ABSTRACT: Although hydrogen is expected to play an important role in the storage of energy from renewable energy sources, technology to produce hydrogen at low cost is needed for its widespread use. The key to the low-cost production of hydrogen with a polymer electrolyte membrane (PEM) water electrolysis system, which is widely used today, is to replace the Au- or Pt-coated Ti with a low-cost material that can be manufactured from inexpensive, corrosion-resistant, and conductive components. We studied titanium suboxide (Ti₄O₇)-coated titanium (Ti) bipolar plates, which can be substituted for commonly used Pt-coated Ti bipolar plates, as an inexpensive way of producing the PEM water electrolysis system. The water electrolysis characteristics of the cell were evaluated using Ti₄O₇-sputtered Ti for the bipolar plates of the water electrolysis cell, and the applicability of Ti₄O₇-sputtered Ti was investigated. The Ti₄O₇-sputtered Ti had a very low contact resistance (4−5 mΩ cm²) before and after voltage application that was equivalent to that of gold or platinum plating. The efficiency of water electrolysis in this study was comparable to those of previous reports using bipolar plates coated with precious metals. This development opens the door for fabrication of low-cost electrolyzers as well as related electrochemical devices such as fuel cells, sensors, catalysts, and air or liquid cleaning devices.

1. INTRODUCTION

Electrical power generation using renewable energy in the form of wind and solar energy is increasing at a remarkable rate. These technologies are expected to make a major contribution to the mitigation of anthropogenic climate change effects caused by the accumulation of CO₂ in the atmosphere. It is difficult, however, to balance the demand for energy with intermittent supplies from renewable energy sources. The commonly used solution to this problem depends on converting excess power into chemical energy or potential energy that can be stored.

Hydrogen is considered to be one of the most promising energy carriers and is expected to play an important role in the storage of energy from renewable energy sources in the future. Hydrogen is currently produced mainly by steam reforming of natural gas and gasification of coal and petroleum. This method is a cost-effective way to produce hydrogen, but at the same time, it hinders the transition to a renewable and sustainable energy source because it is associated with emission of significant amounts of carbon dioxide.

In contrast, high-purity hydrogen can be produced in a water electrolysis cell using a polymer electrolyte membrane (PEM); the process does not involve emission of CO₂ if the electrolyzer is fed by electricity produced from renewables and does not depend on fossil fuels. A PEM water electrolysis system consists of a stack of cells, power electronics, a gas conditioning component, and balance of plant. The cost of the stack, which can be said to be the key parts of a PEM water electrolysis system, accounts for 60% of the cost of the entire system. Within the PEM water electrolysis stack, bipolar plates account for 51% of the cost; the porous transport layers account for 17%, and the catalysts at the anode and cathode account for only 8%.

PEM water electrolysis has the advantages of an excellent response for the load variations, a wide operating current density range, easy production of high-pressure and high-purity hydrogen, and high durability against start-up and shutdown. However, this strategy necessitates operating at relatively high voltages, i.e., operating in a highly corrosive environment. Because the bipolar plates are exposed to a highly oxidizing atmosphere, titanium parts plated with gold or platinum are widely used in current PEM water electrolysis cells to avoid corrosion. However, it is necessary to remove the oxide film on the surface of the substrates before application of the plating because the oxide film causes the resistance to be high. In addition, pinholes are inevitable in plating, and the resistance of these pinholes to corrosion is less than that of the plating. Rolling is therefore often done after plating to eliminate pinholes.
The pinholes are problematic with respect to corrosion resistance if the substrates are simply plated. To solve this problem, it is necessary to increase the plating thickness to reduce the number of pinholes. However, formation of a thick plating film is not practical in terms of cost. The thickness of the plating film is the greatest cause of the high cost of parts and high cost of the whole PEM water electrolysis system.

One approach to producing a remarkably low-cost PEM water electrolysis system is to replace the Au- or Pt-coated Ti with a low-cost material that can be manufactured from inexpensive, corrosion-resistant, and conductive components and that enables operation of the system under high-current-density conditions so as to reduce the amount of materials that are used.

