Modification of the liquid cooling channel of PEMFCs for their operation with dry reactant gases

Jin-Cherng Shyu a, *, Kan-Lin Hsueh b, Fanghei Tsau c, Fa-Lin Chen c

a Department of Mechanical Engineering, National Kaohsiung University of Applied Sciences, Kaohsiung 80778, Taiwan, ROC
b Department of Energy and Resources, National United University, Miaoli 36003, Taiwan, ROC
c Energy and Environment Laboratories, Industrial Technology Research Institute, Hsinchu 31040, Taiwan, ROC

Article info

Article history:
Received 8 October 2008
Received in revised form 29 October 2009
Accepted 22 June 2010
Available online 22 July 2010

Keywords:
PEM fuel cell
Circulating electrolyte
Dry reactant gases
Electrochemical impedance
Interfacial resistance

Abstract

In order to tackle both water and thermal problems, a modified PEMFC is proposed in the present study for its operation with dry reactant gases via the modification of liquid cooling channel with circulating liquid electrolyte. Fuel cell with both circulating liquid electrolyte and solid polymer membrane operated with either dry or humidified H2/O2 is compared in the present study at temperatures of 40, 50, 65, and 80 °C, respectively. The measured E–I data show that such single cell can be operated at 80 °C without humidification.

Besides, a semi-empirical equation to predict the current/voltage relationship, and the electrochemical impedance method are also employed in the present study for cell resistance analysis. The analysis results show that the high interfacial resistance should be one of the major reasons for the inferior performance of the present cell. Based on the discovery, an improvement of the present fuel cell is further proposed by Nafion ionomer spreading on the electrode before the assembly of membrane and electrode. The maximum power density of the cell after electrode treatment reaches 75 mW/cm2 for dry H2/O2 operation at 0.4 V, which is almost threefold improvement compared with that without electrode treatment.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

In order to reduce global warming and to lower the dependency of fossil fuel, hydrogen/fuel cell has been considered as one of the most promising energy technologies due to its high conversion efficiency of energy and zero CO2 emission. Among all kinds of current fuel cells, polymer electrolyte membrane fuel cells (PEMFC), which employ perfluorosulfonic acid polymer membranes, such as Nafion®, have attracted a great deal of attention due to their widespread application areas such as automobile, distributed power generation, as well as portable electronics.

For operation of a PEMFC, water management has been identified as a critical issue. Santarelli and Torchio [1] performed an experiment to analyze the temperature effect on the performance of PEMFCs with Nafion 115 fed with H2/air. Their results showed that an increase in humidification improved the cell performance at high cell temperature due to higher membrane conductivity but decreased the cell performance at low cell temperature and high current density due to cathode flooding. Therefore, it can be concluded that insufficient humidification causes high membrane resistance whereas excessive humidification may lead to flooding of electrode. Either case results in lower cell performance.

In addition, Berning et al. [2] developed a non-isothermal, three-dimensional computational model incorporating a complete cell with both the MEA and gas distribution flow channel of a PEM FC. Al-Baghdadi and Al-Janabi [3] further performed a three-dimensional, non-isothermal, multi-phase model of a PEM fuel cell to investigate the key factors affecting fuel cell performance. Besides single PEM fuel cell, the effects of flow variance and temperature distribution on the performance of a PEM fuel cell stack were also analyzed by a non-isothermal stack model proposed by Park and Li [4]. All simulation results mentioned above indicated that temperature distribution inside fuel cell is another major factor affecting cell performance. Therefore, besides water management, thermal management of fuel cell stack is also a crucial issue in the operation of PEMFCs. In practice, heat generated within stack has to be removed by either water-cooling such as the numerical heat exchanger design performed by Lasbet et al. [5] and the fuel cell stack model proposed by Park and Li [4], or air-cooling technique like the configuration studied by Adzakpa et al. [6]. Since water cooling removes heat more efficiently than that of air cooling, Corbo et al. [7] demonstrated a 20 kW H2/air proton exchange membrane fuel cell stack for stationary and mobile application.
employing a water cooling system to assure an approximately uniform temperature distribution through the cells. Consequently, PEMFC system is usually operated with both an external humidification system and a water cooling system for higher performance. This would complicate stack design, fabrication, and assembly.

