Corrosion resistance of Au/Ni thin film-coated stainless steel used as a polymer electrolyte fuel-cell separator

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Abstract

Recently, as a new clean and renewable energy, much attention has been paid to the polymer electrolyte fuel cell (PEFC) because of energy and environmental problems, such as depletion of petroleum and global warming. PEFC has the characteristics of a simple structure, is easy to maintain and has a low cost. One of the parts of the PEFC is called the 'separator'; metal separators have a major issue regarding compatibility with corrosion resistance and electrical conductivity, in addition to low cost. Using current technology, a stainless steel AISI316L with an Au/Ni skin film has here been selected. Therefore, there is a need to make a thinner skin film, especially an Au top film for suppressing the PEFC total cost. When thinking about skin film, defects in the Au top film increase gradually as the thickness of Au film decreases. As a result, extensive corrosion is generated due to defects in the Au/Ni skin film. There are few reports evaluating the correlation between the corrosion characteristics of stainless steel with an Au/Ni skin film under a PEFC environment and existing defects in the Au/Ni skin film. Therefore, in this study, the pinhole defect ratio especially in Au film was evaluated using the critical passivation current density (CPCD) method. Au/Ni double layered coating was formed on AISI316L stainless steel employing the sputtering method because of its high adhesion strength. As the quasi-PEFC environment, 1 M H₂SO₄ aqueous solution was selected and then the pinhole defect ratio was evaluated by the CPCD method. As a result, the pinhole defect area ratio of 80 nm thick Au film was obtained to be about 1.1% in 1 M H₂SO₄ aqueous solution.

Keywords: PEFC separator, AISI316L stainless steel, Au/Ni skin film, corrosion, pinhole defect area ratio evaluation, CPCD method.

1 Introduction

Recently, as a new clean and renewable energy, much attention has been paid to the polymer electrolyte fuel cell (PEFC) because of energy and environmental problems, such as depletion of petroleum and global warming. PEFC has the characteristics of a simple structure, is easy to maintain and has a low cost. One of the parts of PEFC is called “separator”; metal separators have a major issue regarding compatibility with corrosion resistance and electrical conductivity, in addition to low cost [1, 2]. Using current technology, stainless steel AISI316L with Au/Ni skin film has here been selected. Therefore, there is a need to form a thinner skin film, especially Au top film, for suppressing the PEFC total cost [3]. When thinking about a skin film, defects in Au top film increase gradually as the thickness of the Au film decreases. As a result, extensive corrosion is generated due to defects in Au/Ni skin film. There are few reports evaluating the correlation between corrosion characteristics of stainless steel with Au/Ni skin film under PEFC environment and existing defects in Au/Ni skin film. Therefore, in this study, the pinhole defect ratio, especially in Au film, was evaluated using the critical passivation current density (CPCD) method [4–7]. Also, the corrosion resistance of Au/Ni thin film-coated stainless steel under quasi-PEFC environment was investigated.

2 Experimental procedures

2.1 Pinhole defect area ratio in Au skin film

The substrate material used in this study was a pure Ni plate specimen with a size of $11 \times 11 \times 1 \text{ mm}^3$. The surface of the substrate was polished until #2000 emery paper and then given mirror finish by buff polishing. For forming Au films with four different kinds of thickness, from 20 nm to 120 nm, a DC sputtering system (L-332S-FH, Canon ANELVA) was employed (Table 1) [8]. The pinhole defect ratio, especially in Au film, was evaluated using the CPCD method. This method is based on the critical passivation current density, just before the corrosion state shifts from active to passive with the potential sweep toward the noble direction, being proportional to the ratio of the pinhole defect area through the coating film.

First, to determine the optimal concentration of H_2SO_4 in an aqueous solution for obtaining larger current density data, solutions from 1 M to 5 M H_2SO_4 were employed and the anodic polarization measurement of substrate Ni specimen was conducted under the conditions shown in Table 2. When evaluating the pinhole defect area ratio of Au coating film, it is necessary to make sure the suppression of exfoliation of formed Au film. The corroded morphologies of the coating film surface were examined in detail by optical microscope, scanning electron microscope (SEM) and atomic force microscope (AFM).

Electrochemical measurement by three-electrode methods was conducted in H_2SO_4 aqueous solution after de-aeration treatment of more than one hour using N_2 gas.

Table 1: Details of specimen used for Au pinhole defect ratio evaluation.

Specimen	Remarks
Substrate: Pure Ni	#2000 emery paper polish and buff finish
Au coating	Au film thickness: 20, 50, 80, 120 nm made by sputtering

Table 2: Conditions of anodic polarization measurement for Au pinhole defect area ratio evaluation.