One such method is the use of corrosion-resistant, conductive materials themselves; Nb, Ta, and materials containing a large proportion of Ti such as Inconel 625 and stainless steel 321 have been reported. In such cases, however, oxide layers form on the surface, and the resistance increases after a long period of water electrolysis. A method of forming a TiN film on the Ti surface by heat treatment or plasma treatment has been reported as a method that imparts corrosion resistance and maintains conductivity by modification of the surface. A method that involves nitriding by heat treatment is more stable, but the materials have been found to be oxidized after a long period of water electrolysis. In addition, when used at the hydrogen electrode, the material reacts with hydrogen and increases in weight. Corrosion-resistant, conductive coating methods include coating with Au, TiN, and Nb; in these cases, the surface becomes oxidized, and the resistance is increased during water electrolysis.

The development of inexpensive materials for coating parts of a PEM water electrolysis system, which can be substituted for commonly used Pt, has been a great challenge. Table 1 summarizes the electric conductivity of Ti4O7, TiO2, TiN, Pt, Au, Nb, and Ta.

| Parameter | Ti4O7 | TiO2 | TiN | Pt | Au | Nb | Ta |
|-----------|-------|------|-----|----|----|----|----|
| Electric conductivity (S m\(^{-1}\)) | 1.0 \times 10^{-1} | <10^{-6} | 4.0 \times 10^{-6} | 9.4 \times 10^{-7} | 4.6 \times 10^{-7} | 6.2 \times 10^{-7} | 7.4 \times 10^{-7} |

Table 1. Electric Conductivity of Ti4O7, TiO2, TiN, Pt, Au, Nb, and Ta

(Ti4O7) was investigated as a material for low-cost, corrosion-resistant coating. The purpose was to determine whether Ti4O7-sputtered Ti could be used as a corrosion-resistant coating in PEM water electrolysis cells. A bipolar plate of Ti4O7-sputtered Ti was incorporated into a PEM water electrolysis cell, and the water electrolysis characteristics of the cell were evaluated. It was found that the Ti4O7-sputtered Ti exhibited high conductivity and corrosion resistance. The efficiency of water electrolysis in this study was comparable to those of previous reports using bipolar plates coated with precious metals.

2. RESULTS AND DISCUSSION

2.1. Chronoamperometric Measurements. Figure 1 shows the chronoamperometric measurements at 2.0 V versus a reversible hydrogen electrode (RHE) constant potential of Ti coated with Ti4O7 (red line) and Ti without coating (blue line).

![Figure 1. Chronoamperometric measurements at 2.0 V vs an RHE constant potential of Ti coated with Ti4O7 (red line) and Ti without coating (blue line).](https://dx.doi.org/10.1021/acsomega.0c04786)

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of 1, and there were almost no uncoated areas over the entire surface.

2.3. Raman Spectroscopy. Raman spectroscopic analysis was carried out to determine possible material changes before and after the chronoamperometric measurements. Figure 3 shows the Raman spectra of a Ti$_4$O$_7$ target and the Ti$_4$O$_7$-sputtered part after chronoamperometric measurements. A peak derived from Ti$_4$O$_7$ was confirmed in the vicinity of 150 cm$^{-1}$ in both samples, and it became clear that Ti$_4$O$_7$ was elaborated as a film on the Ti substrate. The peak derived from TiO$_2$ at 235 cm$^{-1}$ was not dominant. From these results, the corrosion resistance of Ti$_4$O$_7$-sputtered Ti was effective in preventing oxidation.

2.4. Contact Resistance. Figure 4 shows the contact resistance before and after chronoamperometric measurements of Ti$_4$O$_7$-sputtered Ti parts and Ti parts without coating. In the case of the Ti substrate without coating, the resistance increased greatly after chronoamperometric measurements. It is considered that this increase was due to the formation of a highly resistive oxide film on the surface. In contrast, in the case of the Ti$_4$O$_7$-sputtered Ti parts, the contact resistance was as low as 5.0 mΩ cm$^2$ before the chronoamperometric measurements. This low contact resistance was due to the formation of a titanium suboxide conductor on the Ti substrate. Even after chronoamperometric measurements, the contact resistance was as low as 5.2 mΩ cm$^2$. The Ti$_4$O$_7$-sputtered Ti parts had an extremely low contact resistance after chronoamperometric measurements. It can be concluded that the Ti parts coated with Ti$_4$O$_7$ by sputtering did not undergo oxidation and that a titanium suboxide coating superior in conductivity and corrosion resistance was elaborated on the substrate surface.