Since the water management of fuel cells is to ensure good conductivity of the solid polymer electrolyte, the external humidifier can thus be eliminated for such fuel cells without solid polymer electrolyte. In fact, fuel cells with circulating electrolyte have been successfully used for alkaline fuel cell (AFC), such as the 7-kW fuel cell with circulating KOH solution as liquid electrolyte demonstrated by Strasser [8]. Above all, the circulating liquid electrolyte can also cool the fuel cell. In other words, the electrolyte circulating between the electrodes not only conducts ions but also works as cooling medium, and thus results in the exclusion of the external humidifier from PEMFC. However, one of the drawbacks of such membraneless fuel cell with circulating liquid electrolyte between two electrodes is that more hydrophobic treatment of the electrode by PTFE would be indispensable to determine the three-phase reaction zone within the electrode as stated by both Wagner and Schulze and Christenn [10]. Undoubtedly, the PTFE content would play a significant role in the cell performance due to the dependency of both electric conductivity and porosity of the electrode on the PTFE content. Both results proposed by Velayutham et al. [11] and Tian et al. [12] showed that heavier PTFE content in the GDE significantly reduced the performance of PEMFCs. Moreover, the optimal PTFE content in the treatment of GDE in Tian et al. [12] experiment was found to be 20% within their tested PTFE content ranged from 0% to 40%.

Therefore, this study aims to propose a modified PEMFC that can be operated with dry reactant gases by circulating liquid electrolyte. Moreover, a commercially available electrode and a solid polymer electrolyte membrane will both be employed in the present study for eliminating the extra PTFE treatment of electrodes. The latter is for the prevention of possible leakage of the liquid electrolyte into the porous electrode. A fuel cell with circulating electrolyte will be built and tested without the need of humidification. Such cell will be operated under either dry or humidified inlet gas at 40, 50, 65, and 80 °C. Furthermore, a semi-empirical equation accounting for various influencing parameters such as internal resistance, exchanging current density, and charge transfer coefficient will be employed to calculate the voltage losses. The electrochemical impedance method will also be applied to analyze the material resistance and the interfacial resistance for further improvement of such fuel cell. Finally, according to those analysis results, a revised design of such fuel cell will be presented with a dramatic improvement of the cell performance.

2. Experimental apparatus

2.1. Configuration of single cell

The configuration of the present fuel cell with electrolyte circulation is shown in Fig. 1. The current collectors of the single cell are gold-plated copper plates. Graphite plates with serpentine gas flow channel are used as gas flow field plates for both anode and cathode. Note that both gas flow plate and sealing gasket have two additional openings for the circulation of liquid electrolyte. Besides, a polymer channel plate acting as the liquid electrolyte flow channel with thickness of 2 mm was placed between the electrodes.

The electrolyte used in the present experiments was sulfuric acid with 2 M concentration. Fig. 1b is the cross-section plot of this cell. The electrolyte was circulated by a peristaltic pump from a 1-L gas flask wrapped in a temperature control system.

The gas diffusion electrode for both anode and cathode of the present fuel cell was commercially available product (E-Tek, LT120EW) with catalyst loading of 0.5 mg Pt/cm². In order to prevent possible leakage of the liquid electrolyte into the porous electrode, a polymer membrane (Nafion 112, Du Pont) was hot pressed on the catalyst side of each GDE at 130 °C under pressure of 100 atm for 90 s. Prior to the hot-pressing, Nafion 112 was cleaned and treated to ensure that the membrane is completely in the protonic form. The membrane was boiling in 3 wt.% H₂O₂ for 60 min, followed by boiling for 60 min in deionized water. The membrane was then boiled for 60 min in 0.5 M H₂SO₄ solution, followed by boiling for 60 min in deionized water twice. The effective area of these electrodes is 25 cm². Finally, the cell was tightened with bolts and nuts clamped to 70 kgf-cm of torque for subsequent experimental tests.

2.2. Description of testing system

The relationship between cell output voltage (E) and current (I) was measured at ambient pressure with pure hydrogen as the fuel and oxygen as the oxidant. The effects of operating temperatures (40, 50, 65, and 80 °C) and the effects of humidification (with/without) on the E–I curve were studied.

All the measurements were carried out on a testing system as shown in Fig. 2. It contains a test-station, circulation system of the liquid electrolyte, and the single cell. The test station includes five parts: gas supply system, flow rate control system, temperature control system, humidity system, and electric load system.

