Corrosion resistance of Au/Ni thin films coated stainless steel used for a PEFC separator

Y. Kimura[1] & M. Hirano[2]
[1]Department of Environmental and Energy Chemistry,
Kogakuin University, Japan
[2]Graduate school, Kogakuin University, Japan

Abstract

Recently, as a new clean and renewable energy much attention has been paid to the PEFC (Polymer Electrolyte Fuel Cell) because of energy and environmental problems, such as depletion of petroleum, global warming and so on. PEFC has the characteristics of a simple structure, easy to maintain and 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, we have selected a stainless steel AISI316L with an Au/Ni skin film. 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 increases gradually as the thickness of Au film decreases. As a result, intensive corrosion is generated due to defects in the Au/Ni skin film. However, there are few reports evaluating 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 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 1M H_2SO_4 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 80nm thick Au film was obtained to be about 1.1% in 1M H_2SO_4 aqueous solution.

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

WIT Transactions on Engineering Sciences, Vol 77,
www.witpress.com, ISSN 1743-3533 (on-line)
doi:10.2495/MC130191

1 Introduction

Recently, as a new clean and renewable energy much attention has been paid to the PEFC (Polymer Electrolyte Fuel Cell) because of energy and environmental problems, such as depletion of petroleum, global warming and so on. PEFC has the characteristics of a simple structure, easy to maintain and a low cost. One of the parts of PEFC, 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, we have selected stainless steel AISI316L with Au/Ni skin film. Therefore, there is a need to make a thinner skin film especially Au top film for suppressing PEFC total cost [3]. When thinking about skin film, defects in Au top film increases gradually as the thickness of Au film decreases. As a result, intensive corrosion is generated due to defects in Au/Ni skin film. However, there are few reports evaluating 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 CPCD method [4–7]. And also, Corrosion resistance of Au/Ni thin films coated stainless steel under quasi-PEFC environment was investigated.

2 Experimental procedures

2.1 Evaluation of pinhole defect area ratio in Au skin film

The substrate material used in this study was pure Niplate specimens whose size of 11×11×1mm. The surface of substrate was polished until #2000 emery paper and then made mirror finish by buff polishing. For making Au film with four different kinds of thickness from 20 nm to 120nm 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 (Critical Passivation Current Density) method. The CPCD method was based on the critical passivation current density, just before corrosion state shifted from active to passive with the potential sweep toward noble direction, is proportional to ratio of the pinhole defect area through coating film.

At first, for determining optimal concentration of H_2SO_4 in aqueous solution for obtaining larger current density data from 1M to 5M H_2SO_4 solutions were employed and 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 coating film surface were examined in detail by optical microscope, scanning electron microscope (SEM) and atomic force microscope (AFM).

Electrochemical measurement by three electrodes methods was conducted in H_2SO_4aqueous solution after deaeration 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, 120nm made by sputtering

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

Potential sweep range	−500mV ~ 500mV(SCE)
Sweep rate	60mV/min
Temperature	303±0.5 K
Solution	1, 3, 5M H_2SO_4

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

$$R = \frac{1}{fs} \times \frac{i_{crit}\ (\text{Coating/Substrate})}{i_{crit}\ (\text{Substrate})} \times 100[\%] \qquad (1)$$

where, i_{crit} (Coating/Substrate) is the critical passivation current density of Au thin film coated Ni specimen and i_{crit} (Substrate) is that of non-coated substrate Ni specimen. The value of the shape factor of corrosion pit fs is evaluated to be 2, because the morphology of corrosion pit is expected to be semielliptical.

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

For evaluating corrosion resistance of Au/Ni coated stainless steel AISI 316L stainless steel under quasi-PEFC environment AISI 316L (chemical composition were shown in Table 3) plate specimens whose size of 11×11×2.5 mm was selected as substrate material because of having good corrosion resistance, low hydrogen embrittlement susceptibility and actual results using as separator. The surface of substrate was finished as the same as Ni palate described in previous section. Au/Ni double layered coating film was formed under the conditions as shown in Table 4. Then for quasi-PEFC environment 0.5M H_2SO_4 aqueous solution at 353K was employed and static immersion test of 24hrs was conducted (Table 5) using corrosion cell shown in Fig. 1.

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

Material	Ni	Fe	C	Cr	Mo
AISI 316L	12.2	Bal	0.01	16.3	2.10

Table 4: Details of Au/Ni coated SUS316L specimen for H_2SO_4 corrosion test.

