Analysis on the corrosion behavior of Al-alloy bipolar plate and pH value of water product for the PEMFC

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Abstract—The energy crisis and global warming are two urgent problems in the world currently. Owing to these major advantages of high efficiency and low emission, proton exchange membrane fuel cell (PEMFC) has become a promising candidate of power sources. The performance of Al-alloy bipolar plate for the PEMFC system was investigated in this paper. Due to the light weight and easy machining, the 5052 Al-alloy is considered as the good candidate for the bipolar plate substrate. In the experimental analysis, aluminum bipolar plates without coating were measured by current-voltage curve and constant current test. Furthermore, the chronological water acidity varied tardily and its pH value ranged 4.2 to 5 initially. The more acid product would corrode the aluminum bipolar plate severely and shorten the fuel cell lifetime. After the experiment operated for 100 hours, the bipolar plate corrosion behavior and membrane degradation decrease the pH value and cell performance. It was available that the fuel cell performance degradation can be quantified by our method. These above results will be useful for the metallic bipolar plate preliminary design.

Keywords—PEMFC, pH value, aluminum bipolar plate, water

I. INTRODUCTION

Fuel cells are used for power generation with low emission and high efficiency. The major advantages of proton exchange membrane fuel cell (PEMFC) are low-temperature operation, quick starting, high energy density, clean, and simple design. Therefore, the PEMFC extensively applied to power generation, portable electric equipment, ship and hybrid vehicles. The fuel cell provided the electric power when it was supplied with hydrogen and oxygen gas. Electrons and H⁺ ions released from the hydrogen gas consumption at the anode side. The reaction at the negative electrode is:

\[ 2H_2 \rightarrow 4H^+ + 4e^- \] (1)

The hydrogen gas electrochemical reaction was enhanced by the catalysis. Electrons flow from the anode to cathode side via the external circuit. Hydrogen ions transport to the cathode side and react with the oxygen gas. The reaction at the positive electrode is:

\[ O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad E_o=1.229 \text{ V} \] (2)

The fuel cell performance considerably degraded with the chemical catalyst change over the proton membrane. Cai et al. [1] had proved platinum catalyst would react with water and form free radical •OH. The carbon dioxide (CO₂) and hydrofluoric acid (HF) form easily when the free radical •OH react with the perfluorosulfonic membrane at high temperature. Above result involved the pH value change of water that drained from the fuel cell as following reactions:

\[ 2R_f - CF_2COOH + OH^- \rightarrow R_f - CF_2^+ + CO_2 + H_2O \]

\[ R_f - CF_2^+ + OH^- \rightarrow R_f - CF_2OH \rightarrow R_f - COF + HF \]

\[ R_f - COF + H_2O \rightarrow R_f - CF_2OH + HF \]

There were many researches focused on the degradation mechanism to increase the H₂O₂ formation rate [2-9] in the fuel cell. It has been found that the deteriorated membrane would enhance the water acidity at the cathode compartment. Sethuraman et al. [7] measured the H₂O₂ concentration under the constant temperature and relative humidity. It can be predicted as a function of humidity and temperature by studying the oxygen reduction reaction. Abundant H₂O₂ formed when the experiment set as higher temperature, relative humidity and oxygen concentration. The free radical formed when the H₂O₂ reacted with metal ions. Meanwhile, another mechanism was discussed by the electrochemical reaction potential in PEMFC as below:

\[ H_2O_2 + M^{2+} \rightarrow M^{3+} + OH^- + HO^- \]

\[ O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad E_o=0.695 \text{ V} \] (3)

