

Corrosion-resistant component for PEM fuel cells

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Abstract

Thin sheets of stainless steel are low-cost material for fuel cell components that can be easily formed to yield compact volume. But corrosion of the stainless steel bipolar plates is a problem in the PEMFC. Corrosion affects the performance and cell life of a fuel cell. The goal of this study is to find out appropriate surface treatment technology to protect the stainless steel bipolar plates against electrochemical corrosion. The feasible surface treatment process should be able to make significant improvement on the corrosion-resistance and the electrical resistance at a reasonable cost. After the treatment, the surface composition and/or the surface morphology may be modified. The modification of the surface composition may improve the corrosion-resistance of the metallic bipolar plate. The corrosion rate is determined by linear-polarization method from the polarization curve. The differences in polarization behaviors are attributed to a surface treated layer. The electrical resistance is the other factor which may affect the performance of the fuel cell. A smoother surface may reduce the interfacial resistance. The treated layer is a passive film. The thickness of the passive film after the surface treatment is thinner and the surface resistance is reduced.

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1. Introduction

The most widely used bipolar plate material of the PEM fuel cell is graphite. It is brittle and lacks mechanical strength. Therefore, thickness of the plates can not be reduced. This results in thicker plates, bulkier size, and heavier weight. There are many researchers focused on developing substitute material that is cheaper, lighter, and easy to manufacture. The most often mentioned new materials for bipolar plates are injection molding of the graphite filled polymer, compression molding, and metal [1].

In comparison to the graphite material, metallic bipolar plates provide many advantages such as cheaper material cost, good electrical and thermal conductivity, variety of manufacturing processes, excellent mechanical properties, and zero permeability. The volumetric size of the cell could be significantly reduced. The power/volume ratio of a cell will be improved.

Stainless steel is a good choice for metallic bipolar plate due to its excellent corrosion-resistance. However, because of the electrochemical reactions in a fuel cell,

the corrosion-resistance capability of stainless steel under such stringent operating conditions still need to be addressed. In a fuel cell, oxidation reaction occurred in the anode which ionized the hydrogen and produced electrons, shown in Eq. (1). The hydrogen ions passed through the membrane electrode assembly (MEA) and reached the cathode side to react with the oxygen and generated water Eq. (2):



Because of the hydrogen ions in the anode and moisture content in the MEA, it becomes acid. In addition, due to the discharging process of the cell's reaction, there were potential differences between the micro-gaps of the metallic bipolar plates and the MEA. Therefore, both chemical and electrochemical corrosion may erode the metallic plates. Also, the metallic bipolar plates losing electrons may result in dissolution of metallic ions which may poison the MEA. On the cathode, metallic oxide grows due to recovery reaction by gaining the electrons. It may increase the surface's electrical resistance.

The stainless steel contains about 70% Fe, 18% Cr, and 12% Ni. In acidic environment, both the Fe and Ni elements and their oxides were unstable and may be corroded

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or dissolved. On the other hand, although, the Cr element was very active, it quickly became oxide, Cr_2O_3 , which was both chemically and electrochemically stable. The existence of Mo and N will enhance chemical stability on the surface. However, the metallurgical structure of the protective passive film of the stainless steel, Cr_2O_3 , formed in normal manufacturing process was not solid and uniform. It may also have many surface defects such as inclusions, contaminants, scratches, and micro-cracks. It will accelerate localized corrosion.

There have been some studies on corrosion-resistance of stainless steel. Hornung and Kappelt [2] studied the ferric-based metallic bipolar plates. Their goal was to investigate cheaper ferric-base metal to replace more expensive gold-plated nickel-base metal. They found that the corrosion-resistance of the ferric-base metallic bipolar plate was about the same as that of the gold-plated nickel-base metallic bipolar plate. However, the gold-plated bipolar plate had better electrical conductivity.

Davies et al. [3] had reported that there was a high resistance surface layer of oxide film among many stainless steels such as ss316, ss310, and ss904L. The thickness of the oxide film will affect contact resistance and degrade cell performance. Their results showed that the cell performance was rated as followed: ss316 < ss310 < ss904L. The higher contents of the nickel and chromium will result in thinner oxide film and, thus, better cell performance. It was verified from the measurement of contact resistance of the ss904L was better than that of the ss316.

Wang et al. [4] studied the characteristics of stainless steels with different Cr contents. The results showed that the Cr contents were ss349TM > ss904L > ss317L > ss316L. The performance of corrosion tests also showed ss349TM > ss904L > ss317L > ss316L. The results of both Davies et al. [3] and Wang et al. [4] verified that the Cr forms passive film on the surface of the stainless steels. The more the Cr content in the stainless steel the better its corrosion-resistance.

