AC impedance characteristics of a 2 kW PEM fuel cell stack under different operating conditions and load changes

Xiqiang Yana, Ming Houb,*, Liyan Sunb, Dong Liangb, Qiang Shenc, Hongfei Xua, Pingwen Minga, Baolian Yib

aDalian Sunrise Power Co. Ltd., Dalian 116025, China
bDalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

Received 25 January 2007; received in revised form 14 June 2007; accepted 23 June 2007
Available online 30 August 2007

Abstract

This paper mainly presents the AC impedance characteristics of a 2 kW PEMFC stack under different operating conditions and load changes. The AC impedances of the fuel cell stack are examined by a fuel cell impedance meter. Air stoichiometry, air humidity, and operation temperature are shown to have significant effects on the AC impedance of stack. When air stoichiometry decreases, the mass transfer resistance of stack increases obviously, but the influences on other resistances are very slight. The air humidity and operation temperature mainly influence the charge transfer resistance of stack. The influences of load changes on the AC impedance of stack are also investigated, and the results of which show that it is quite necessary to adjust the humidity of reactant gas according to the fuel cell load changes during fuel cell running. The AC impedance diagnosis of stack can provide some useful information for the running of fuel cell stack.

Keywords: AC impedance; PEMFC; Stack

1. Introduction

The proton-exchange membrane fuel cells (PEMFCs) with the advantages of low-operating temperature, high current density, high potential for low cost and volume, fast start-up ability, and suitability for discontinuous operation [1–4] become the most promising and attractive candidate for electric vehicle power [5–7]. The load on fuel cell stack frequently changes during running especially in vehicular application, which will accelerate the fuel cell degradation. Diagnosis of fuel cell stack is of importance to PEMFC research. Generally, polarization curves are the common method to characterize the electrochemical performance of the fuel cell stack. However, details of the underlying mechanisms are difficult to obtain by this method. The electrochemical impedance spectroscopy (EIS) has been demonstrated to be a powerful experimental technique to examine the complexity of the different processes that take place in fuel cells. The measured EIS can help to explain the performance of fuel cell and offer more information [8,9]. Hence, EIS has been applied widely to measure ohmic resistance of fuel cell [10–15], optimize the membrane electrode assembly (MEA) fabrication [16–20], and obtain optimal operation conditions [21–24].

Although many efforts have been made to diagnose the PEM fuel cell by applying EIS, most studies focus on single cell [25–30]. Only limited work has been done with fuel cell stacks [31–35]. However, the evaluation of high power stack performance is of great importance for PEM fuel cell applications, especially in fuel cell vehicle. Yuan et al. studied AC impedance characteristics of a 500 W stack under various operating conditions, and obtained some very useful information, but the stack measured was very short, only 6-cell. And they did not study the impedance characteristics under load changes, which are very important for fuel cell vehicle. In this study, the AC impedance characteristics of a 2 kW stack with 20-cell were measured under various operating conditions and load changes using fuel cell test station and a fuel cell impedance meter.
2. Experimental

The fuel cell stack tested in this work was assembled with 20 cells, and the active area of each cell is 270 cm². The bipolar plates in the stack were metal composite bipolar plates, which consisted of thin metal plates and expanded graphite flowfields. The flowfields were parallel channel pattern formed by stamped method. The MEAs consisted of Nafion 212 membranes, catalyst layers with a total Pt loading of 0.8 mg cm⁻², and Toray carbon paper as gas diffusion layers. The experiments were conducted in the automation mode using a fuel cell test station (FCATS-H36000, Hydrogenics, Canada) and a fuel cell impedance meter (KFM2150, Kikusui Electronics, Japan). The hydrogen and air flow rates were controlled by smart mass flow meters (Brooks Instrument, USA). The hydrogen and air were humidified by adding high pressure steam, and the relative humidity of anode and cathode sides was accurately adjusted by changing dew point temperature.

In this work, the AC impedance measurements were carried out by a fuel cell impedance meter. The impedance spectra were recorded by sweeping frequencies over the range of 20 kHz to 60 mHz with 8 points per decade. The amplitude of the AC current was always kept at 10% of the DC current. The fuel cell stack was operated steadily for at least 1 h before starting each impedance measurement. The hydrogen and air flow rates were kept at stoichiometries of 1.5 and 2.5, respectively. Both the anode and cathode sides were kept at relative humidity of 80%, operation temperature of 60 °C, and ambient pressure, unless otherwise stated. During the AC impedance measurements only one variable was allowed to change while the other variables were kept constant for each measurement. The AC impedance characteristics of PEM fuel cell stack under various operating conditions and load changes were measured.

