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Measurement and analysis on variable parameters of in-plane segment electrochemical impedance spectroscopy of polymer electrolyte membrane fuel cells#

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ABSTRACT

In the study of in-plane segment electrochemical impedance spectroscopy (EIS) distribution of polymer electrolyte membrane fuel cells, it is necessary to use effective data analysis methods to fit the segment test results, so as to quantify and compare the polarization process between the segments at different frequencies. Further, more information about the electrochemical reaction behavior inside the cell can be obtained, which is helpful to further analyze the complex multi-domain and multi-scale change process inside the fuel cell. Therefore, on the basis of using the FFT algorithm of MATLAB software to successfully obtain the in-plane segment EIS distribution, the equivalent circuit model (ECM) and the control parameter variable method can be used to further explore the corresponding changes between in-plane EIS. Using this analytical method, the difference in EIS between in-plane segments was quantified and compared under the condition of setting variable cell temperature.

Keywords: polymer electrolyte membrane fuel cell, in-plane segment electrochemical impedance spectroscopy, equivalent circuit model, variable parameters measurement

NONMENCLATURE

Abbreviations	
PEMFC	Polymer electrolyte membrane fuel cell
EIS	Electrochemical impedance spectroscopy
FFT	Fast Fourier Transform
PCB	Printed circuit board
FPC	flexible printed circuit
n	Segment number
S_n	Segment name
ECM	Equivalent circuit model

1. INTRODUCTION

Polymer electrolyte membrane fuel cell (PEMFC) has the advantages of high energy conversion efficiency, low operating noise, and zero pollution in operation [1-2]. In recent years, it has been greatly developed and applied in the field of new energy vehicles. The EIS technology is widely used in the field of fuel cells [3]. Because PEMFC usually has a large active area, it is difficult to ensure the consistency of electrochemical reactions in different regions [4-5]. Therefore, it is necessary to analyze the EIS distribution and characteristics of the cell in the plane. H. Yuan et al. Have systematically tested the EIS of a single cell and analyzed the sensitivity of the EIS curve of a single cell [6-7]. Dengcheng Liu et al. experimentally measured the local EIS of a single-cell in-plane [8]. Honda has adopted flexible printed circuit technology and developed a distributed impedance measurement sensor for measuring the water content of fuel cells in real vehicles [9].

However, due to the differences in the EIS between in-plane segments, effective data analysis methods need to be used to fit the test results of the segments in order to quantify and compare the polarization process

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between different frequency bands. Therefore, on the basis of using the FFT algorithm of MATLAB software to successfully obtain the plane segment distribution [10], this paper uses the ECM and the control parameter variable method [6-7] to quantify and compare the EIS difference between the in-plane segments under the condition of setting the variable cell temperature. These works can be used to further understand and explore the internal mechanism of fuel cells.

2. EXPERIMENT

2.1 In-plane segment EIS test system

The in-plane segment EIS test system is built based on the Scribner 850e fuel cell test bench [6-7]. The test bench can complete the supply and transportation of experimental gas, and the online control and monitoring of the parameters of the experimental operation. A high-precision mass flow controller can control the gas flow, and the inlet pressure is controlled by the back-pressure module. The fuel cell temperature is adjusted by a thermocouple arranged on the cathode graphite plate and two heating rods respectively inserted in the two end plates. The relative humidity of the intake air can be adjusted by changing the dew point temperature of the humidifier and the temperature of the fuel cell. The test bench includes both an electronic load and a frequency response analyzer (FRA).

To obtain single-cell and segment EIS simultaneously, three core components are introduced in the test circuit. They include a PCB signal amplification sensor and a specific cathode collector arranged in the single-cell, and a series-connected small resistance shunt. The in-plane segment EIS test system diagram is shown in Fig. 1. And the assembly style of the segment PCB sensor with the single-cell is detailed in Ref. [10]. The PCB signal amplification sensor has a resolution of 3*3 measurement units corresponding to the MEA 25cm^2 active area. The layout of the in-plane segment array of the single cell is defined in turn as S_n (n=1~9) corresponding to the active area in Fig. 2. Both current collectors at the cathode and anode of the single cell are connected with the positive and negative of the electronic load, respectively. The FRA can generate AC excitation and superimpose it on the load current for different types of EIS experiments.

2.2 In-plane segment variable parameter EIS test

Before the in-plane segment EIS variable parameter test, it is necessary to preset a standard operating condition for the test system, as shown in Tab.1.

