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The durability of Mn–Mo–Sn–W–Sb–O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti oxygen evolution anode for hydrogen production from seawater electrolysis

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Abstract

New types of electrodeposited nanocrystalline Mn–Mo–Sn–W–Sb–O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti anode is successfully tailored for hydrogen production from seawater electrolysis. Simultaneous additions of tungsten and antimony in an electrodeposited Mn–Mo–Sn–W–Sb–O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti anode are found to be more effective for better durability than that of the electrodeposited Mn–Mo–Sn–O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti anode for long period seawater electrolysis. The examined Mn–Mo–Sn–W–Sb–O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti anode showed nearly 100% oxygen evolution efficiency at the current density of 1000 A.m⁻² in 0.5 M NaCl solution of pH 1 at 25°C and it is guaranteed the stable anode performance with 99.7–99.8% oxygen evolution efficiency for more than five months in seawater electrolysis for hydrogen production.

Keywords: Global warming; CO₂ recycling; Electrodeposition; Hydrogen production; Seawater electrolysis

1. Introduction

Koji Hashimoto and his research groups of Japan have been proposed global CO₂ recycling project to prevent global warming and to supply abundant energy converted from solar energy for last twenty years [1–10] considering the facts that a continuous increase in primary energy consumption results in continuous increase in CO₂ emissions [11,12] and such a huge CO₂ emissions resulting from complete exhaustion of fossil fuel reserves will induce intolerable global warming. 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. In general, for large-scale seawater electrolysis to produce hydrogen at cathode for the CO₂ recycle project, environmentally harmful chlorine release is not allowed. Therefore, oxygen production is prerequisite without forming environmentally harmful chlorine for safety production of hydrogen from seawater electrolysis. One of the most difficult subjects in tailoring key materials for the global CO₂ recycling project was the development of stable and more efficient anodes for seawater electrolysis, because for CH₄ 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 γ -MnO₂ type double, triple or quadrate oxides were prepared by anodic deposition on the Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti electrode and these anodes showed about 99.50–99.85% oxygen

evolution efficiency (OEE) after electrolysis for about 4200 h in 0.5 M NaCl solution of pH 1 at current density of 1000 A.m^{-2} [13–22]. The intermediate $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}$ layer 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 [13,14,16]. It has been reported that $\gamma\text{-MnO}_2$ type Mn–Mo–Sn–O/ $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}$ /Ti anode showed about 99.6% oxygen evolution efficiency (OEE) after electrolysis for about 4200 h in 0.5 M NaCl solution of pH 1 at 1000 A.m^{-2} [16,17]. In this context, present work is aimed to develop a more stable, efficient and nanocrystalline Mn–Mo–Sn–W–Sb–O/ $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}$ /Ti oxygen evolution anode for hydrogen production from seawater electrolysis.

2. Materials and 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 . The treated-titanium metal was used as a substrate for coating of the intermediate $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}$ 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 Sb_2O_5 , respectively, from XPS analysis [13].

The intermediate $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}$ layer, coated on the titanium is called as $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}$ /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} for 5 minutes in 1 M H_2SO_4 solution. The Mn–Mo–Sn–W–Sb–O electrocatalyst for oxygen evolution was anodically deposited on the clean and activated $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}$ /Ti electrode at 600 A.m^{-2} in 0.2 M $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ + 0.003 M $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ + 0.006 M $\text{SnCl}_2 \cdot 5\text{H}_2\text{O}$ + 0.0045 M $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ + 0.003 M SbCl_5 solutions at pH –0.1 and 90°C for 90 minutes. The electrodeposition of the Mn–Mo–Sn–W–Sb–O electrocatalysts was carried out by exchanging electrolyte for every 30 minutes. The performance of the electrodeposited Mn–Mo–Sn–W–Sb–O/ $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}$ /Ti anode was examined by oxygen evolution and galvanostatic polarization measurements. The oxygen evolution efficiency of the electrodeposited anode 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 [13,14]. The amount of chlorine formed was analyzed by iodimetric titration of chlorine and hypochlorite.