The analysis of the compositions in the MEA reported by Wind et al. [5] indicated that large quantity of Fe and Ni atoms released from the stainless steel. It means that, under the PEM fuel cell operating environment, the Fe and Ni atoms may be dissolved by the electrochemical effect while the Cr atoms is more stable. In order to improve the effect of this oxide film, Wind had investigated metallic coatings on the metallic plates. They found that the coating reduces the contaminants of nickel, chromium, and iron in the membrane electrode assembly. The cell had a steady performance of over 1000 h.

For most reported data, a fuel cell with stainless steel bipolar plates has a cell life between 1000 and 3000 h. For computer, communication, and consumer (3C) products, it is a feasible direction. Therefore, in this paper, a surface treatment method was developed in order to improve the surface quality of the oxide film, to reduce contact resistance and to increase corrosion-resistance.

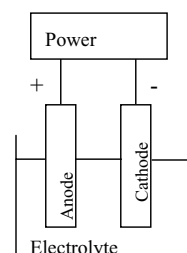


Fig. 1. Schematic plot of the surface treatment method.

2. Experimental and the results

2.1. Process procedures

The proposed surface treatment method employed the electrochemical theory. The work specimen is the anode and is immersed in the electrolyte. When it was connected with a cathode, the metallic ions will be released from the work specimen to form a passive film. Fig. 1 shows the schematic plot of the electrochemical process. Because the passive film had different metallurgical compositions from those of the substrate, the capability of corrosion-resistance may be improved. The surface morphology also became smoother and shining. The surface roughness was greatly improved and exhibited hydrophobic property. It may improve the flow of gas and water in the gas channel of the bipolar plate. The surface resistance was reduced. Therefore, the cell performance may be more stable and cell life is longer.

The stainless steel ss316L (American Society for Testing and Material) was selected as the bipolar plate material. The size of the work specimen was 50 mm × 30 mm × 1 mm. The cathode material was copper. The experimental procedures were shown in Fig. 2. First, the specimen was prepared by grinding, degreasing, ultrasonic cleaning, and de-ionization, a standard cleaning process for chemical treatment. The stainless steel plate went through the electrochemical surface treatment. Finally, the treated specimens were tested for corrosion-resistance, surface metallurgical compositions, and contact resistance.

2.2. Analysis of passive film

The treated specimen was analyzed by ESCA for surface metallurgical compositions. From the ESCA spectrum the binding energy will be compared with data bank to identify the amount of chemical shift and the chemical compositions of the elements [6].

From the results, Cr/Fe elemental ratios, chemical species for Cr and Fe and independent estimates of Cr, Fe, and Ni oxide thickness, were described. Cr/Fe elemental ratio, and metal/oxide species ratios for Cr, Fe, and Ni were determined from measurements of the Cr(2p_{3/2}), Fe(2p_{3/2}), and Ni(2p_{3/2}). The oxide thickness of Cr, Fe, and Ni estimation

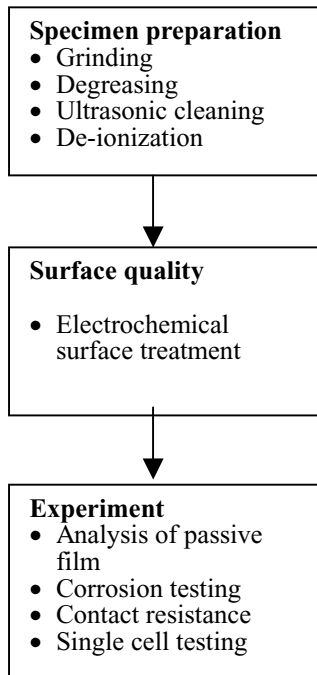


Fig. 2. Flow chart of the experimental procedure.

followed the Eqs. 3–5 [7]:

$$\text{Cr oxide thickness} \approx 20 \text{ \AA} \times \ln \left[\frac{\text{Cr oxide area}}{\text{Cr metal area}} 2.15 + 1 \right] \quad (3)$$

$$\text{Fe oxide thickness} \approx 20 \text{ \AA} \times \ln \left[\frac{\text{Fe oxide area}}{\text{Fe metal area}} 2.01 + 1 \right] \quad (4)$$

$$\text{Ni oxide thickness} \approx 20 \text{ \AA} \times \ln \left[\frac{\text{Ni oxide area}}{\text{Ni metal area}} 1.7 + 1 \right] \quad (5)$$

2.3. Corrosion test

During the operation of a H₂–air PEM fuel cell, the ionic exchange membrane may dissolve acidic ions such as SO₄⁻, SO₃⁻, and HSO₄⁻ [8]. Because of ionic and electronic transfer exchange, the electrochemical corrosion will occur due to the potential difference.

