

Overviews on internal resistance and its detection of microbial fuel cells

L. P. Fan and J. J. Li

Abstract—Microbial fuel cell is a bio-electrochemical system that drives a current by using bacteria and mimicking bacterial interactions found in nature. Internal resistance is an important factor which affects the fuel cell performance and is of great help to the fault diagnosis of the fuel cell. Monitoring the internal resistance of the microbial fuel cell effectively is not only the necessary condition for realizing the maximum power output, but also a key action to ensure the health and performance of the microbial fuel cell. The main measurement methods for determining the internal resistance of microbial fuel cell are summarized in this paper. Some usually used measurement methods such as polarization curve method, current interruption method, electrochemical impedance spectroscopy, phase locked amplifier, are briefed and compared.

Keywords—electrochemical impedance spectroscopy, internal resistance, Microbial fuel cell, measuring method, polarization curve method

INTRODUCTION

Microbial fuel cell (MFC) is a biochemical reaction device which can directly convert chemical energy into electrical energy by the catalysis of microorganism. It is an optional mode of "green" power generation in twenty-first Century. The researchers applied this principle to the process of wastewater treatment, and found that the wastewater treatment and power generation can be carried out simultaneously, so that the microbial fuel cell has received wide attention, and has become one of the hot spots in the fields of wastewater treatment and new energy [1], [2].

In recent years, microbial fuel cell technology has been made great progress, but it still faces great challenges in practical application. Microbial fuel cell is a complex bio electrochemistry process, and the electrode activity, temperature, and many other factors affect its performance. Compared with conventional battery, the output power of MFC is relatively low, which is one of the main bottlenecks restricting its popularization and application in large area. High internal resistance is an important factor affecting the output power [3-5]. Therefore, many recent studies focus on reducing the internal resistance of microbial fuel cell by

material improvement, structure optimization, operation control, and so on, so as to improve the output power effectively [6-8].

The internal resistance of a microbial fuel cell is the resistance it suffers when current passes through in its operation process [9]. Like other electrochemical cells, the internal resistance of the microbial fuel cell can also be divided into ohmic resistance (R_{Ω}), charge transfer resistance (also known as active resistance) and diffusion resistance (also known as concentration resistance) [10], [11]. Ohmic resistance property grows out of electrolyte and proton exchange membrane, and active resistance and diffusion resistance appears in the electrode surface which is surrounded by the electrolyte. So, sometimes the internal resistance of the microbial fuel cell is divided into ohmic resistance, anodic resistance and cathode resistance. The three sources of ohmic resistance are: (a) resistance to ion migration within the electrolyte, (b) resistance to electron transport within the cell components, and (c) contact resistances. A large part of internal power loss of the microbial fuel cell is caused by ohmic resistance [12].

From the point of an engineering circuit, the fuel cell can be equivalent to an electrical model which is series of an ideal voltage source and an impedance. The maximum output power of the fuel cell is proportional to the square of the open-circuit voltage, and is inversely proportional to its internal resistance. When the load resistance is equal to the internal resistance, the output power of the fuel cell can achieve the maximum. So, monitoring the internal resistance of the microbial fuel cell effectively is not only the necessary condition for realizing the maximum power output, but also a key action to ensure the health and performance of the microbial fuel cell. However, microbial fuel cell is a complex system which has the inherent characteristics of nonlinearity, multi-variable, strong coupling, pure lag and unmeasured disturbances. The internal resistance of a MFC will change with the variation of microbial community and activity, the environmental conditions, temperature, and some other factor, and some electronic effects occur in the reaction process of the fuel cell will also affect the effect of internal resistance measurement. So, it is difficult to measure the internal resistance accurately.

Fuel cell testing methods are derived from general electrochemistry techniques. At present, a range of testing approaches have been used for full fuel cells. The measurement methods of microbial fuel cell internal resistance contain polarization curve method, power density curve peak method, electrochemical impedance spectroscopy, current interruption method and computer simulation method [13]. Due to the existence of equivalent capacitance, different measurement methods may get different values of internal resistance [14].

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I. MAIN MEASUREMENT METHODS

A. Polarization Curve Method

Polarization curve method is the most widely used method for measuring internal resistance in the electricity generation system. This method obtain the current voltage curves by detecting the response of voltage and current to the external load resistance, and then get the internal resistance of the fell cell by linear fitting. After the fuel cell is stable, change the external resistance, and measure the stable discharge voltage corresponding to different external resistance, then the current I can be calculated according to the steady discharge voltage U and the external resistance R by the Ohm's law equation (i.e. $I=U/R$), and the polarization curve of voltage and current can be gain. After linear fitting according to the Ohm law of the whole circuit, the linear relationship between voltage and current can be derived, and its slop is just the total internal resistance R_i of the microbial fuel cell [15], [16].