Potential sweep range	-500 mV ~ 500 mV (SCE)
Sweep rate	60 mV/min
Temperature	303 ± 0.5 K
Solution	1, 3, 5 M H ₂ SO ₄

Then the defect area ratio R [%] of Au thin film was evaluated from the following equation

$$R = \frac{1}{f_s} \times \frac{i_{crit}(\text{coating/substrate})}{i_{crit}(\text{substrate})} \times 100 (\%) \quad (1)$$

where, $i_{crit}(\text{coating/substrate})$ is the critical passivation current density of Au thin film-coated Ni specimen and $i_{crit}(\text{substrate})$ is that of non-coated substrate Ni specimen. The value of the shape factor of corrosion pit f_s is evaluated to be 2, because the morphology of corrosion pit is expected to be semi-elliptical.

2.2 Corrosion resistance of Au/Ni thin films coated stainless steel under quasi-PEFC environment

For evaluating the corrosion resistance of Au/Ni-coated stainless steel AISI316L under quasi-PEFC environment, AISI316L plate specimens with the chemical composition shown in Table 3 and a size of $11 \times 11 \times 2.5 \text{ mm}^3$ were selected as substrate material because of having good corrosion resistance, low hydrogen embrittlement susceptibility and actual results used as separator. The surface of the substrate was finished in the same manner as the Ni palate described in the previous section. A Au/Ni double layered coating film was formed under the conditions shown in Table 4. Then, for quasi-PEFC environment, 0.5 M H₂SO₄ aqueous solution at 353 K was employed and a static immersion test of 24 hrs was conducted (test conditions are described in Table 5) using the corrosion cell shown in Fig. 1.

Table 3: Chemical composition of material used in this study (wt. %).

Material	Ni	Fe	C	Cr	Mo
AISI316L	12.2	Bal	0.01	16.3	2.10

Table 4: Details of Au/Ni coated SUS316L specimen for H₂SO₄ corrosion test.

Specimen	Au film thickness
Au / Ni coated AISI316L (Ni thickness: 100 nm)	20, 50, 65, 80 nm

Table 5: Conditions of immersion corrosion test in H₂SO₄ aqueous solution.

Immersion time	24 H
Solution temperature	353±1 K
Solution	0.5 M H ₂ SO ₄ aqueous solution

Figure 1: Setup of immersion corrosion test in H₂SO₄ aqueous solution.

2.3 Corrosion resistance of Au/Ni thin films coated stainless steel under quasi-PEFC environment by anodic polarization measurement

Electrochemical measurements were conducted using the three-electrode method (HZ-3000, Hokutodenkou, Japan) composed of the specimen (working electrode), Pt (counter electrode) and the saturated calomel electrode (SCE) (reference electrode). All tests were performed in 0.5 H₂SO₄ aqueous solution of 348 K. Potentio-dynamic corrosion tests were conducted with the sweep rate of 60 mV/min from -200 mV to 1500 mV (vs. SCE) considering the real potential range under actual usage (100–800 mV SCE) [9]. Through considering the separator's actual operating conditions, anodic polarization measurements were conducted under the conditions summarized in Table 6. In this case, specimens with 200 nm thick Ni intermediate film whose Au top film thickness was 50, 65 and 80 nm, were also prepared for understanding the effects of Ni intermediate film thickness upon corrosion resistance of Au/Ni/AISI316L specimen (Table 7).

Table 6: Conditions of anodic polarization measurement.

Potential sweep range	−200 mV–1500 mV (SCE)
Sweep rate	60 mV/min
Solution temperature	348 ± 0.5 K
Solution	0.5 M H ₂ SO ₄ aqueous solution

Table 7: Details of Au/Ni/AISI316L specimen for anodic polarization measurement.

Ni intermediate film thickness	Au top film thickness
100 nm	50, 65, 80, 120 nm
200 nm	50, 65, 80 nm

3 Experimental results and discussions

3.1 Pinhole defect area ratio in Au skin film

First, to determine the optimal concentration of H₂SO₄ in aqueous solution for highly accurate measurements, aqueous solutions from 1 M to 5 M H₂SO₄ were employed and the anodic polarization measurement of substrate Ni specimen was conducted under the conditions described in Table 2. From the obtained results shown in Fig. 2, the 1 M H₂SO₄ aqueous solution was selected as the optimal concentration of H₂SO₄ aqueous solution for the CPCD method because of showing maximum current density within the potential range at which no anodic dissolution of Au was generated.