Hence, the H₂O₂ formation rate may not too little owing to the high electrochemical drive force. The perfluorosulfonic membrane would be attacked when the oxygen reduction reaction occurred. It could be inferred that H₂O₂ formation rate involved the pH value change. Abdullah et al. [10, 11] discussed the water character that drained from the fuel cell at different relative humidity. The very acidic...
water drained from the cathode compartment easily under the low relative humidity (35%). But, the opposite trend occurred at high relative humidity (100%). Furthermore, the pH value of water changed with the load owing to the chemical reaction rate. The water approximated the neutrality when the load operated at large current density except for the low temperature and low relative humidity condition. The pH value of water chronological change was attributed to the OH production rate of the selectivity in the oxygen reduction reaction. The lower temperatures would enhance the stability of H₂O₂ molecules in the fuel cell. Oppositely, it was obvious that the pH value fluctuated severely at high temperature. Above result indicated the lower proton crossover reaction was caused by the higher concentration hydrogen peroxide. Meanwhile, the hydrogen peroxide affected the cell performance significantly. Hentall et al. [12] considered the complex flow-field and adopted a new process technique for making the bipolar plate. Hence, they suggest the material fabricated into the bipolar plate must be machined easily. The stainless steel was coated with a thin gold that offered superior power performance than the graphite. The gold film has the good corrosion resistance and electricity conductivity property. The current-voltage (I-V) curve had proven the metallic bipolar plate was really feasible. There were also many researches focused on the chronological change of the metallic bipolar plate [13-15] in the fuel cell. This accomplishment would benefits to the metallic bipolar plate preliminary design.

II. EXPERIMENT

The manufactured PEMFC used in this experiment has been assembled with commercial membranes (Nafion-112), aluminum bipolar plates and gas diffusion layers. The active area of the Nafion 112 membrane set as 25cm² (5cm × 5 cm). The fuel gas was supplied with oxygen (140 c.c/Min) in the cathode side and hydrogen gas (210 c.c/Min) in the anode side. The temperature of fully humid flow gas and cell were set as 60°C. The range of electric load set as 0.85 to 0.2V (voltage scan rate was set as 0.1 V/hour) and the limit current set as 33A. The water produced from PEMFC cathode was measured by the pH meter (from HACH Inc Benchtop series model number H260G). The acidity of water droplet was recorded as per thirty seconds and the average value was obtained for twenty points.

The single serpentine gas flow bipolar plate made from the 5052 Al-alloy was machined as Fig 1. The inset shows the SEM topographies of the 5052 Al-alloy bipolar plate. Owing to the light weight and ease of machining, the aluminum is considered as the good candidate for the bipolar plate.

Figure 1. The 5052 Al-alloy bipolar plate morphology

III. RESULTS AND DISCUSSION

A. Assembly test

After the PEMFC operation environment test as Table I. The chronological performance change of 5052 Al-alloy was recorded as Fig 2. The performance decayed with the operation time due to the variation on the sheet surface. The single cell performance would decay as the thicker oxide film and the corrosion over the sheet surface. The relation between the single cell performances corresponds to mathematical model as Eq (4).

\[ E = E_0 - \beta \log(i) - R \]

The term \( E_0 \) yields the electrode kinetic parameter for oxygen reduction in the PEMFC. The term \( \beta \) is the Tafel parameter for the oxygen reduction and \( R \) represents the ohmic resistance. The 5052 Al-alloy substrate performance data were fitted as Fig 3. The root mean square error value approximate 9.47E-04 the Tafel parameter for the oxygen reduction and \( R \) represents the ohmic resistance. The single cell matched well with the mathematical model. These fitting values of metallic bipolar plates were shown as Table I. Basically, the \( R \) value increased with time as a whole and displayed linearization property as Fig 4.
Figure 2. Polarization curve chronological change under the experiment setup.

Figure 3. Fitting curve for 5052 Al-alloy polarization curve.

Figure 4. Parameter R variation in the fitting model.

Table I. The fitting parameter of cells under the experiment setup.

<table>
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<tr>
<th>No</th>
<th>Time(hours)</th>
<th>$E_0$ (V)</th>
<th>b (V/dec)</th>
<th>R (mOhm)</th>
<th>mean square error</th>
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<tr>
<td>1</td>
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<td>0.937</td>
<td>0.02426</td>
<td>2.60</td>
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</tr>
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</table>

B. Corrosive behavior of the metallic bipolar plate

The SEM result under the fuel cell operation was shown as Fig 5. Both bulks in the different environment have the identical morphology over the sheet surface.