2.5. SEM. Figure 5 shows SEM images before and after chronoamperometric measurements of Ti$_4$O$_7$-sputtered Ti parts and Ti parts without coating. In the SEM images of Ti$_4$O$_7$-sputtered Ti parts, there was little change after the chronoamperometric measurement. In contrast, in the SEM images of Ti parts without coating, there were many
pitted structures that appeared to be TiO₂ after the chronoa"mperometric measurement. The implication is that the surface of the Ti metal on the Ti parts that lacked coating was oxidized by chronoa"mperometry.

2.6. Cell Performance. Figure 6 depicts the current-potential characteristics of a cell with a Ti₄O₇-sputtered Ti bipolar plate and a cell with a Pt-plated Ti bipolar plate after measurements up to a current density of 3.0 A cm⁻². In both cases, the voltage increased when the current density increased. Onsets of water splitting were determined by extrapolation of the ohmic (linear) region of the polarization curves. There was no significant difference in the voltages associated with the onset of water electrolysis of a cell using a Ti₄O₇-sputtered Ti bipolar plate and a Pt-plated Ti bipolar plate. The onset for the cell using the Ti₄O₇-sputtered Ti bipolar plate was 1.51 V. The onset for the cell using the Pt-plated Ti bipolar plate was 1.50 V. The potential for the cell using the Ti₄O₇-sputtered Ti bipolar plate at a current density of 3.0 A cm⁻² was 1.83 V. The potential for the cell using the Pt-plated Ti bipolar plate at a current density of 3.0 A cm⁻² was 1.76 V. The current-potential characteristics of the cell using the Ti₄O₇-sputtered Ti bipolar plate were almost equivalent to those of the cell using the Pt-plated Ti bipolar plate.

A Ti₄O₇-sputtered Ti bipolar plate was used to make PEM water electrolysis cells. Figure 7 shows the cell voltages of the water electrolysis cells with these plates at a constant current density of 3 A cm⁻² as a function of electrolysis time. The cell voltage was almost constant over time for 20 h. The information about the stability of the Ti₄O₇-sputtered Ti bipolar plate could not be analyzed satisfactorily from Figure 7. In the near future, we need to perform more detailed analyses for longer electrolysis time.

The temperatures of the samples during the coating process increased up to ~40 °C. There was little risk of cracking or spalling due to mismatch of the thermal expansion of Ti substrates and coated Ti₄O₇ films.

Figure 8 compares the current-potential curve of the cell for PEM cells in this study and previously reported results. The previously reported results were obtained with the bipolar plates coated with precious metals. Cell voltages and efficiencies at a nominal current density of 1.0 A cm⁻² are in the range of 1.57–2.18 V and 68–94%, respectively. At a current density of 2.0 A cm⁻², the cell voltage of those cells increases to 1.63–2.44 V and efficiency decreases to 61–91%. At a higher current density of 3.0 A cm⁻², the cell voltage increases to 1.73–2.72 V and efficiency decreases to 54–86%. The cell voltage in this study was as low as 1.83 V and efficiency was 81% at current densities of 3.0 A cm⁻². These low voltage and high efficiency were obtained with the bipolar plate without a precious metal. The efficiency of water electrolysis in this study was comparable to those of previous reports using bipolar plates coated with precious metals.

3. CONCLUSIONS

To fabricate a truly low-cost PEM water electrolysis system, it was considered replacing the commonly used Pt plating on the bipolar plates of the water electrolysis system with a low-cost coating. Water electrolysis characteristics were evaluated using Ti₄O₇-sputtered Ti for the bipolar plates of the water electrolysis cell, and the applicability of the Ti₄O₇-sputtered Ti was investigated. The Ti₄O₇-sputtered Ti had a very low contact resistance (about 5 mΩ cm²) before and after voltage application. The Ti₄O₇-sputtered Ti could be applied to the bipolar plate of the PEM water electrolysis system. The efficiency of water electrolysis in this study was comparable to those of previous reports using bipolar plates coated with precious metals.

