Improvement of intermediate layer by formation of tin-iridium dioxide in oxygen evolution anodes for seawater electrolysis

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INTRODUCTION

In order to prevent global warming and to supply renewable energy origin fuel, Hashimoto et al. are proposing global CO₂ recycling and have tailored the necessary key materials, that is, the anodes and cathodes for seawater electrolysis and catalysts for CO₂ methanation [1].

The most difficult was the anode for seawater electrolysis. For energy production a great quantity of chlorine emissions are not allowed, and hence the anode should evolve only oxygen even in seawater electrolysis. Anodically deposited γ-MnO₂-type MnₓMo₅Sn₂O₇₋ₓ anodes showed the 100% oxygen evolution efficiency in the electrolysis of 0.5 M NaCl electrolysis [2].

These electrodes were composed of three layers; the outer electrocatalyst, the intermediate iridium dioxide and the inner titanium substrate. During anodic polarization iridium dioxide, IrO₂, with sufficiently high electrical conductivity can act as the barrier to inward diffusion of oxygen preventing oxidation of titanium, and can form double oxide IrₓTi₂O₄ preventing the formation of isolated insulting TiO₂ if titanium is oxidized because of the same rutile structure as TiO₂. However, in order to meet the future hydrogen demand in the world, the amount of iridium is not sufficient for seawater electrolysis at all.

The alternative materials to IrO₂ for prevention of oxidation of the titanium substrate during anodic polarization should have high stability at high potentials and the same rutile structure as TiO₂. Tin oxide, SnO₂, has the same rutile structure and is more stable than IrO₂. Thus, tin was thought to be a candidate of alternative elements to iridium in the intermediate layer. In our previous research, it found that the substitution of Ir⁴⁺ with Sn⁵⁺ and Sb⁵⁺ was quite effective in decreasing the iridium content to less than 1/70 and the performance of the anodes was significantly better than the MnₓMo₅Sn₂O₇₋ₓ/Ti anodes without degradation in seawater electrolysis. It is, moreover, expected that even if antimony is not added, the MnₓMo₅Sn₂O₇₋ₓ/SnₓIr₂O₇/Ti anodes will show good performance because the presence of Ir⁴⁺ will provide sufficiently high electrical conductivity.

The present work aimed to decrease the amount of IrO₂ by substituting Ir⁴⁺ with Sn⁵⁺, maintaining excellent performance for oxygen evolution in seawater electrolysis.

EXPERIMENTAL

Punched titanium metal substrates were immersed to the air-formed oxide film in HF solution. The surface roughening enhancing the anchor effect of the substrate for the electrocatalyst layer was performed by immersion in 11.5 M H₂SO₄ at 363 K. Chloroiridic acid (H₂IrCl₆·6H₂O) and tin chloride (SnCl₂·5H₂O) were dissolved in butanol, in which the total concentration of cations in the butanol solutions in the present study was 1/5.2 of the solution for the preparation of the traditional IrO₂ layer. The solutions were coated on the titanium substrate with a brush, dried at 353 K for 10 min in air, and then baked at 723 K for 10 min in air. This procedure was repeated three times but the final baking of the specimen was continued for 60 min at 723 K in air for calcination.

The MnₓMo₅Sn₂O₇₋ₓ electrocatalyst for oxygen evolution was anodically deposited on the SnₓIr₂O₇/Ti at 600 Am⁻² in 0.2 M MnSO₄·4H₂O·0.003 M NaClO₄·0.006 M SnCl₂ aqueous solution at pH 0.1 and 353 K for 30 min, three times. The electrodeposition of the MnₓMo₅Sn₂O₇₋ₓ was carried out by exchanging electrolyte for every 30 min.

The performance of the electrodes was examined by oxygen evolution efficiency measurement and galvanostatic anodic polarization. The characterization of the electrode was carried out by XRD and XPS.

RESULTS AND DISCUSSION

The x-ray diffraction revealed that the intermediate layer consisted of a double oxide of a single rutile structure.

The initial oxygen evolution efficiency of the MnₓMo₅Sn₂O₇₋ₓ oxide electrocatalysts on the SnₓIr₂O₇/Ti formed from 0.005-0.1 M IrCl₆·6H₂O solutions was around 99% and independent of the concentration of Ir⁴⁺.

The anode with the intermediate layers formed from the 0.04 M IrCl₆·6H₂O solution kept more than 99% oxygen evolution efficiency for 4300 h without any degradation. On the other hand, the MnₓMo₅Sn₂O₇₋ₓ anode with the 100% IrO₂ intermediate layer formed from 0.1 M IrCl₆·6H₂O solution without SnCl₂, showed about 96.5% oxygen evolution efficiency for only several hundred hours in spite of the fact that the anode with the same electrocatalyst and with 100% IrO₂ formed from 0.52 M H₂IrCl₆ butanol solution showed more than 98% oxygen evolution efficiency for 3200 h. In this manner, thinning of the 100% IrO₂ layer to 1/5.2 was quite detrimental. Nevertheless, the MnₓMo₅Sn₂O₇₋ₓ/SnₓIr₂O₇/Ti anodes with the thin SnₓIr₂O₇ layer containing Ir⁴⁺ of less than 1/70 and Sn⁺ showed no degradation for 4300 h.

Furthermore, although the presence of a low concentration of Ir⁴⁺ was necessary, the anodes with lower Ir⁴⁺ contents in the intermediate layer showed better performance without degradation. Consequently, the SnₓIr₂O₇ layer is significantly more effectively prevent oxidation of substrate titanium acting as a better barrier than the IrO₂ layer against inward diffusion of oxygen.

CONCLUSION

An attempt was made to decrease the amount of IrO₂ in the intermediate layer in the MnₓMo₅Sn₂O₇₋ₓ/Ir₂O₇/Ti anodes for the oxygen evolution in seawater electrolysis. The substitution of Ir⁴⁺ with Sn⁵⁺ was quite effective in decreasing the iridium content to less than 1/70 and the performance of the anodes was significantly better than the MnₓMo₅Sn₂O₇₋ₓ/Ir₂O₇/Ti anodes without degradation in seawater electrolysis.

REFERENCE