The uniform corrosion rate of a metal can be estimated by the electrochemical corrosion measurement. The linear polarization method was employed for uniform corrosion evaluation [9]. From Faraday’s law, the corrosion rate, *R*_{corr}, can be obtained under known surface area, *A* and process time [10].

$$R_{\text{corr}} = 0.0032 \frac{I_{\text{corr}} A}{nD} \quad (6)$$

$$R_p = \frac{\beta_a \beta_c}{2.3 I_{\text{corr}} (\beta_a + \beta_c)} \quad (7)$$

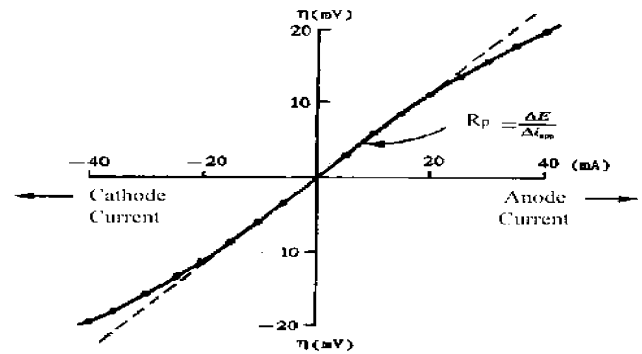


Fig. 3. Typical uniform corrosion curve of linear polarization test.

where *I*_{corr} is the corrosion current, *A*/*n* is the gram-equivalent weight, *D* the weight density, $\beta_a \beta_c / 2.3 (\beta_a + \beta_c)$ is the constant. A typical uniform curve from a linear polarization test was shown in Fig. 3 [10]. The slope from Fig. 3 is the *R*_p. When substituted into Eq. (7), the *I*_{corr} can be calculated. This method is faster than the measurement of weight loss by putting the specimen in acid solution for a long time. There are different standards to perform the corrosion test. Because, the pH value in the fuel cell environment is between 0 and 3.5 and the ionic exchange is equivalent to 1 M of H₂SO₄ [11], the ASTM G5 standard [10] was employed for the uniform corrosion test. The specimen was tested under room temperature with 0.5 M H₂SO₄ Solution. A Solartron 1285 potentiostat was used for the corrosion test which included reference electrode (REF), working electrode (WE), and auxiliary electrode (AUX). The scanning range was between –0.5 and 0.5 V (versus OCP) and the scanning rate was 10 mV/s.

2.4. Contact resistance measurement

In order to obtain optimal parameter for cell assembly, tests were conducted to establish the relationship of the pressure versus contact resistance. Because of the sandwich layered structure, the surface characteristics, and the surface passive (oxide) film may affect the contact resistance between the bipolar plate and the MEA.

The contact resistance test method as Fig. 4 was described by Wang et al. [4]. This basically involved measuring the

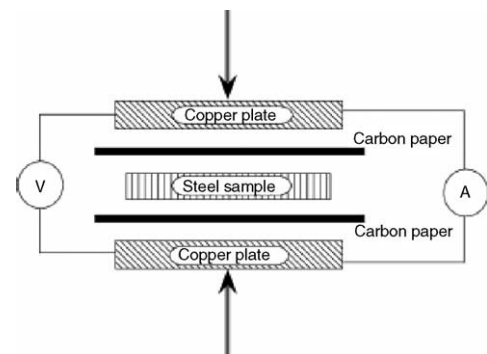


Fig. 4. Schematic of the test assembly for interfacial contact resistance.

potential difference across two pieces of the plate material, which sandwiched two pieces of a gas diffusion layer, whilst a fixed electrical current was passed through the arrangement. The potential difference was monitored as the compaction on the assembly was periodically increased. Thus, the relative surface resistance for each material could be determined. The bipolar plate specimens were tested, apart from thorough degreasing and cleaning in DI water.