3. Results and discussion

3.1. AC impedance characteristics of stack

The impedances of a 20-cell stack with large active area of 270 cm² are measured using the FC impedance meter. The measured results of the 2 kW stack can be seen in Figs. 1 and 2. The spectra consist typically of a high frequency straight line and two overlapping arcs in medium and low frequency regions. The high frequency intercept part (intersection with the real axis in impedance spectrum) reflects the ohmic resistance of stack \( R_{\text{ohm}} \); the arc at medium frequency reflects the combination of charge transfer resistance \( R_{\text{ct}} \) due to the oxygen reduction reaction and double layer capacitance within the catalyst layer, which is considered to be a constant phase element \( \text{CPE}_1 \); the arc at low frequency reflects the mass transport resistance of oxygen in the catalyst layer \( R_{\text{mt}} \) and the associated constant phase element \( \text{CPE}_2 \). The anodic polarization is very small and can be neglected. Thus, the obtained impedance spectrum mainly reflects the cathode polarization.

To better understand the electrochemical processes involved in the operation of PEMFC stack, in accordance with the characteristics of fuel cell reaction and our measured impedance spectra of stack, an equivalent circuit has been set up as seen in Fig. 3. The measured electrochemical impedance spectra are fitted using Zsimwin software. The AC impedance spectrum and its fitting curve are shown in Fig. 4. It provides a good fit for these responses. So the electrochemical processes of stack can be analyzed by the equivalent circuits.
3.2. Effect of output current

As seen in Fig. 5, the high frequency intercept part only changes slightly with output current changes, but the diameter of two overlapping arcs changes greatly with output current changes. As for the high frequency intercept part, the reason for its slight change may be that the water generated will be more with current density increasing, thus the membrane will be more hydrated, leading to the slight decrease of the ohmic resistance of stack. At low output current region the diameter of two overlapping arcs gradually reduces with output current increasing, but after the output current exceeds a certain value about 108 A, the two overlapping arcs begin to distort and increase as the output current increases. As output current increases, the driving force for the oxygen reduction reaction gradually increases, so the charge transfer resistance of stack gradually decreases. Also, the amount of generated water will increase, therefore, mass transport limitation will become more significant, which causes the mass transport resistance to increase gradually. Because of the mutual effect of charge transfer resistance and mass transport resistance, the two overlapping arcs begin to distort and increase after the current exceeds a certain value.

3.3. Effect of air stoichiometry

As seen in Fig. 6, air stoichiometry has a significant effect on the AC impedance of stack. With air stoichiometry decreases, the diameter of the two overlapping arcs becomes larger, indicating mass transport limitation occurring when air stoichiometry is very low. The diameter of the two overlapping arcs evidently grows when air stoichiometry is lower than 2.5, especially the second arc at low frequency, which reflects the mass transport limitations in the gas phase because of the shortage of air supply when operating at low air stoichiometries. The similar result can also be demonstrated from the performance curves of stack under different air stoichiometries in Fig. 7.

As shown in Fig. 8, the value of $R_{\text{int}}$ increases acutely when air stoichiometry decreases. The main reason is that the decrease of oxygen concentration of reactant gas inside fuel cell with air stoichiometry decreasing causes the mass transport limitation. In addition, at low air stoichiometry, the liquid water formed at the cathode cannot be completely blown away, which affects the transport of oxygen in the diffusion layer and the catalyst layer. The changes of $R_{\text{ohm}}$ are slight, since the membrane can remain well hydrated by the water generated in the cell at this current density and relative humidity. As air stoichiometry increases, the $R_{\text{ct}}$ gradually decreases owing to the increase of oxygen concentration of reactant gas. But the change of $R_{\text{ct}}$ with air stoichiometry is very small compared with that of $R_{\text{int}}$. The results above show that the transport of oxygen is a controlled and dominant factor at low air stoichiometry. From these testing results, we can obtain that the optimal operation condition of cathode air stoichiometry is from 2.5 to 3.
3.4. Effect of air relative humidity

From AC impedance spectra of stack in Fig. 9, it is found that the high frequency intercept part with the real axis gradually increases and the diameter of the two overlapping arcs at medium and low frequency regions increases observably, when RH of cathode reactant gas varies from 100% to 20%. It indicates that the insufficient stack humidification results in the impedance of stack increasing observably and the losses of cell performance, which can be observed in Fig. 10. Fitting of the spectra in Fig. 9 to the equivalent circuit model in Fig. 2 shows that the $R_{\text{ohm}}$ of the stack gradually decreases as RH of cathode reactant gas increases. As seen in Figs. 9 and 11, $R_{\text{ct}}$ of the stack gradually decreases as RH of cathode reactant gas increases. With the RH of cathode reactant gas increasing, the proton mobility becomes sufficient to affect the ORR kinetics and leads the $R_{\text{ct}}$ of the stack to gradually decrease. And the $R_{\text{mt}}$ of the stack observably changes as RH of cathode reactant gas increases. The $R_{\text{mt}}$ gradually decreases as RH of cathode reactant gas increases, because water content at the interface contributes to the transport of the protons. However, an extremely high water level can block oxygen transport due to water flooding in the diffusion layer, which leads to the increase of mass transport resistance. So the stack performances lose slightly at high RH in Fig. 10. The results show that the optimal cathode reactant gas RH is from 60% to 80%.

Fig. 7. The performance curve of stack with different air stoichiometries.