In fact, the oxide film covered on aluminum plate surface was thicker with time owing to the higher $O_2$ concentration in the cathode environment shown as Fig 5a. By the way, the oxide film on the anode surface would not develop easily under the $H_2$ environment as Fig 5b. The analysis by examined with EDAX, results stated that oxide in the cathode side (54.5%) much higher than in anode side (10.78%). Above results verified the acid electrolyte result in serious corrosion in the fuel cell as Fig 5.

C. The time series analysis of the fuel cell

It takes 50 hours single cell operation to attain the stable system before the time series was recorded. The cell on load operated at constant current (100mA/cm²) and recorded as chronological data (50-55 hours). The time series was recorded per minute to analyze the cell voltage loss trend. The chronological change stated the fuel cell could not keep at the constant voltage as Fig 6. There are two reasons led to the cell voltage loss. Firstly, the long term descend trend was due to the ohmic resistance loss. The temperature set at 333K which is fairly standard for the operation of PEM fuel cells. Owing to the acid environment, the thicker oxide film formed in the cathode side and corrosive phenomenon occurred in the anode. The interfacial contact resistance and dielectric constant would vary with time. Furthermore, the
ohmic loss led to the overall fuel cell performance descends tardily.

Secondly, the short term variation was affected by the operation condition. The cell voltage involved by the electrochemical reaction, mass transfer phenomenon, catalyst layer, temperature and pressure. The reaction stayed at equilibrium when the forward and backward reaction occurred simultaneously. Hence, the cell voltage perturbation is considered as a random signal.

The descend trend occurred obviously in single cell. The graph of the cell voltage data fitting were used by the linear model as Eq (5-6):

\[ T_v = \beta_0 + \beta t + \epsilon \]  
\[ \hat{T}_v = \beta_0 + \beta t \]

Figure 6. The chronological trend of the fuel cell voltage

Where \( T \) and \( \epsilon \) are known as the trend component and error, respectively [17]. The over all performance durability test was analyzed by the above model. A linear regression fitted as voltage data at 100 mA/cm\(^2\) for the fuel cell operating period of the experiment (from 50 to 55 hours) voltage decay rates \( \beta \) of single cell was 35.4 \( \mu \)V/min. The experiment initial value \( \beta_0 \) was 0.665 Volt. Above result verified the aluminum bipolar plates possess weak corrosion resistance in the high temperature and low pH value environment.

D. pH character and cell performance

The chronological water acidity was stated by pH value change and ranged from 4.2 to 5 initially as Fig 7. Furthermore, abundant metal ions release rate would enhance the water acidity owing to abundant free radical \(*OH\) production. The more acid product would corrode the metallic material severely and shorten the fuel cell lifetime. Hence, the degradation of the cell performance could be observed at Fig 7.

At current density 250 mA/cm\(^2\), the cell voltage was 0.52 (V) and the pH value of water was 4.7. After the Experiment operated for 100 hours, the cell voltage and pH value decreased to 0.2 (V) and 3.9, respectively. It was obvious the bipolar plate corrosion behavior and membrane degradation decrease the pH value and cell performance. Furthermore, the pH value chronological change of water could be an important index of the membrane degradation.

Figure 7. The performance and pH value change of water about the cell.

IV. CONCLUSIONS

1) The aluminum bipolar plate possess weak corrosion resistance in the high temperature and low pH value environment. These results were valid by the time series analysis and the mathematical model which induced by Kim.

2) The fuel cell environment led to the different corrosion behavior in two sides (Anode and Cathode side). The oxide film would increase the interfacial contact resistance and descend the overall performance. The thicker oxide film formed in the cathode side than the anode.

3) It was obvious the bipolar plate corrosion behavior and membrane degradation decrease the pH value and cell performance. Furthermore, the pH value chronological change of water could be an important index of the membrane degradation. By the way, the metallic components (end plates, collectors and fuel inlet) in the fuel cell were corroded by the acid water easily. As for the cell lifetime, it is important to manipulate the cell at moderate thermal condition and decrease the \(*OH\) production. These above results will benefit to the metallic bipolar plate preliminary design.

REFERENCES