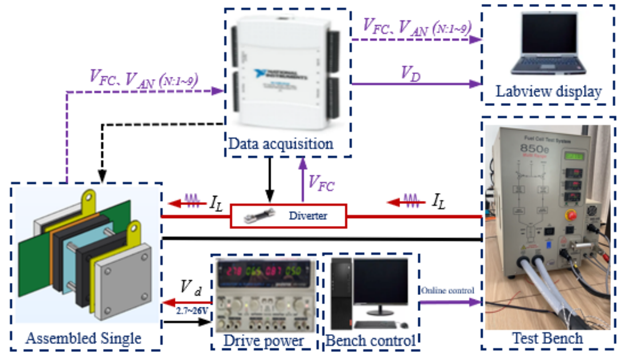

Fig. 1 In-plane segment EIS test system diagram

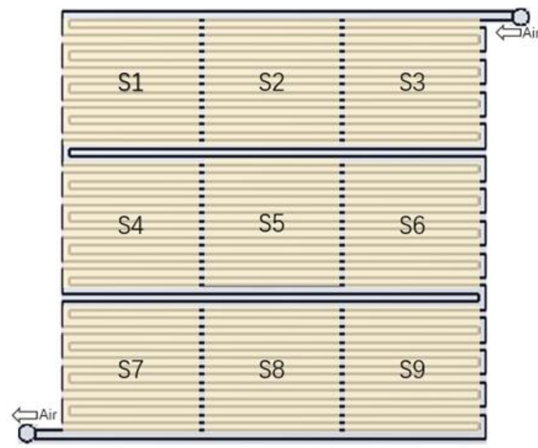

Fig. 2 In-plane segment layout array location

The operating condition remain unchanged, and the cell temperature adjustment is the research object. The preset values are 50℃/60℃/70℃/80℃. According to the in-plane EIS acquisition method in Ref. [10], the in-plane segment EIS group for the cell temperature at 70℃ is shown in Fig. 3. This group of curves can reflect the non-uniform characteristics of the electrochemical reaction inside the single cell. Although there are some differences between the segment EIS group, the different values cannot be accurately identified. Therefore, it is necessary to quantify and analyze the test results.

Tab 1. Test operating conditions

Operating conditions	Value	Unit
Dew point temperature(A/C)	59.5/59.5	℃
Relative humidity(A/C)	50/50	%
Current density	0.4	A/cm^2
Stoichiometry(A/C)	1.5/2	-
Pressure(A/C)	130/110	Kpa
Cell temperature	50/60/70/80	℃
Scan frequency	0.2~2000	Hz

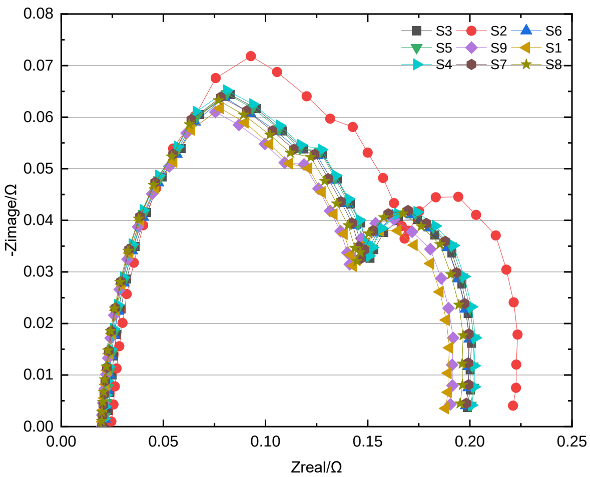

Fig. 3 In-plane segment EIS group at 70 ℃ cell temperature

2.3 In-plane segment equivalent circuit model

*The loss process of EIS mainly includes ohmic loss, an*ode activation loss, cathode activation loss, and cathode mass transfer loss. Zhang shaozhe et al. quantified the loss process of the EIS of a single cell using the ECM approach [7]. With this approach, the equivalent circuit fitting of the impedance spectrum of the segment is carried out respectively in this paper, and the loss types of the segment EIS can be quantized and compared. Therefore, the variation characteristics of different loss types of segment EIS under variable cell temperature parameters can be obtained.

The polarization loss of each frequency band of the segment EIS can be identified and quantified by the third-order R-CPE model in Fig. 4. Rohm is ohmic resistance, R_{ct-a} is anode resistance, and R_{mt} is the mass transfer resistance. The constant phase components CPE1, CPE2, and CPE3 are equivalent to anode double-layer capacitance, cathode double-layer capacitance, and uneven gas diffusion capacitance respectively. On the basis of the ECM and the test results of under 70℃ cell temperature, the segment EIS data groups are fitted using Zview software.