Specimen	Au film thickness
Au / Ni coated AISI 316L (Ni thickness:100nm)	20, 50, 65, 80nm

Table 5: Conditions of immersion corrosion test in H_2SO_4aqueous solution.

Immersion time	24H
Solution temperature	353±1 K
Solution	0.5M H_2SO_4aqueous solution

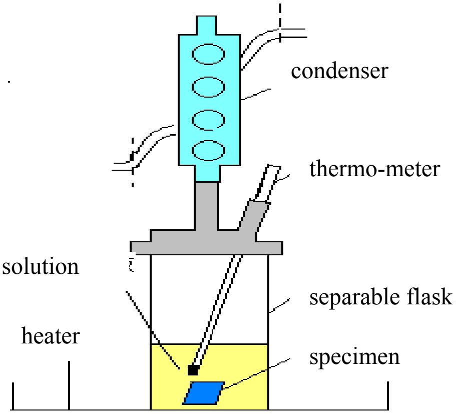


Figure 1: Setup of immersion corrosion test in H_2SO_4aqueous solution.

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

Electrochemical measurement was conducted using three electrode method (HZ-3000, Hokutodenkou, Japan) composed of specimen (working electrode), Pt (counter electrode) and the saturated calomel electrode (S.C.E.) (reference electrode). All tests were performed in 0.5 H_2SO_4 aqueous solution of 348K. Potentio-dynamic corrosion test was conducted with the sweep rate of

60mV/min from –200 mV to 1500 mV (vs. S.C.E.) considering real potential range under actual usage (100~800mV SCE) [11]. Through considering separator's actual operating conditions anodic polarization measurement were conducted under the conditions summarized in Table 6. In this case, specimens with 200nm thick Ni intermediate film whose Au top film thickness were 50, 65 and 80 nm, were also prepared for understanding the effects of Ni intermediate film thickness upon corrosion resistance of Au/Ni/AISI 316L specimen (Table 7).

Table 6: Conditions of anodic polarization measurement.

Potential sweep range	－200mV–1500mV(SCE)
Sweep rate	60mV/min
Solution temperature	348±0.5 K
Solution	0.5M H_2SO_4aqueous solution

Table 7: Details of Au/Ni/AISI 316L specimen for anodic polarization measurement.

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

3 Experimental results and discussions

3.1 Pinhole defect area ratio in Au skin film

At first, to determine optimal concentration of H_2SO_4 in aqueous solution for highly accurate measurement from 1M to 5M H_2SO_4aqueous solutions were employed and anodic polarization measurement of substrate Ni specimen was conducted under the conditions shown in Table 2. From the obtained results shown in Fig. 2, 1M H_2SO_4aqueous solution was selected as the optimal concentration of H_2SO_4 aqueous solution for 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 Au top skin film was evaluated employing CPCD method [4–7].Results obtained by anodic polarization measurements of specimens with different Au top skin film thickness on Ni substrate were shown in Fig. 3. Critical passivation current density ($i_{crit.}$) of 20nm thick Au film coated specimen showed almost the same level as that of substrate pure Ni specimen. Other specimens with thicker Au coating showed relatively smaller $i_{crit.}$ as the thickness of the film became larger. Drastic suppression in critical passivation current density ($i_{crit.}$) was recognized in specimen with Au film thickness between 50nm and 80 nm.

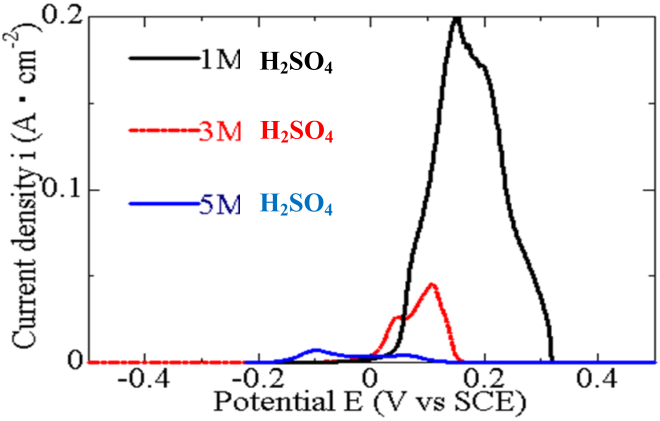


Figure 2: Results of anodic polarization measurements in aqueous solutions with different H_2SO_4concentration.