In the humidity system of this test-station, the reactant gas is forced to pass through humidification bottles at the same temperature as the single cell. Water in humidification bottles was drained out completely before the experiment for non-humidification condition. In the liquid electrolyte system, a peristaltic pump is used to circulate the liquid electrolyte between the electrolyte circulation tank and fuel cell. A controller and a heater were used to maintain the electrolyte temperature in the tank. The temperatures of fuel cell, humidification system, liquid electrolyte, and reactant gases were kept at the same during experiment.

The electrochemical impedance measurements were carried out with a Potentiostat/Galvanostat (AutoLab, PGSTAT20) and an external FRA2 module. The present impedance measurements were performed in potentiostatic mode with voltage amplitude of 10 mV over a frequency range from 0.1 to 10,000 Hz in a logarithmic distribution.

2.3. Experimental procedure and uncertainty

The present experiment was performed based on the following procedures:

1. Connect the cell to the test station, including the gas connections and electric connections.
2. Turn on the test station.
3. Open the gas lines (hydrogen, oxygen and nitrogen) and purge the cell and piping by nitrogen gas.
4. Set the temperature of the liquid electrolyte and start to circulate the liquid electrolyte when temperatures reaches the setting value.
5. Set the gas flow rates by the computer with test software connected to the test station.
6. Set the temperatures of the cell, gas humidifiers and inlet piping.
7. Turn on the electric load and start the test when all temperatures have reach the setting values.
8. Disconnect the electric connections between the cell and the test station when E–I curve measurement has finished.
9. Connect the cell to the Potentiostat/Galvanostat and set the gas flow rate.
10. Start to measure the electrochemical impedance of the cell at fixed voltage.
11. The measurement range and accuracy of all the measurement devices are shown in Table 1.

3. Results and discussion

3.1. Effects of operating temperature on cell performance

The cell performance fed with dry H2/O2 is given in Fig. 3. The cell voltages (E, volt) at different operating temperatures (40, 50,
3.2. Effects of humidification on cell performance

Both of the E–I curve and P–I curve are plotted in Fig. 4 for cell performance operated with humidified H₂/O₂. The value of |dE/dI| is decreased as the temperature changed from 40 to 80 °C. Maximum power density is increased from 20 to 27 mW/cm² as the cell temperature increased from 40 to 80 °C. The dependence of OCV, slope of E–I curve, and maximum power density on temperature with humidified gas inlet is similar to those with dry gas inlet (Fig. 3). At 40 °C with a given current density (for instance, at 50 mA/cm²), the cell voltage with dry inlet gas (0.4 V) is higher than that with humidified inlet gas (0.37 V). However, the difference (0.49 V vs. 0.48 V) becomes less pronounced when the temperature is raised to 80 °C. At 80 °C, humidification of gas or not seems to make insignificant difference on cell performance.

3.3. Breakdown of cell over-potentials

The E–I curves mentioned before are further analyzed by a semi-empirical equation in a similar form to that proposed by Tu et al. [13]. The voltage losses of a fuel cell can be generally divided into three parts, including activation over-potential, and internal resistance, as well as concentration over-potential. In the present case, the output current of single cell (~100 mA/cm²) is much lower than the supplying rate of reactant gas (104 cc H₂/min and 70 cc O₂/min). The voltage loss due to mass transfer over-potential could thus be negligible.

Therefore, the semi-empirical equation used in the present analysis takes both the activation over-potential and internal resistance into consideration. The first term of Eq. (1), 𝐸₀, is the equilibrium potential of the cell. The second and third terms account for the activation over-potential of electrode. Although the electrode over-potential includes the over-potential from both anode and cathode over-potential, only the cathode over-potential is needed to be considered. This is because the anode over-potential due to hydrogen oxidation reaction is much smaller than the cathode over-potential due to oxygen reduction reaction. The forth term is the over-potential due to the internal resistance of the entire cell. Here “a” is the charge transfer coefficient, “I₀” represents the exchanging current, “T” is the cell temperature in Kelvin scale, and “R” is the internal resistance.

\[
E = E_0 + \frac{RT}{nF} \log(I_0) - \frac{RT}{nF} \log(I) - R \cdot I
\]

The values of “I₀”, “a”, and “R” are calculated from E–I curve data by least square curve fitting method. Values of these three parameters (I₀, a, R) are found by minimizing the difference of cell voltage between the measured data and calculated results from Eq. (1). Detailed calculation procedure is given in Appendix A. The fitting results are then compared with the measured ones for dry gas.