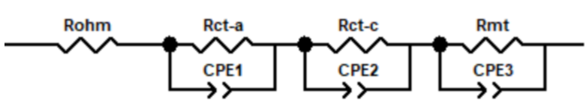

Fig. 4 Third-order equivalent circuit model

The measured in-plane segment EIS group and segment ECM fitting curves are shown in Fig. 5, and the shape of the fitting curve is basically consistent with the EIS for each segment. The segment EIS loss fitting values and segment ECM parameter change trend are shown in Tab.2 and in Fig. 6(c), respectively. The four curves in Fig. 6(c) represent the relevant losses at different frequencies, and the variation trend of the curves reflects the variation value of in-plane segment polarization loss. The R_{ct-a} and R_{ohm} values of the 9 segments change little, but the R_{ct-c} and R_{mt} values of the segments near the inlet and outlet fluctuate to some extent.

2.4 Variable cell temperatures segment test results quality and analysis

Under the operating condition that other parameters remain unchanged to adjust the cell temperature according to 50 ℃, 60 ℃, 70 ℃, and 80 ℃, and the in-plane segment EIS group under variable cell temperatures are acquired in turn. The changes in parameters in ECM of the in-plane segment EIS under different cell temperatures are shown in Fig. 6.

Due to the hydration of polymer electrolyte membranes, the performance of fuel cells will increase with the rise of the cell temperature. It can be seen from Fig.7 that the higher the cell temperature is, the lower the impedance values of the cell tend to be. The slower redox reaction at low temperature leads to higher activation impedance, while the impedance value of the cell will decrease with the rise of the cell temperature. However, the Rohm increases at 80 ℃, which also verifies that the fuel cell has a more appropriate operating temperature. If the temperature exceeds the optimal temperature, the performance of the fuel cell will decline. Meanwhile, it can also be found that with the increase of the cell temperature, the temperature has a more obvious impact on R_{ct-c} and R_{mt}, and their values have decreased by about half in the process of temperature increase. At the temperature of 50 ℃ and 60 ℃, R_{ct-c} and R_{mt} at the inlet and outlet area of the in-plane segments have obvious fluctuations. Comparatively, R_{ct-a} and R_{ohm} between in-plane segments have little influence on temperature.

3. ***CONCLUSION***

In this paper, based on the single-cell segment impedance spectrum test, the in-plane segment EIS test with variable temperatures was conducted under standard operating conditions. The ECM was used to fit the segment impedance spectrum test data, quantify the loss resistance values in different frequency bands, and analyze and compare the effect of different temperatures *on the in-plane segment EIS.*

Tab 2. In-plane segment EIS ECM parameter fitting result at 70 ℃ cell temperature

Segment	Rohm/Ω	Rct-a/Ω	CPE1-T $/(s^{-n}/\Omega)$	CPE1-P	Rct-c/Ω	CPE2-T $/(s^{-n}/\Omega)$	CPE2-P	Rmt/Ω	CPE3-T $/(s^{-n}/\Omega)$	CPE3-P
S1	0.02256	0.01534	0.03289	1.216	0.09815	0.05351	1.08	0.05378	1.799	1.104
S2	0.02846	0.01851	0.02043	1.267	0.10932	0.04156	1.109	0.06698	1.467	1.075
S3	0.026	0.01724	0.02063	1.278	0.0962	0.04484	1.121	0.06148	1.617	1.065
S4	0.02318	0.01558	0.0372	1.198	0.10679	0.05366	1.066	0.05688	1.709	1.127
S5	0.02428	0.01612	0.0279	1.242	0.10205	0.05065	1.088	0.05935	1.672	1.105
S6	0.02446	0.0172	0.02665	1.245	0.09883	0.05112	1.097	0.059	1.679	1.105
S7	0.02193	0.01522	0.03867	1.191	0.10456	0.05466	1.068	0.05761	1.742	1.127
S8	0.02116	0.01424	0.05084	1.162	0.1068	0.05975	1.046	0.05411	1.815	1.151
S9	0.02242	0.01491	0.03413	1.226	0.0984	0.05681	1.076	0.05596	1.806	1.121