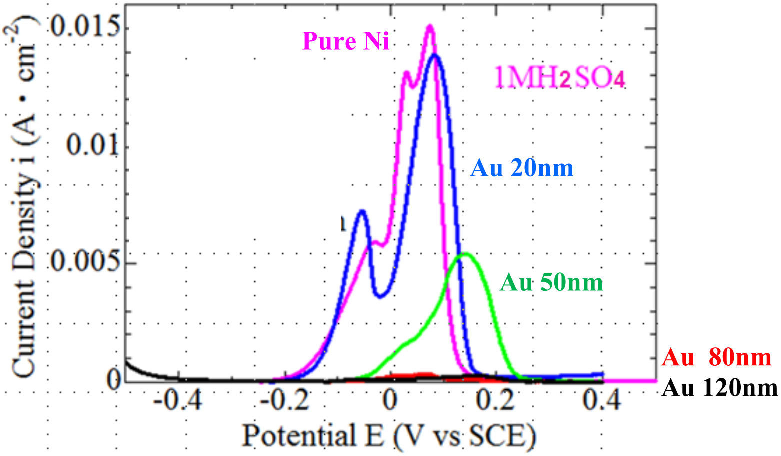
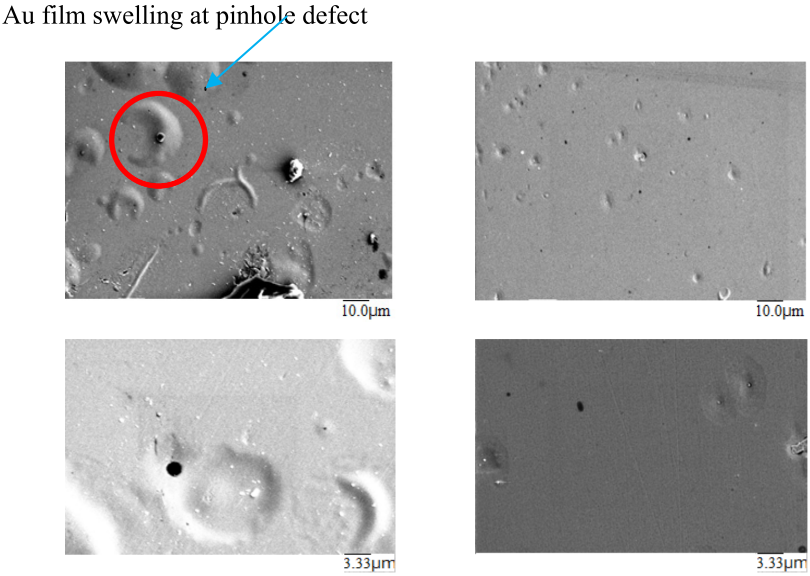


Figure 3: Results of anodic polarization measurements with different Au skin film thickness on Ni substrate.

In the case of 20nm 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 by using equation (1) and shown in Table 8. At the same time, an Au pinhole defect area ratio evaluation was also conducted by microscopic surface observation.

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



(a) Au thickness: 50nm (b) Au thickness: 80nm

Figure 4: Surface morphology after polarization measurement.

Also in this Table 8, Au pinhole defect ratio [%] evaluated by surface observation was summarized. From these results, clear difference in pinhole defect area ratio values was recognized between data obtained by CPCD method and microscopic surface observation for 50nm thick Au film. In case of specimens with thicker Au films than 50 nm, there were no large difference between evaluated values both by the CPCD method and microscopic surface observation. Therefore, coherency of evaluated results between two different evaluating methods was recognized. For making clear the reason of the deference in evaluated results obtained in 50nm thick Au film coated specimen, surface morphology after polarization measurement was investigated by SEM and shown in Fig. 4. As a result, surface morphology of specimen with 50nm thick Au film showed clear deference to specimens with thicker Au film. In case of specimen with 50nm thick Au film some trace of Au film swelling [9, 10] was recognized and shown by circle in Fig. 4(a). In this case, anodic dissolution of Ni substrate was expected to generate and extended inside of pinhole. For this reason some excess current density may be detected in this case.

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

Then for quasi-PEFC environment 0.5M H_2SO_4 aqueous solution at 353K was employed and static immersion test of 24hrs was conducted using corrosion cell shown in Fig. 1 under the conditions shown in Table 5. From these tests effect of Au film thickness upon corrosion resistance of Au/Ni thin films coated AISI 316L stainless steel under quasi-PEFC environment was evaluated. Then, corrosion rate was calculated and shown in Table 9. As a result, both of evaluated corrosion rates were suppressed. From these results, sufficient corrosion resistance of Au/Ni thin films coated AISI 316L stainless steel under static quasi-PEFC environment of 0.5M H_2SO_4 aqueous solution at 353K was obtained within thin Au top film thickness range of 20nm and over.