Then, the pinhole defect area ratio in the Au top skin film was evaluated employing the CPCD method [4–7]. The results obtained by anodic polarization measurements of specimens with different Au top skin film thickness on Ni substrate are shown in Fig. 3. The critical passivation current density, $i_{crit.}$, of the 20 nm thick Au film coated specimen was shown to be at almost the same level as that of the substrate pure Ni specimen. Other specimens with thicker Au coating showed relatively smaller $i_{crit.}$ as the thickness of the film became larger. A drastic suppression in critical passivation current density was recognized in specimens with Au film thickness between 50 nm and 80 nm.

In the case of 20 nm thick Au film coated specimen, almost all of the Au film was exfoliated after polarization measurement. Therefore, the Au top film defect area ratio R_{Au} in this case was not evaluated. Then, the defect area ratio R_{Au} with thicker Au film was evaluated using eqn (1) and is shown in Table 8. At the same time, an Au pinhole defect area ratio evaluation was also conducted by microscopic surface observation.

Figure 2: Results of anodic polarization measurements in aqueous solutions with different H_2SO_4 concentration.

Figure 3: Results of anodic polarization measurements with different Au skin film thickness on Ni substrate.

Table 8: Results of Au film defect area ratio evaluation.

Au film thickness [nm]	Au pinhole defect ratio: R_{Au} [%] (CPCD method)	Au pinhole defect ratio [%] (Surface observation)
20	—	—
50	18.0	6.34
80	1.12	0.84
120	0.854	1.45

Also, in this Table 8, the Au pinhole defect ratio [%] evaluated by surface observation was summarized. From these results, a clear difference in pinhole defect area ratio values was recognized between data obtained by CPCD method and microscopic surface observation for 50 nm thick Au film. In the case of specimens with Au films thicker than 50 nm, there were no large differences between obtained values by both the CPCD method and microscopic surface observation. Therefore, consistency of evaluated results between two different evaluating methods was recognized. For making clear the reason of the difference in evaluated results obtained from 50 nm thick Au film coated specimen, its surface morphology after polarization measurement was investigated by SEM and shown in Fig. 4. In that figure, the surface morphology of the specimen with 50 nm thick Au film clearly shows to be different from that of the specimens with a thicker Au film. In the case of the specimen with 50 nm thick Au film, some trace of Au film swelling [10, 11] was recognized and shown by a circle in Fig. 4(a). In this case, the anodic dissolution of Ni substrate was expected to arise and be extended within the pinhole. For this reason, some excess current density may be detected in this case.

3.2 Corrosion resistance of Au/Ni thin film-coated stainless steel under quasi-PEFC environment

Next, for quasi-PEFC environment, a 0.5 M H_2SO_4 aqueous solution at 353 K was employed and a static immersion test of 24 hrs was conducted using the corrosion cell shown in Fig. 1 under the conditions shown in Table 5. From these tests, the effect of Au film thickness upon corrosion resistance of Au/Ni thin films coated AISI316L stainless steel under quasi-PEFC environment was evaluated. Then, the corrosion rate was calculated and shown in Table 9. As a result, both evaluated corrosion rates were suppressed. From these results, sufficient corrosion resistance of Au/Ni thin films coated AISI316L stainless steel under static quasi-PEFC environment of 0.5 M H_2SO_4 aqueous solution at 353 K was obtained within thin Au top films of thickness in the range of 20 nm and over.

For evaluating the corrosion resistance of Au/Ni thin films coated AISI316L stainless steel under a quasi-PEFC environment, a potentiodynamic corrosion test was conducted with the sweep rate of 60 mV/min from -200 mV to 1500 mV (vs. SCE) considering the real potential range under actual usage (100–800 mV SCE) [9].

Au film swelling at pinhole defect

Figure 4: Surface morphology after polarization measurement.

Table 9: Calculated corrosion rate.

Au/Ni thickness (nm)	Corrosion rate (mg/dm ² day)	Corrosion rate (mm/year)
20/100	9.30×10^{-3}	4.27×10^{-4}
50/100	9.38×10^{-3}	4.29×10^{-4}
65/100	9.72×10^{-3}	4.45×10^{-4}
80/100	15.8×10^{-3}	7.22×10^{-4}

3.3 Corrosion resistance of Au/Ni thin films coated stainless steel under quasi-PEFC environment evaluated by anodic polarization measurement

The obtained anodic polarization curves are shown in Figs. 5 and 6.

