hypochlorite.

Galvanostatic polarization measurement of the electrodeposited Mn–W–X(X=Sn,Mo,Mo)–O electrocatalysts on the Ir_{1–x}–Sn_{x}–Sb_{y}O_{2.5}/Ti electrode was carried out in 0.5 M NaCl solution of pH 1 at 25°C. The ohmic
drop was corrected using a current interruption method. The
potential written in this paper is overpotential and is relative
to Ag/AgCl reference electrode using electrolysis with saturated KCl solution. The Ir_{1–x}–Sn_{x}–Sb_{y}O_{2.5}/Ti electrodes and the anodically
deposited Mn–W–X(X=Zn,Sn,W)–O/Ir_{1–x}–Sn_{x}–Sb_{y}O_{2.5}/Ti anodes were characterized by X–ray diffraction (XRD)
patterns with α–20 mode using CuK_{a} radiation at a glancing angle α of 5°. The changes in the surface morphologies of the
anodically deposited Mn–W–X(X=Sn,Mo,Mo)–O/Ir_{1–x}–
Sn_{x}–Sb_{y}O_{2.5}/Ti anodes were observed using confocal
scanning laser microscope (CSLM). The laser source used
was He–Ne having wavelength of 633 nm.

RESULTS AND DISCUSSION
Figure 1 shows X–ray diffraction patterns of the intermediate Ir_{1–x}–Sn_{x}–Sb_{y}O_{2.5} layer on titanium substrate and the
electrodeposited Mn–W–Mo–O/Ir_{1–x}–Sn_{x}–Sb_{y}O_{2.5}/Ti anode. There are no separate peaks for IrO_{2}, SnO_{2} and SbO_{2},
at the XRD patterns of the intermediate Ir_{1–x}–Sn_{x}–Sb_{y}O_{2.5} layer on titanium substrate, as shown in Fig. 1(a), indicating
the formation of single–phase IrO_{2}–SnO_{2}–SbO_{2} layer. It is
noteworthy to mention here that iridium, tin and antimony
oxides on the titanium substrate were identified as IrO_{2}, SnO_{2}
and SbO_{2}, respectively, from XPS analysis. These results
revealed that the intermediate Ir_{1–x}–Sn_{x}–Sb_{y}O_{2.5} layer is
composed of triple oxides of a rutile structure with fine grains
instead of the mixture of oxides of iridium, tin and antimony.
On the other hand, there are no separate peaks for manganese,
tungsten and molybdenum oxides on the anodically deposited
Mn–W–Mo–O/Ir_{1–x}–Sn_{x}–Sb_{y}O_{2.5}/Ti anode. The XRD patterns of the anodically deposited Mn–W–Mo–O/Ir_{1–x}–
Sn_{x}–Sb_{y}O_{2.5}/Ti anode show only the reflections of γ–MnO_{2}
as shown in Fig. 1(b). Similarly, the XRD patterns of the all
the other anodically deposited Mn–W–X (X=Sn,Mo,Mo)–O/Ir
_{1–x}–Sn_{x}–Sb_{y}O_{2.5}/Ti anodes showed only the reflection of
γ–MnO_{2}. Furthermore, the apparent grain size of the
anodically deposited Mn–W–X (X=Zr,Sn,W)–O/Ir
_{1–x}–Sn_{x}–Sb_{y}O_{2.5}/Ti anodes was estimated from full width at
half maximum (FWHM) of the most intense XRD reflection
by using the Scherrer’s formula. The estimated apparent
grain size of the electrodeposited Mn–W–X (X=Sn,Mo,Mo)
elecrocatalysts was found to be in the ranges of 5–11 nm. These results revealed that the anodically deposited Mn–
W–X (X=Sn,Mo,Mo)/Ir_{1–x}–Sn_{x}–Sb_{y}O_{2.5}/Ti anodes consisted of a nanocrystalline γ–MnO_{2}–type triple/quadrate
oxides consisting of Mn^{2+}, W^{6+}, Sn^{4+}, Sb^{5+} or Mo^{6+} ions.
Figure 1: XRD patterns of the (a) Ir$_{1-x-y}$Sn$_x$Sb$_y$O$_{2+0.5}$ / Ti electrode and (b) anodically deposited Mn–W–Mo–O electrocatalyst on the Ir$_{1-x-y}$Sn$_x$Sb$_y$O$_{2+0.5}$ / Ti electrode.