By measuring the voltage drop, it was possible to calculate the total resistance according to:

$$V = IR \quad (8)$$

3. Results and discussion

3.1. Analysis of passive film

The elemental compositions of the passive films were analyzed and the results were listed in Table 1. The percentage composition of Cr has increased by two-folds from 26.88 to 59.69%. The specimen also went through AES for the depth profile to verify the compositional changes throughout the thickness. The results were shown in Fig. 5. At a depth of around 10–20 Å the Cr composition is much higher than that of the Fe. At the depth of substrate, the percentage compositions went back to normal ss316L compositions when Fe consists of 70% and Cr was about 16–18%.

The experimental data showed that the Cr content had doubled from its original value. It proved that this surface treatment method can effectively increase the Cr content and decrease the corrosion-prone Fe content of the surface. The thickness of the oxide layer of the Cr, Fe, and Ni were estimated to be 16.5, 5.5, and 6.9 Å. This dense and integral oxide film had much less thickness.

Under optical microscopy, the smooth and shining surface exhibits hydrophobic characteristics which may

Table 1
Results of ESCA analyses (wt.%)

Element	Original specimen	Processed specimen
Cr	26.88	59.69%
Fe	52.40%	15.68%
Ni	20.71%	24.63%
Cr/Fe ratio	0.51	3.81

Table 2
List of surface roughness values (μm)

No.	R_{max}	R_{a}
Original	1.1	0.12
1	0.410	0.042
2	0.383	0.038
3	0.451	0.045
4	0.550	0.058
5	0.500	0.050
6	0.367	0.032

improve the flow of gas and fluid. The reduction in surface roughness value may also decrease micro-potential difference. The values of surface roughness after treatment were listed in Table 2. Figs. 6 and 7 show the microscopy pictures of the surface profiles of the original and treated specimen. The original specimen, Fig. 6, had rough surface profile, loose and damaged structure, inclusions, and rolling marks. Fig. 7 shows smooth and integral structure with no above mentioned defects. The improvement in surface roughness was also obvious when comparing Figs. 6 and 7.

3.2. Results of corrosion test

Fig. 8 shows typical result of the uniform corrosion test. The electrochemical corrosion rate of the original specimen is 0.1 mmPy. The corrosion rates of the processed specimen

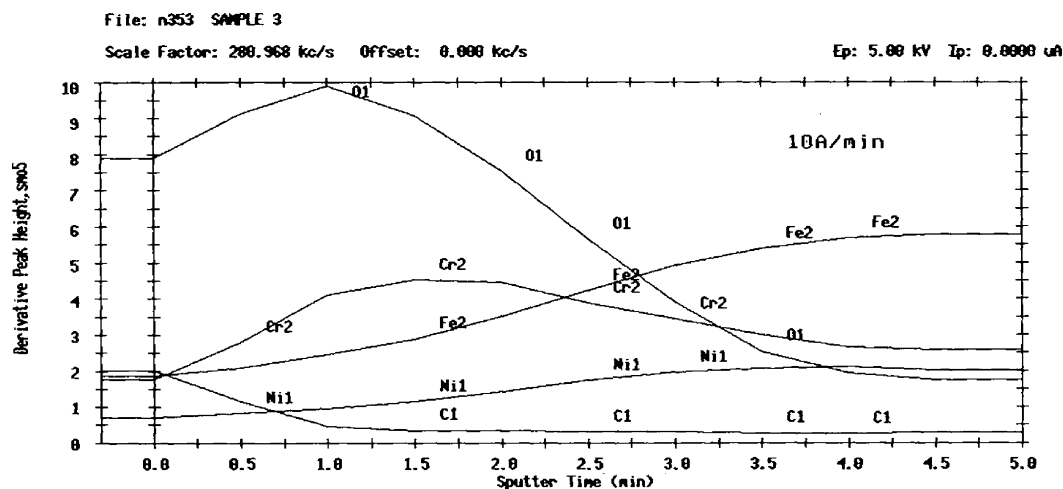


Fig. 5. Depth profile from AES analysis.

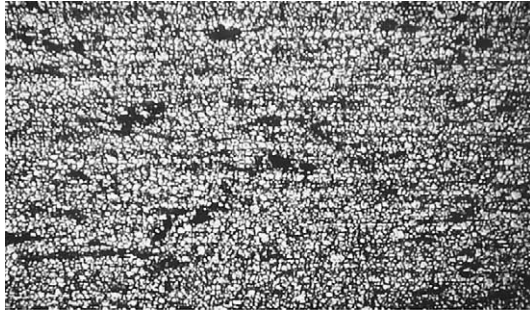


Fig. 6. Microscopy picture of original specimen (surface roughness: R_a 0.12 μm , R_{max} 1.1 μm).