Fig. 8. The dependence of the ohmic resistance ($R_{\text{ohm}}$), the charge transfer resistance ($R_{\text{ct}}$), and mass transfer resistance ($R_{\text{mt}}$) with different stoichiometries at 500 mA cm$^{-2}$.

Fig. 9. AC impedance spectra of stack with different RHs at 500 mA cm$^{-2}$.

Fig. 10. The performance curve of fuel cell stack with different RHs.
Fig. 11. The dependence of the ohmic resistance \( (R_{\text{ohm}}) \), the charge transfer resistance \( (R_{\text{ct}}) \), and mass transfer resistance \( (R_{\text{mt}}) \) with different RHs at 500 mA cm\(^{-2}\).

Fig. 12. AC impedance spectra of stack with different operating temperatures at 500 mA cm\(^{-2}\).

3.5. Effect of operating temperature

As seen in Fig. 12, the high frequency intercept part and the diameter of the two overlapping arcs gradually decrease as the temperature increases. From Fig. 14, it can be found that the values of \( R_{\text{ohm}} \), \( R_{\text{ct}} \), and \( R_{\text{mt}} \) gradually decrease as the temperature increases. The two figures above show the same trend of impedance change of stack with different operating temperatures. The AC impedance diagnosis of stack is consistent with the performance of stack with different operating temperatures in Fig. 13. When the temperature increases, the proton mobility increases and the membrane conductivity improves. Therefore, \( R_{\text{ohm}} \) gradually decreases as the temperature increases (Fig. 14). On the other hand, as the temperature increases the gas molecule becomes more active which will accelerate the transport of oxygen in the diffusion layer and the catalyst layer, and the liquid water can be removed easily due to the reduced surface tension of the interface between the liquid water and the electrode material, as a result the mass transport resistance will decrease as the temperature increases. Furthermore, the catalyst kinetic becomes faster as the temperature increases, which makes the charge transfer more quickly. So, the charge transfer resistance gradually decreases as the temperature increases. From Fig. 11, it can also be seen that the change extent of \( R_{\text{ct}} \) is larger than those of \( R_{\text{ohm}} \) and \( R_{\text{mt}} \) with temperature increasing. These results indicate that the operating temperature mainly affects the charge transfer resistance of stack, and they coincide with Springer et al.’s [36] classical spectra, although the cell measured and the operational conditions are different.

Fig. 13. The performance curve of stack with different operating temperatures.

Fig. 14. The dependence of the ohmic resistance \( (R_{\text{ohm}}) \), the charge transfer resistance \( (R_{\text{ct}}) \), and mass transfer resistance \( (R_{\text{mt}}) \) with different operating temperatures at 500 mA cm\(^{-2}\).
3.6. The impedance of load changes

The measurement of $R_{\text{ohm}}$ of fuel cell stack gives important information on water management, which is a crucial issue for the successful operation of a PEM fuel cell. The high frequency impedance mainly reflects ohmic resistance of fuel cell stack ($R_{\text{ohm}}$). In our measurement, a simulated fuel cell vehicle loading process is designed. The AC impedances at frequency of 2 kHz are measured keeping temperature at 60°C and RH of 60%. The measured AC impedances of stack can be considered as the ohmic resistance of stack which can be obtained from the intercept with real axis at frequency about 2 kHz in impedance spectra. As seen in Fig. 12, the impedance of stack gradually increases at state of idle speed (current about 5 A) and gradually decreases at relative high load (current above 81 A). It indicates that when running at low load (especially, at idle state) the membrane cannot be maintained fully humidified by the generated water of stack, and the water content in membrane reduces gradually, which will result in the increase of impedance of stack. Therefore, it is necessary to increase the humidity of reactant gas for keeping membrane humidification at low load. We can also know from Fig. 15 that the impedance of stack gradually decreases at relative high load. The main reason is that the amount of generated water increases at high load, and the membrane becomes more hydrated, so the impedance of stack decreases. However, if there is too much of water in fuel cell, the water management will become complicated and can affect mass transfer and cell performance. Thus, it is necessary to adjust the humidity of reactant gas according to the load changes during the operation of a fuel cell stack.

4. Conclusions

The AC impedance characteristics of the 2 kW PEM fuel cell stack under various operating conditions and load changes are measured and the optimal operation conditions of fuel cell stack are obtained. The results of the AC impedance show that air stoichiometry, air humidity, and operation temperature have obvious effects on AC impedance of stack. When air stoichiometry decreases, the mass transfer resistance of stack increases obviously, but the influences on other resistances are very slight. The stack humidity and operation temperature mainly influence the charge transfer resistance of stack. Furthermore, the influences of load changes on the AC impedance are investigated. The AC impedance of stack gradually increases at state of idle speed (current about 5 A) and gradually decreases at relative high load (current above 81 A). Therefore, it is quite necessary to adjust the humidity of reactant gas according to the fuel cell load changes during running. The AC impedance diagnosis of stack could provide some useful information for fuel cell stack, especially in vehicular application.

Acknowledgment

The authors gratefully acknowledge the Japan Kikusui Electronics Corporation for supplying fuel cell impedance meter.

References