Table 9: Calculated corrosion rate.

Au/Ni thickness(nm)	Corrosion rate(mg/dm^2· day)	Corrosion rate(mm/year)
20/100	9.30 x 10^{-3}	4.27 x10^{-4}
50/100	9.38 x 10^{-3}	4.29 x10^{-4}
65/100	9.72 x 10^{-3}	4.45 x10^{-4}
80/100	15.8 x 10^{-3}	7.22 x10^{-4}

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

For evaluating corrosion resistance of Au/Ni thin films coated AISI 316L stainless steel under quasi-PEFC environment potentio-dynamic corrosion test was conducted with the sweep rate of 60mV/min from –200 mV to 1500 mV (vs. S.C.E.) considering real potential range under actual usage (100~800mV S.C.E.) [11].

Obtained anodic polarization curves were summarized in Figs 5 and 6.

In Fig. 5, results obtained from the Au/Ni/AISI316L specimen with100 nm thick intermediate Ni film were indicated. On the contrary, those obtained from specimens whose intermediate Ni film thickness is 200 nm were shown in Fig. 6.

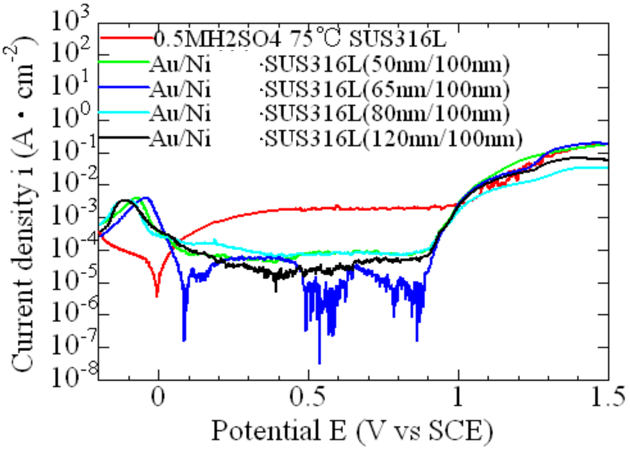


Figure 5: Results of polarization measurement obtained from Au/Ni/AISI316Lspecimen whose intermediate Ni film thickness is 100 nm.

Current density of Au/Ni thin films coated AISI 316L stainless steel was suppressed until about 1/100 levels comparing to that detected in bare substrate AISI 316L stainless steel.

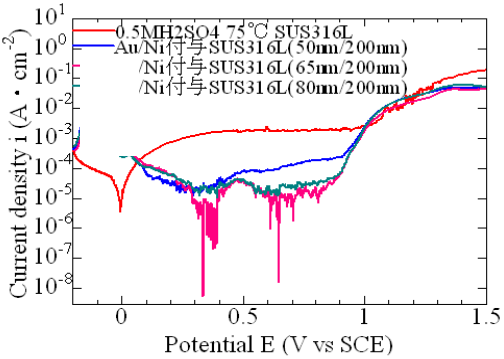
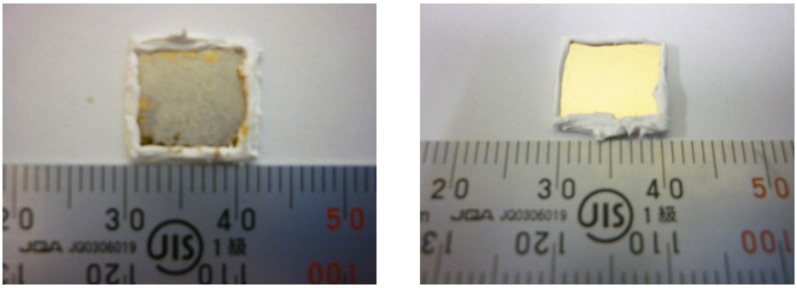


Figure 6: Results of polarization measurement obtained from Au/Ni/AISI316Lspecimen whose intermediate Ni film thickness is 200 nm.

And also, under the potential range of actual usage (100~800mVSCE) double layers coated AISI316L specimen indicated to stay still in passive state. Current density of Au/Ni thin films coated AISI 316L 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 thinner intermediate Ni thickness of 100 nm. And also, improvement in corrosion resistance due to increase of Au top film thickness was more remarkable in case of specimens with thicker intermediate Ni film.