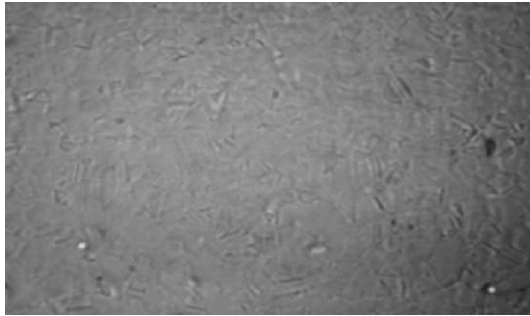


Fig. 7. Microscopy picture of treated specimen (surface roughness: R_a 0.02 μm , R_{max} 0.24 μm).

are listed in Table 3. This indicates that the corrosion rate was improved by about 66%. It meant that the processed plates may run longer without electrochemical corrosion under normal PEM fuel cell operation.

The corrosion tests, shown in Fig. 8, indicates that the corrosion current, I_{corr} , of the treated specimen was smaller than that of the original specimen due to the increased Cr

Table 3

Results of the corrosion-resistance tests

Test number	Uniform corrosion (mmPy)	Result of corrosion test improvement (%)
Original	1.0E-01	–
1	3.54E-02	62.852
2	2.78E-02	70.811
3	3.03E-02	68.232
4	3.99E-02	58.200
5	3.82E-02	59.968
6	2.10E-02	78.027
Average	3.21E-2	66.230

content. At 0.6 V potential which is the operating voltage of the fuel cell, the corrosion current of the treated specimen is 15 $\mu\text{A}/\text{cm}^2$ as compared with 60 $\mu\text{A}/\text{cm}^2$ of the original specimen.

When the treated specimen went through the corrosion test in the 0.5 M H_2SO_4 solution, Fig. 9 shows the anodic behavior of the original state and after 24 and 48 h. The surface condition is stable and the corrosion currents remain constant at about 25 $\mu\text{A}/\text{cm}^2$. The corrosion rates were 0.035, 0.038, and 0.039 mmPy, respectively. This indicated that the treated specimen had a stable protective passive film and may survive a long time fuel cell operating conditions.

3.3. Results of contact resistance measurements

In order to obtain optimal parameters for cell assembly, tests were conducted to establish the relationship of the pressure versus contact resistance. Because of the sandwich layered structure, the surface characteristics, and the surface passive (oxide) film may affect the contact resistance

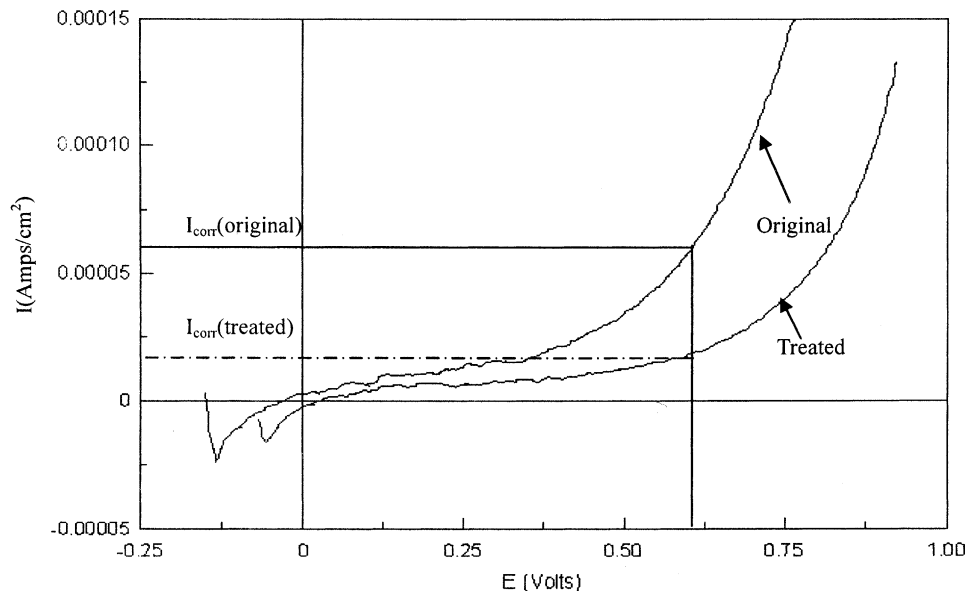


Fig. 8. Anodic behavior in 0.5 M H_2SO_4 at 70 °C (original vs. treated).