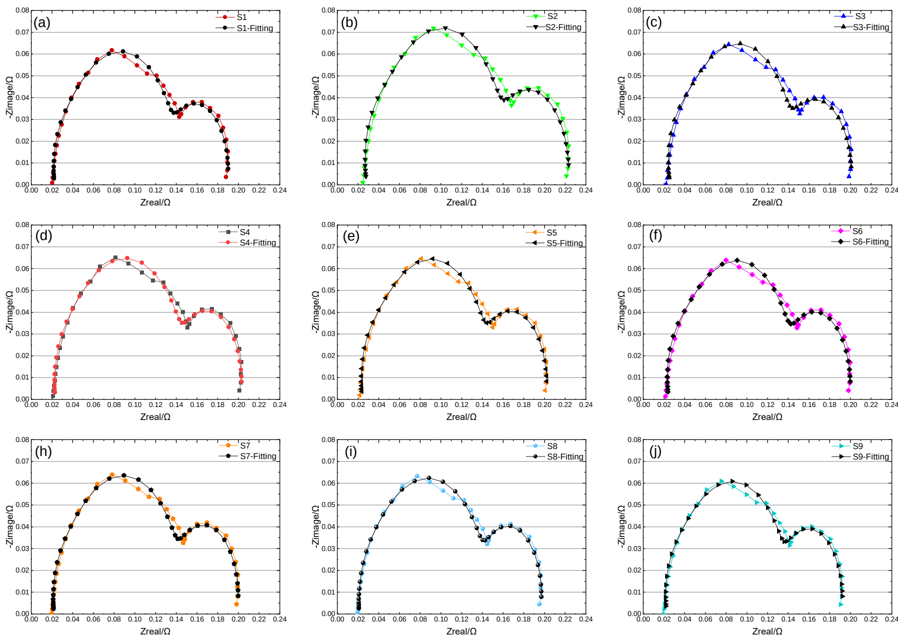

Fig. 5 ECM fitting in-plane segment EIS at 70 ℃ cell temperature

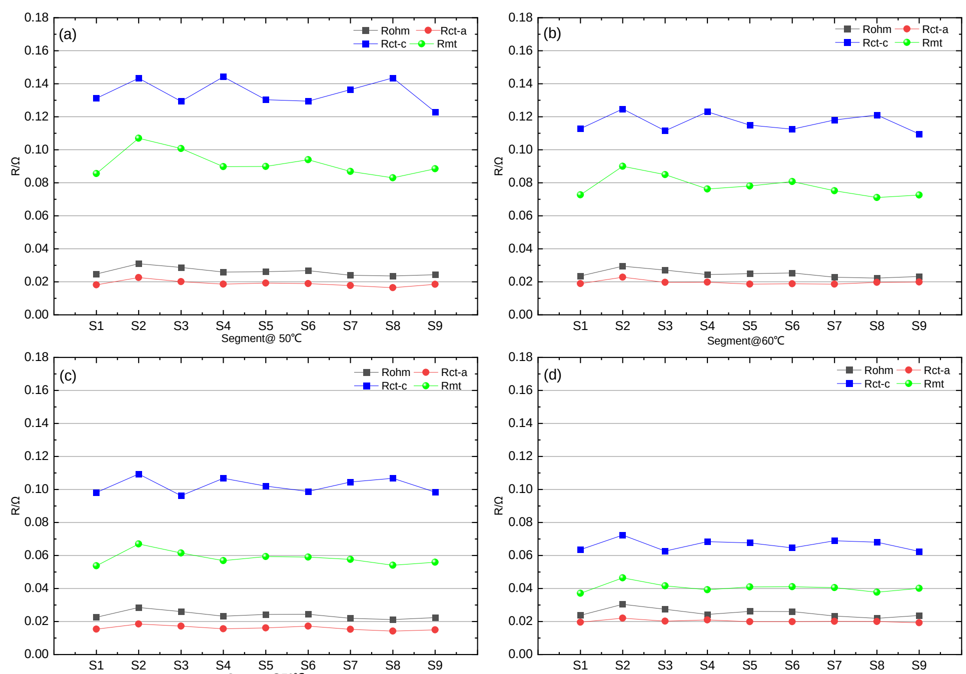

Fig. 6. In-plane segment polarization loss at variable cell temperatures

The research found that the temperature has a more obvious impact on the in-plane segment loss values with the rise of the cell temperature. Compared with R_{ct-a} and R_{ohm}, R_{ct-c} and R_{mt} values are subject to greater fluctuations. The measurement and study of the in-plane segment impedance spectrum of the single cell will be of important reference significance for the study of the non-uniformity of fuel cells with large active areas.

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