From abovementioned results, improvement of corrosion resistance was recognized in all the double layered Au/Ni coated AISI 316L stainless steel. Contribution of intermediate Ni film thickness increase upon improvement in corrosion resistance became more remarkable when Au top film thickness became larger. 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. Best corrosion resistance in Au/Ni coated AISI 316L 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 [10]improvement and fill up of pinhole in Au top film by thicker Ni film formation. For this reason increase of intermediate Ni film thickness results in remarkable corrosion resistance improvement together with suppressing top Au film thickness.

From these results, it was made clear that CPCD method was applicable to Au top film defect area ratio evaluation of Au/Ni double layered coated AISI 316L stainless steel. And 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, outlook of specimen after anodic polarization measurement was investigated and typical results of these observations were indicated in Fig. 7. As shown in Fig. 7(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 24hrs static immersion test in 0.5M H_2SO_4 aqueous solution of 353K, as shown in Table 9.



(a) 50nm Au/100nm Ni/AISI 316L (b) 120nm Au/100nm Ni/AISI 316L

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

On the contrary, in 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 condition shown in Table 6.

4 Conclusions

There are few reports evaluating 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 Au top film was evaluated using the CPCD method. And also, corrosion resistance of Au/Ni thin films coated AISI 316L stainless steel under quasi-PEFC environment was evaluated.

Results obtained are summarized as follows:

1. CPCD method was applicable to Au top film defect evaluation of Au/Ni double coated AISI 316L stainless steel. The pinhole defect area ratio in Au thin film depends upon thickness of film itself.
2. The coherency of 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 AISI 316L stainless steel. Current density of Au/Ni thin films coated AISI 316L stainless steel suppressed until about 1/100 levels compared with that detected in bare substrate AISI 316L stainless steel. And 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 AISI 316L stainless steel specimen was obtained when Au/Ni is 65 nm/200 nm under the condition of polarization measurement. However, specimen whose top Au film thickness is less than 50nm indicated sufficient corrosion resistance under the conditions of 24hrs static immersion into 0.5M H_2SO_4 aqueous solution of 353K.

References

[1] Takagi, S., Development of New Metallic Separator Material for PEFC "NANOCLAD", Electric Furnace Steel, **77(4)**, pp. 321-326, 2006.

[2] Ueda, M., *et al.* Development of Metallic Separator for Polymer Electrolyte Membrane Fuel Cell (PEFC) (Report 1), pp. 2-6, Kurimoto Technical Report, No.55, 2006.

[3] Ueda, M., *et al.* Development of Carbon Coated Stainless Separators and Their Polarization Performance for Polymer Electrolyte Cell, J. of Japan Inst. of Metals, **71(7)**, pp. 545-552, 2007.

[4] Sugimoto, K., 95th JSCE symposium, pp. 1-11, JSCE, 1993.

[5] JSME standard S-010 "Standard Method for Evaluating the Defects in the Coatings Made by Dry Processing", JSME, 1996.

[6] Nitta, S. and Kimura, Y., Evaluation of Defects in Ceramic Coating Films by Various Electrochemical Techniques, Trans. Japan Soc. Mech. Engineers, **61(589)**, pp. 1914-1920, 1995.

[7] Nitta, S. and Kimura, Y., Evaluation of Defects in TiN Thin Films by Various Electrochemical Techniques, Advances in Surface Engineering, Volume II: Process Technology, Edited by P. K. Datta and J. S. Burnell-Gray, pp. 39-47, The Royal Society of Chemistry 1997.

[8] The Surface Finishing Society of Japan, "Basics and applications of PVD and CVD Coatings", Tokyo, Makishoten, 1994.

[9] Nitta, S. and Kimura, Y., Morphologies and Quantitative Evaluation by Electrochemical Methods of the Defects in Ceramic Coating Films, Journal of Material Testing Research Association of Japan, **42(1)**, pp. 4-14, 1997.

[10] Ohata, M. and Kimura, Y., Correlation between Localized Corrosion Morphology and the State of Interface of Coated TiN Thin Film, Surface Treatment IV, Editors, C. A. Brebbia *et al.* pp. 23-32, WIT Press, 1999.

[11] Chiba, H., *et al.* Influence of Mechanical and Structural Factors on Durability of PEFC with Gel Electrolyte Membranes, Electrochemistry, **75(2)**, pp. 238-242, 2007.