4. EXPERIMENTAL SECTION

4.1. Coating Process. Ti₄O₇ (Toshima Manufacturing Co., Ltd., Japan) in the form of a powder was placed in a target folder for sputtering. Presputtering for the removal of surface oxide layers of Ti bipolar plates was not performed. A Ti₄O₇-thin film was elaborated on Ti bipolar plates in an Ar plasma using an ULVAC ACS-4000-C2 RF-sputter coater at 150 W for 3600 s. The result was a coating approximately 50 nm thick. The chamber pressure was 3.1 × 10⁻¹ Pa. The coating was applied on all sides of the bipolar plates. The bipolar plates had parallel flow paths with 5 mm-wide grooves.

4.2. Corrosion Evaluation. Corrosion measurements were carried out in a half cell using Ti plates coated with or without Ti₄O₇ so as to expose an active area of 3.0 × 3.0 cm² to the 0.01 M H₂SO₄ electrolyte solution. A working electrode, a Pt reference electrode, and a Pt counter electrode were used for the chronoa"mperometric measurements at 2.0 V (vs RHE) constant potential and cyclic voltammetry (CV) to simulate the conditions of PEM electrolysis on the anode side. The results were recorded using a potentiotstat/galvanostat (ALS2323, BAS) at 80 °C. Cyclic voltammetry was measured at 0.0–2.0 V versus RHE at a scanning rate of 5 mV s⁻¹. A chronoa"mperometric measurement was then made at 2.0 V versus an RHE constant potential for 6 h, and lastly, a cyclic voltammetry was performed at 5 mV s⁻¹ to determine whether
there had been any changes in the electrochemical properties of the samples.

4.3. Contact Resistance Measurement. The contact resistance of the sample was measured. The voltage was measured when a current of 0–0.5 A was applied in the direction perpendicular to the sample surface, and the contact resistance was calculated.

4.4. Raman Spectroscopy. The measurement of Raman spectroscopy was performed with a laser Raman spectroscopic apparatus (NRS-3300 manufactured by JASCO Corporation). The laser wavelength and power were 532 nm and 100 mW, respectively. The diffraction grating was 600 gr mm$^{-1}$, and the detector was a 2048 $\times$ 512 pixel CCD detector. For the wavenumber correction, diamond was used as the reference sample.

4.5. Water Electrolysis Cell. A catalyst sheet was prepared by adding an ionomer. A membrane electrode assembly consisting of an oxygen electrode catalyst, an electrolyte membrane, and a hydrogen electrode catalyst was prepared via a thermal transfer printing method. IrO$_2$ (ELC-1005 (SAS), Tanaka Kikinzoku Kogyo K.K.) was used for the oxygen electrode catalyst with the catalyst loadings of 0.5 mg cm$^{-2}$. Naion (NR212 DuPont, USA) was used as an electrolyte membrane, and platinum/carbon (Pt/C) (Tanaka Kikinzoku Kogyo K.K.) was used for a hydrogen electrode catalyst with the catalyst loadings of 1.0 mg cm$^{-2}$. The Ti$_4$O$_7$-sputtered Ti bipolar plates used in the PEM water electrolysis cell were produced by a sputtering method in the manner described in Section 4.1.

4.6. Water Electrolysis Evaluation Test. Evaluation tests were carried out with the PEM water electrolysis cell described in Section 4.5. The cell temperature was kept constant at 80 °C. The current density was maintained at 3.0 A cm$^{-2}$ for 20 h. During the evaluation test, the current density, the cell voltage, and the AC resistance at a frequency of 10 kHz were recorded. The efficiency of an electrolyzer is defined using the thermoneutral voltage for water decomposition as $(1.481/V) \times 100$, where $V$ is the cell voltage of the PEM electrolyzer.

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**Notes**

The authors declare no competing financial interest.

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