Galvanostatic polarization measurement of the electrodeposited Mn–Mo–Sn–X(X=W & Sb)–O electrocatalysts on the $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}$ /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 and structure of the anodically deposited Mn–Mo–Sn–W–Sb–O/ $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}$ /Ti anode were observed using confocal scanning laser microscopy (CSLM) and X-ray diffraction (XRD) patterns, respectively.

3. Results and Discussion

Figure 1 shows the result of the durability of the Mn–Mo–Sn–W–Sb–O/ $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}$ /Ti anode in 0.5 M NaCl solution of pH 1 at 25°C . The durability result of the Mn–Mo–Sn–O/ $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}$ /Ti anode is also shown for comparison. The Mn–Mo–Sn–W–Sb–O/ $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}$ /Ti anode shows about 99.7 to 99.8% oxygen evolution efficiency after electrolysis for about 500–3650 h in 0.5 M NaCl of pH 1 at 25°C , which is slightly higher OEE than that of the Mn–Mo–Sn–O/ $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}$ /Ti anode, although initial oxygen evolution efficiency of it was about 99.0% only. Consequently, the simultaneous additions of tungsten and antimony are more effective for better durability of the electrodeposited Mn–

Mo–Sn–W–Sb–O/ $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}$ /Ti anode than that of the Mn–Mo–Sn–O/ $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}$ /Ti anode for long period electrolysis of seawater for hydrogen production.

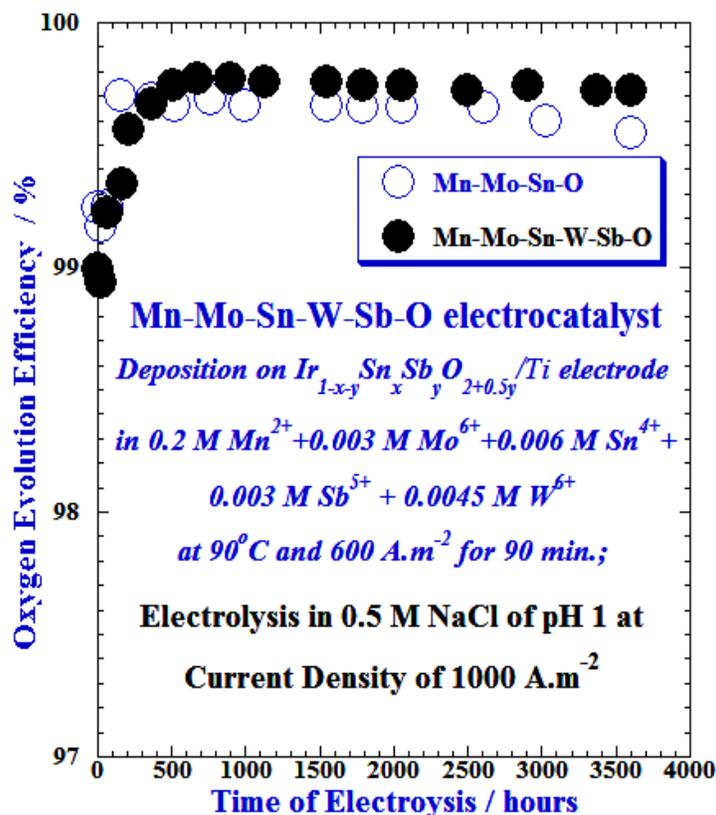


Fig.1: Changes in the oxygen evolution efficiency of the Mn–Mo–Sn–W–Sb–O/ $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}$ /Ti and Mn–Mo–Sn–O/ $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}$ /Ti anodes in 0.5 M NaCl of pH 1 at the current density of 1000 A.m^{-2} , as a function of electrolysis time.