Table 1

Measurement ranges and accuracy of the measurement devices in the present experiment.

<table>
<thead>
<tr>
<th>Devices</th>
<th>Measurement range and accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electric load (Agilent 6060B)</td>
<td>Max. operating current: 60 A</td>
</tr>
<tr>
<td></td>
<td>Accuracy: ±0.1% of full scale</td>
</tr>
<tr>
<td></td>
<td>Resolution: ±75 mA</td>
</tr>
<tr>
<td></td>
<td>Max. operating voltage: 60 V</td>
</tr>
<tr>
<td></td>
<td>Voltage accuracy: ±0.1% of full scale</td>
</tr>
<tr>
<td></td>
<td>Voltage resolution: ±50 mV</td>
</tr>
<tr>
<td>Mass flow controller</td>
<td>Accuracy ±1% of full scale</td>
</tr>
<tr>
<td></td>
<td>Full scale at anode: 10,000 cc/min</td>
</tr>
<tr>
<td></td>
<td>Full scale at cathode: 30,000 cc/min</td>
</tr>
<tr>
<td>T-type thermocouple</td>
<td>Accuracy ±0.5 °C</td>
</tr>
</tbody>
</table>

65, and 80 °C) are plotted against the cell current density (i, mA/cm²). The OCVs (open circuit voltage) at different temperature are close to each other. Besides, it could be observed that the slope of the E–I curves at different temperatures are obviously different. The absolute value of the slope of the E–I curve (|dE/dI|) is decreased as the temperature changed from 40 to 80 °C.

Moreover, the power densities (P, mW/cm²) at various temperatures are also plotted against the current density (i, mA/cm²) in Fig. 3. Maximum power density (P_max) is increased from 21 to 28 mW/cm² as the cell temperature is raised from 40 to 80 °C. Since the current density at the P_max (~50–100 mA/cm²) is in the linear region of E–I curve, the low P_max value could be due to a high internal resistance.

After fitting the measured E–I data and the impedance data performed later, besides the ionic conductivity of the electrolyte, it was found that the resistance from the electrode/electrolyte interface of present cell also plays an important role in the internal resistance. Detailed discussion will be given in Section 3.3 and Section 3.4.

Fig. 3. E–I curves and P–I curves for the present cell fed with dry H₂/O₂ at cell temperatures of 40, 50, 65, and 80 °C, respectively. Gas flow rates are 104 cc H₂/min and 70 cc O₂/min, respectively. Marks on the figure are measured data and lines are fitting results.
\[ Z_{pt} = Z_{p1} + Z_{p2} = \frac{Z_{r1}Z_{c1}}{Z_{r1} + Z_{c1}} + \frac{Z_{r2}Z_{c2}}{Z_{r2} + Z_{c2}} \]  
\[ Z_f = R \]  
\[ Z_c = j \frac{1}{2\pi fC} \]  
\[ Z_{pt} = \frac{R}{1 + (2\pi fRC)^2} + j \frac{2\pi fRC}{1 + (2\pi fRC)^2} \]

Eqs. (3)–(6) are derived from above equation. The calculation of RC values is carried out by least square curve fitting method. The error between the measured data and calculated result for a given RC value is 
\[ e = e_r + e_m = \sum \left[ Z_{pt} - \frac{R}{1 + (2\pi fRC)^2} \right]^2 + \left[ Z_{pt} - \frac{2\pi fRC}{1 + (2\pi fRC)^2} \right]^2 \]

where \( e_r \) is the error of real part impedance and \( e_m \) is the error of imaginary part of impedance. The least square curve fitting is to find the values of R and C where \( e \) is minimized. A Fortran program is written for this purpose. During the first round of optimization, the value of R and C are explored over a wide range. The optimal value of R and C is found. The second round of optimization is started with the optimal value of R and C and the explored range is reduced by an order of 1/10. The optimal values of R and C that minimized the \( e \), can be found with desired accuracy. Only data with frequency below 10 Hz are used to find the RC values of reaction. The data with frequency ranged from 10 to 1 kHz are used to find the RC values of interfaces. The RC value is found in the high frequency range where the value of |Z| at phase angle equal to zero.

References