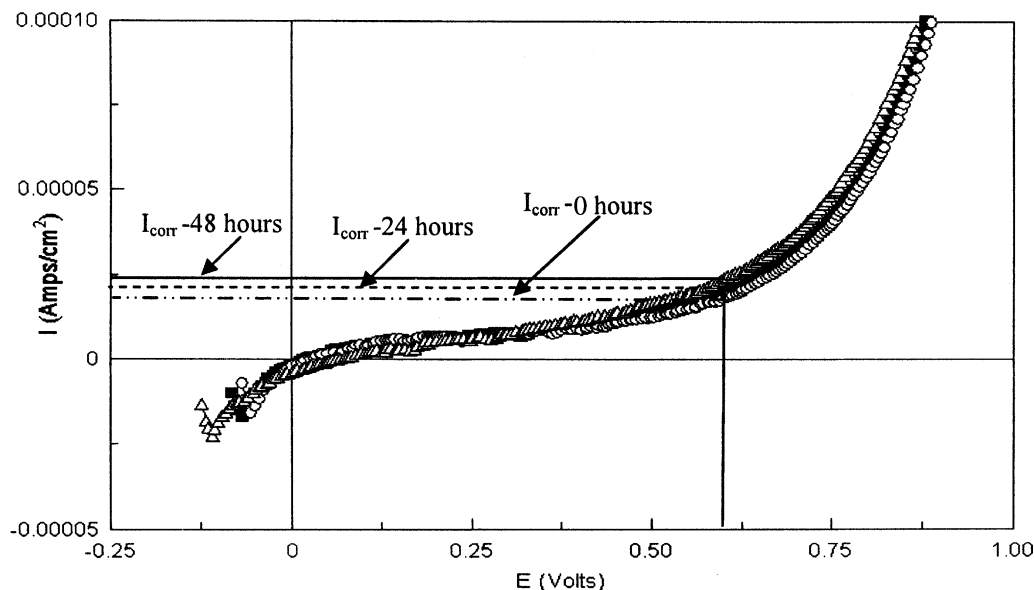


Fig. 9. Anodic behavior in 0.5 M H₂SO₄ at 70 °C-treated specimen (○)-Oh, (■)-24 h, (△)-48 h.

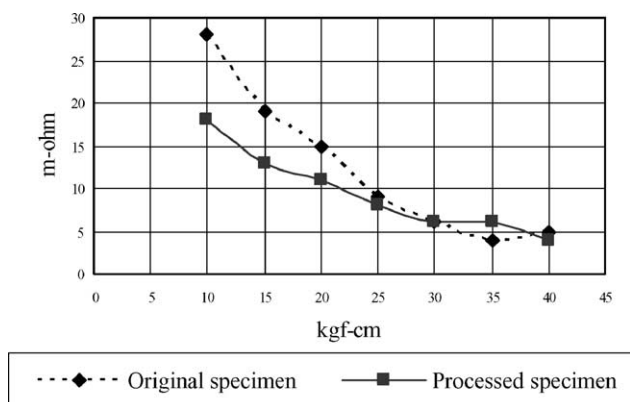


Fig. 10. Contact resistances of the original and the processed specimens.

between the bipolar plate and the MEA. The curves of pressure versus contact resistance of the original and the processed specimens are shown in Fig. 10. This indicates that due to the smoother surface the contact resistance was much lower under low assembly pressure. As the applied pressure increases, the diffusion layer was compressed and the difference became minimal.

4. Conclusions

The metallurgical analysis showed that the Cr content on the surface of the treated stainless steel bipolar plate had been greatly increased through selective dissolution process of the surface treatment method. At the same time, the Fe content was greatly decreased. The metallurgical structure of the surface had become defect-free, solid, and integral.

The Cr oxide, Cr₂O₃, formed a protective passive film which increased the corrosion-resistance of the stainless steel bipolar plates. The corrosion test showed that the corrosion current was reduced to one fourth of the original value. When immersed in the 0.5 M H₂SO₄ 70 °C, the corrosion current remain stable indicating it may survive long term fuel cell operation.

Because of the clean and integral surface, the surface electric conductivity increased despite the increase in Cr content. The surface texture and surface roughness had also been greatly improved. The surface characteristics became hydrophobic which may improve the flow of the fuels and fluid. Because of the smooth surface, the micro-potential difference between the MEA and the metallic bipolar plates was reduced which may further reduce localized corrosion of the metallic bipolar plate.

From this study, the surface treated stainless steel bipolar plate may be a good candidate for PEM fuel cell. Single cell and long term life testing are under preparation.

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