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–Mo–Sn–W–Sb–O, Mn–Mo–Sn or Mn–O}/ $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}$ /Ti anodes to study the effects of tungsten and antimony oxides in the anodes. All the examined double, triple or more oxide electrocatalysts deposited on the $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}$ /Ti electrode showed almost same and lower oxygen overpotential (i.e., about 1.6 V vs Ag/AgCl) than that of Mn–O/ $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}$ /Ti anode in 0.5 M NaCl of pH 1 at 1000 A.m^{-2} . It is noteworthy for mentioning here that the observed oxygen overpotential value of 1.60 V vs Ag/AgCl at 1000 A.m^{-2} in the present study is almost same as that was reported for the anodically deposited Mn–Mo–X(X=W,Sn)–O/ IrO_2 /Ti anodes [3–11]. However, the amount of iridium content in the $\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}$ /Ti electrode is only about 1/22 of the IrO_2 /Ti electrode. These results revealed that the simultaneous additions of molybdenum, tin, tungsten and antimony in the Mn–based oxide electrocatalyst are more effective for high electronic conductivity of the $\text{MnO}_2/\text{Ir}_{1-x-y}\text{Sn}_x\text{Sb}_y\text{O}_{2+0.5y}$ /Ti anode.

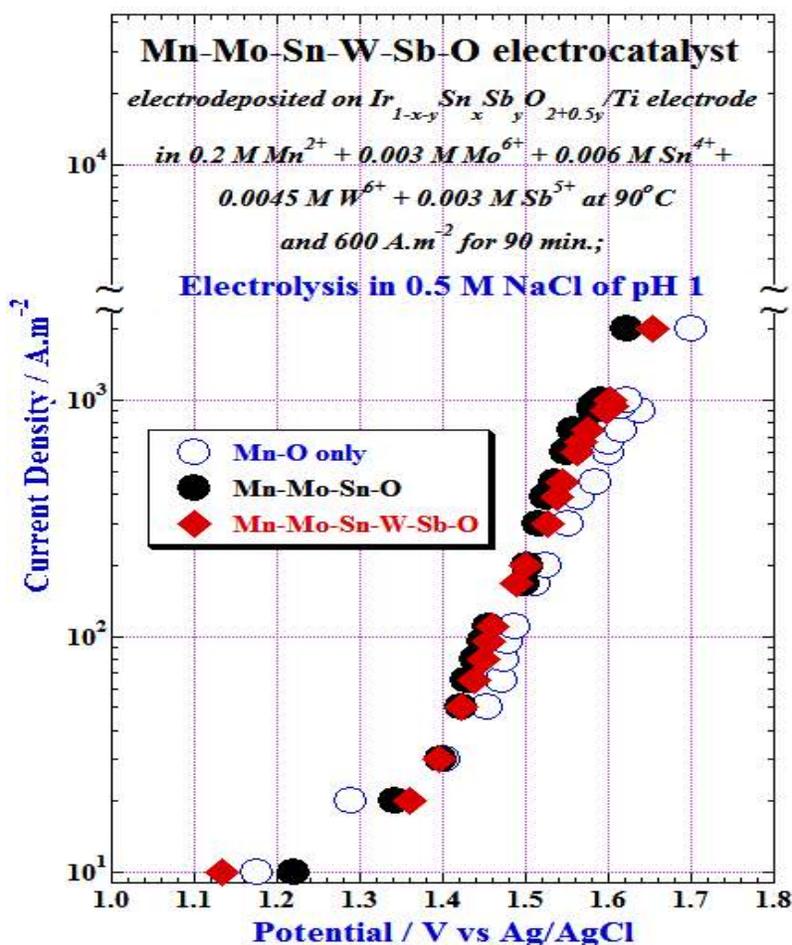


Fig.2: Galvanostatic polarization curves for {Mn-O, Mn-Mo-Sn-O and Mn-Mo-Sn-W-Sb-O}/Ir Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti anodes after electrolysis in 0.5 M NaCl.

Figure 3 shows the changes of the surface morphology of the electrodeposited Mn-Mo-Sn-W-Sb-O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti anode before and after electrolysis for 1545 h in 0.5 M NaCl solution of pH 1 at 1000 A.m⁻². Numbers of cracks and pores on the surface of anode are decreased to form a smooth surface after electrolysis for about 1545 h. This revealed that the filling of cracks and pores by the beneficial ions (e.g., Mn²⁺, Mo⁶⁺, Sn⁴⁺, W⁶⁺ or Sb⁵⁺) in the electrocatalyst was clearly observed after electrolysis for about one week or more time. In accordance of the changes in the surface morphology, the durability of the oxygen evolution efficiency of the Mn-Mo-Sn-W-Sb-O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti anode increased with increasing the electrolysis times and became steady state after electrolysis for about 500 hours as shown in Fig. 1 above.