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–W–X–O (X=Sn,Sb,Mo) electrocatalysts on the Ir$_{1-x-y}$Sn$_x$Sb$_y$O$_{2+0.5}$ / Ti electrode to study the effect of additional elements of tin, antimony and molybdenum in the Mn–W–O electrocatalysts. The anodically deposited Mn–W–Sn–O/Ir$_{1-x-y}$Sn$_x$Sb$_y$O$_{2+0.5}$/Ti anode shows lowest oxygen overpotential at the current density of 1000 A.m$^{-2}$ among all the examined anodes in this study. Furthermore, the Mn–W–Sn–Sb–O/Ir$_{1-x-y}$Sn$_x$Sb$_y$O$_{2+0.5}$/Ti and Mn–W–Mo–Sn–Sb–O/Ir$_{1-x-y}$Sn$_x$Sb$_y$O$_{2+0.5}$/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/Ir$_{1-x-y}$Sn$_x$Sb$_y$O$_{2+0.5}$/Ti and are higher than that of the Mn–W–Sn–O/Ir$_{1-x-y}$Sn$_x$Sb$_y$O$_{2+0.5}$/Ti anode as shown in Fig.3. It is noteworthy to mention here that the oxygen overpotential value of 1.60 V vs Ag/AgCl at 1000 A.m$^{-2}$ observed in the present study is almost same value as reported for the anodically deposited Mn–X–Y–O(X=W,Mo & Y=Sn,Sb)/IrO$_2$/Ti anodes$^{8,9,12,14}$. However, the amount of iridium content in the intermediate oxide layer of the Ir$_{1-x-y}$Sn$_x$Sb$_y$O$_{2+0.5}$/Ti electrode is only 1/22 of the IrO$_2$/Ti electrodes. These results revealed that the addition of SnO$_2$ with small amount of Sb$_2$O$_5$ to the intermediate layer of the Mn–X–Y–O(X=W,Mo & Y=Sn,Sb)/Ir$_{1-x-y}$Sn$_x$Sb$_y$O$_{2+0.5}$/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$_x$Sb$_y$O$_{2+0.5}$/Ti layer on titanium substrate. On the other hand, the additions of tin, antimony and molybdenum on the Mn–W–O/Ir$_{1-x-y}$Sn$_x$Sb$_y$O$_{2+0.5}$/Ti anodes show high activity of the oxygen evolution efficiency of about 98–99% or more in seawater electrolysis. In particular, the initial oxygen evolution efficiency of the Mn–W–Mo–O/Ir$_{1-x-y}$Sn$_x$Sb$_y$O$_{2+0.5}$/Ti and Mn–W–Mo–Sn–O/Ir$_{1-x-y}$Sn$_x$Sb$_y$O$_{2+0.5}$/Ti anodes show about 99% oxygen evolution efficiency in 0.5 M NaCl solution of pH 1 at 25°C (Fig.3).
Figure 3: Changes in the oxygen overpotential and initial oxygen evolution efficiency of the Mn–W–X–O(X=Sn,Sb,Mo)/Ir1–x–ySnxSbyO2+0.5y /Ti anodes in 0.5 M NaCl of pH 1 at the current density of 1000 A.m⁻².

The durability test on the Mn–W-based oxide electrodes was carried out. Figure 4 shows the durability result on the Mn–W–X–O(X=Sn,Sb,Mo)/Ir1–x–ySnxSbyO2+0.5y /Ti anodes in 0.5 M NaCl solution of pH 1 at 25°C. The initial oxygen evolution efficiency of the Mn–W–Sn–O electrocatalyst is about 97.75 %, whereas that of the Mn–W–Mo–O electrocatalyst is about 99%. However, both of these electrocatalysts show almost 100% oxygen evolution efficiency and exhibit better durability for long time electrolysis of 0.5 M NaCl at pH 1. Consequently, the addition of molybdenum is effective in improving the initial oxygen evolution, but tin addition to Mn–W–O electrocatalyst is more active for oxygen evolution reaction with long-term electrolysis. All the three examined 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 3600 hours. The Mn–W–Sn–O/Ir1–x–ySnxSbyO2+0.5y /Ti and Mn–W–Mo–O/Ir1–x–ySnxSbyO2+0.5y /Ti anodes show slightly higher oxygen evolution efficiency of about 99.85% than that of the Mn–W–Mo–Sn–O/Ir1–x–ySnxSbyO2+0.5y /Ti anode.

Figures 5 and 6 show the changes of the surface morphologies of the Mn–W–Mo–O/Ir1–x–ySnxSbyO2+0.5y /Ti and Mn–W–Mo–Sn–Sb–O/Ir1–x–ySnxSbyO2+0.5y /Ti anodes, respectively, before and after electrolysis in 0.5 M NaCl solution of pH 1 at 1000 A.m⁻² for about 1545 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 1545 hours. This revealed that the filling of the cracks by the beneficial ions (Mn²⁺, W⁶⁺, Mo⁶⁺, Sn⁴⁺ or Sb⁵⁺) presence in the electrocatalysts was clearly observed after electrolysis of the anodes for hundreds of hours. In accordance of the

Figure 4: Changes in the oxygen evolution efficiency of the Mn–W–X–O(X=Sn,Sb,Mo)–O electrocatalysts deposited on the Ir1–x–ySnxSbyO2+0.5y intermediate layer on 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.

Figure 5: Changes in the surface morphology of the Mn–W–Mo–O electrocatalyst deposited on the Ir1–x–ySnxSbyO2+0.5y /Ti electrode (a) before and (b) after electrolysis for 1545 h in 0.5 M NaCl solution of pH 1 at 1000 A.m⁻².

Figure 6: Changes in the surface morphology of the Mn–W–Mo–Sn–Sb–O electrocatalyst deposited on the Ir1–x–ySnxSbyO2+0.5y /Ti electrode (a) before and (b) after electrolysis for 1545 h in 0.5 M NaCl solution of pH 1 at 1000 A.m⁻².
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. 4.

CONCLUSIONS

Successfully tailored new types of anodically deposited nanocrystalline Mn–W–Sn–O, Mn–W–Mo–O, Mn–W–Mo–Sn–Sb–O and Mn–W–Mo–Sn–Sb–O electrocatalysts on the intermediate Ir$_{1-x}$Sn$_x$Sb$_y$O$_{2+0.5y}$ layer on titanium substrate for the production of hydrogen gas from seawater electrolysis with forming less than 0.25% of the environmentally harmful chlorine. The high oxygen evolution efficiency of these oxide electrocatalysts maintained during prolonged electrolysis, and even after the electrolysis for five or more months, the Mn–W–X–O(X=Sn,Sb,Mo)/Ir$_{1-x}$Sn$_x$Sb$_y$O$_{2+0.5y}$/Ti anodes showed an oxygen evolution efficiency of about 99.75–99.85%. The addition of tin, antimony and molybdenum in Mn–W–O electrocatalyst is effective to maintain the high electronic conductivity and high activity of oxygen evolution of the anodes for seawater electrolysis at pH 1 at high current density of 1000 A/m$^2$.

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REFERENCES


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