In Fig. 5, the results obtained from the Au/Ni/AISI316L specimen with 100 nm thick intermediate Ni film are indicated. In addition, those obtained from specimens whose intermediate Ni film thickness is 200 nm are shown in Fig. 6.

Figure 5: Results of polarization measurement obtained from Au/Ni/AISI316L specimen whose intermediate Ni film thickness is 100 nm.

Figure 6: Results of polarization measurement obtained from Au/Ni/AISI316L specimen whose intermediate Ni film thickness is 200 nm.

The current density of Au/Ni thin films coated AISI316L stainless steel was suppressed down to about 1/100 level compared to that detected in bare substrate AISI316L stainless steel.

Also, under the potential range of actual usage (100–800 mV SCE), a double layer-coated AISI316L specimen indicated to stay still in passive state. The current density of Au/Ni thin films coated AISI316L stainless steel whose intermediate Ni film thickness was 200 nm showed furthermore suppressed passivation current density compared with that obtained from the same system specimen with the thinner intermediate Ni thickness of 100 nm. Thus, the improvement in corrosion resistance due to the increase of Au top film thickness was more significant in the case of specimens with a thicker intermediate Ni film.

From the results mentioned above, improvement of corrosion resistance was recognized in all the double layered Au/Ni coated AISI316L stainless steel specimens. The contribution of intermediate Ni film thickness increase to the improvement in corrosion resistance became more noticeable when the Au top film thickness became bigger. The adhesion strength improvement due to Ni film thickness increase may result in promotional effect of dense Au film formation together with Au film thickness increase effect itself. The best corrosion resistance in Au/Ni coated AISI316L stainless steel specimen was obtained when Au/Ni is 65 nm/200 nm. These results may be brought about due to optimization of adhesion strength [11] improvement and fill up of pinhole in Au top film by thicker Ni film formation. For this reason, an increase of intermediate Ni film thickness results in significant corrosion resistance improvement together with suppressing the top Au film thickness.

From these results, it was made clear that the CPCD method was applicable to Au top film defect area ratio evaluation of Au/Ni double layered coated AISI316L stainless steel. Through establishing adhesion strength improvement by intermediate Ni film Au/Ni double layered coated film has sufficient corrosion resistance under quasi-PEFC environment. At the same time, the outlook of specimens after anodic polarization measurement was investigated and typical results of these observations are indicated in Fig. 7. As shown in Fig. 7(a), a specimen with thin top Au coating film resulted in remarkable exfoliation of coated layers after anodic polarization measurement under the conditions shown in Table 6. However, this specimen indicated sufficient corrosion resistance under the conditions of 24 hrs static immersion test in 0.5 M H_2SO_4 aqueous solution of 353 K, as shown in Table 9.

In contrast, in the case of 120 nm thick Au top coated specimen, no damage was recognized in this specimen as shown in Fig. 7(b) even after anodic polarization measurement under the conditions listed in Table 6.

(a) 50 nm Au/100 nm Ni/AISI316L (b) 120 nm Au/100 nm Ni/AISI316L

Figure 7: Outlook of specimen surface after anodic polarization measurement.

4 Conclusions

There are few reports evaluating the correlation between corrosion characteristics of stainless steel with Au/Ni skin film under PEFC environment and existing defects in Au/Ni skin film. Therefore, in this study, the pinhole defect area ratio,

especially in the Au top film, was evaluated using the CPCD method. Also, the corrosion resistance of Au/Ni thin films coated AISI316L stainless steel under quasi-PEFC environment was evaluated.

The results obtained are summarized as follows:

1. The CPCD method was applicable to Au top film defect evaluation of Au/Ni double coated AISI316L stainless steel. The pinhole defect area ratio in the Au thin film depends upon the thickness of film itself.
2. The consistency of the evaluated results of Au top film defect between CPCD method and surface morphology observation after polarization measurement was recognized.
3. Improvement of corrosion resistance was recognized in all the double layered Au/Ni coated AISI316L stainless steel. Current density of Au/Ni thin films coated AISI316L stainless steel suppressed down to about 1/100 level compared with that detected in bare substrate AISI316L stainless steel. Also, under the potential range of actual usage, double layered coated AISI316L specimen whose top Au film thickness is larger than 65 nm indicated to stay still in passive state.
4. Best corrosion resistance in Au/Ni double layered coated AISI316L stainless steel specimen was obtained when Au/Ni is 65 nm/200 nm under the condition of polarization measurement. However, a specimen whose top Au film thickness is less than 50 nm indicated sufficient corrosion resistance under the conditions of 24 hrs static immersion into 0.5 M H₂SO₄ aqueous solution of 353 K.

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