It is meaningful to mention here that there is no separate peaks for manganese, molybdenum, tin, tungsten and antimony oxides on the anodically deposited Mn-Mo-Sn-W-Sb-O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti anode and was shown only the reflections of γ -MnO₂ from the analysis of the X-ray diffraction patterns of the anode which is not presented here. Furthermore, the apparent grain size of the anodically deposited Mn-Mo-Sn-W-Sb-O/Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti anode was estimated from full width at half maximum (FWHM) of the most intense XRD reflection using Scherrer's equation [23] and the apparent grain size of the anode was found about 8 nm. These results revealed that the anodically deposited Mn-Mo-Sn-

W-Sb-O/ Ir_{1-x-y}Sn_xSb_yO_{2+0.5y}/Ti anode consisted of a nanocrystalline γ -MnO₂-type oxides consisting of Mn²⁺, Mo⁶⁺, Sn⁴⁺, W⁶⁺ and Sb⁵⁺ ions.

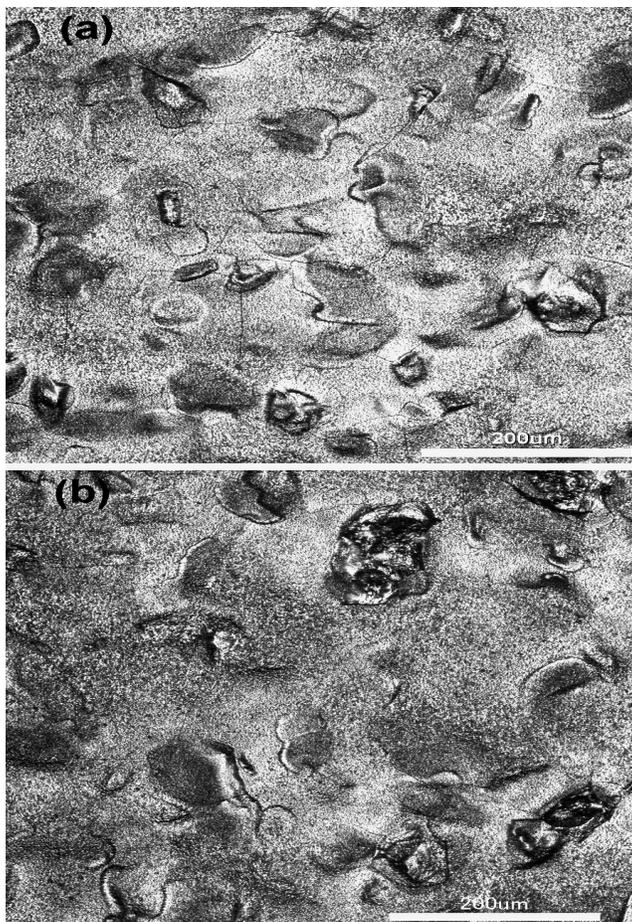


Fig.3: Changes in the surface morphology of the Mn-Mo-Sn-W-Sb-O/Ir Ir_{1-x-y}Sn_xSb_yO_{2+0.5y} /Ti anode (a) before and (b) after electrolysis for 1545 h in 0.5 M NaCl solution of pH 1 at the current density of 1000 A.m⁻².

4. Conclusion

The Ir_{1-x-y}Sn_xSb_yO_{2+0.5y} /Ti supported γ -MnO₂ type nanocrystalline Mn-Mo-Sn-W-Sb-O/ Ir_{1-x-y}Sn_xSb_yO_{2+0.5y} /Ti anode guaranteed the stable anode performance showing 99.7–99.8 % oxygen evolution efficiency from seawater electrolysis for more than five months to produce hydrogen gas necessary for the prototype CO₂ recycling project.

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