The greatest strength of polarization curve method is that it can also determine the distribution of internal resistance components. For the real MFC potential, the relationship between the current and the voltage can be described by [17]

$$U = E - (a + b \times \ln I) - I \times R_{\Omega} - c \times \ln \frac{I_L}{I_L - I} \quad (1)$$

where, U is the output voltage of the fuel cell, E is open circuit potential, a and b are the activation loss constants, I is the current, R_{Ω} is the ohmic resistance, c is the concentration loss, and I_L is the limit current. The activation resistance (R_{act}) and the concentration resistance (R_{conc}) were calculated by [18]

$$R_{act} = (a + b \times \ln I) / I \quad (2)$$

$$R_{conc} = [c \times \ln(I_L / I_L - I)] / I \quad (3)$$

Polarization curve method generally adapts to a fuel cell in which ohmic resistance occupies a main position, in this case, the polarization curves of the ohmic resistance is approximately linear. When the non ohmic resistance accounts for a large proportion, the polarization curve will deviate from the straight line shape, the slope will be difficult to determine, and the internal resistance of the MFC should be determined by other methods [19]. In addition, when using polarization curve method for measuring the internal resistance of the fuel cell, after changing the external resistance, a certain amount of stable time is needed to eliminate the influence of electrode double layer charge and discharge on the measurement of the internal resistance. The research shows that if the discharge stable time for various external resistances can keep over 60s, the accuracy of the measurement of a MFC can be ensured [20].

The polarization curve method is simple and easy to operate, and it has no effect on the normal operation of the fuel cell, so it is widely used. But in the practical application, the determination process by polarization curve method takes a long time, and the measured resistance value is actually the total resistance for the overall measuring time, it cannot be used to characterize the real internal resistance of the fuel cell in a working state [21]. So, the internal resistance determined by this method is not very precise.

B. Current Interruption Method

As a time domain technique, the current interruption method can obtain accurate data of the current and voltage before and after the interruption, and is widely used in the electrochemical system. Suddenly disconnect the external circuit of the fuel cell which is discharging stably, and measure the variation in voltage between anode and cathode by a high frequency sampler, the increased voltage value ΔU during current interruption instantaneous and the current value I before circuit breaking can be obtained. Ohmic resistance is related to current. When the current is interrupted, the ohmic resistance will disappear quickly. So, the ohmic resistance can be got by Ohm's law equation $R_{\Omega} = \Delta U / I$ [22].

Current interruption method obtains the measurement signal by controlling ON and OFF status of the fuel cell. The main advantages of this method are that it does not need additional equipment, simple and easy to operate, etc; and its main drawback is that it imposes an obvious disturbance signal to the fuel cell itself. On the other hand, current interruption method can be used to measure the internal resistance of the fuel cell, but it can not be used to distinguish the ohmic resistance, activation resistance or diffusion resistance, so it is generally applied only to the system which ohmic resistance is dominant [23].

Usually, in order to make full use of the current interrupt data for analyzing the internal resistance, the Randles equivalent circuit can be used to describe the fuel cell, that is, describe the fuel cell as an equivalent circuit model which is a series branch of an ohmic resistance R_{Ω} and a parallel branch of polarization resistance R_{ct} and a double layer capacitance C_{dl} , where R_{ct} is the non-ohmic resistance of the fuel cell, and C_{dl} is the combination capacitors of the anode and cathode of the fuel cell [24]. The non-ohmic resistance R_{ct} is the combinational anodic and cathodic charge transfer kinetic resistance. The simplified Randles equivalent circuit suitable for Current Interruption Method is shown in Fig. 1. Thus, the output voltage of the microbial fuel cell can be described as

$$U = E - I(R_{\Omega} + R_{ct}) + IR_{ct}e^{-\frac{t}{\tau}} \quad (4)$$

where $\tau = R_{ct}C_{dl}$ is the discharge time constant. Ohmic and non-ohmic resistance can be obtained by analyzing the upper equation using the measured current interrupt data, and the internal resistance of the MFC is $R_i = R_{\Omega} + R_{ct}$.

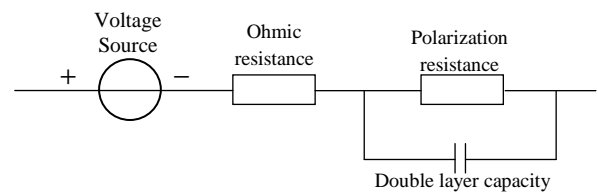


Fig.1 Simplified model of the microbial fuel cell

Sometimes, a frequency-dependent component $Z(\omega)$ may be added to the equivalent circuit to account for diffusion losses [25], as shown in Fig. 2. This circuit has been widely used to model the essential dynamics of a fuel cell, and for interpreting the results of current interrupt and Electrochemical Impedance Spectroscopy test methods.

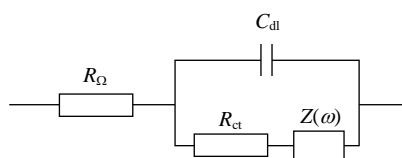


Fig. 2 A impedance model often used

When using the current interruption method for determination the internal resistance, it must be paid attention to that there will be a large deviation in the measurement data because of the existing of the cable inductance. In order to reduce data deviation, the length of used cables must be tried to shorten.

C. Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) is an electrochemical measurement method which use small amplitude sine wave potential (or current) as a perturbation signal. It is a well-established technique used in determining the physiological state of biological tissues from their electrical properties. By exerting a small interference signal to the system, EIS measure the current I or voltage U response to the interference signal, and then get the impedance of the system through the relationship $Z=dU/di$ [26].

The Electrochemical impedance spectroscopy is an important tool in the study of chemical and physical processes in solution and solid, and is widely used in the characterization description and performance diagnosis of fuel cells [27]. Electrochemical impedance spectroscopy can be used to measure the microbial fuel cell without changing its voltage and current characteristic, and it is a very promising electrochemical analysis technology for studying microbial fuel cell deeply. EIS has been used to study the microbial fuel cell these recent years [28-30]. The initial purpose of using EIS for microbial fuel cell research is to measure the internal resistance, because the method provides easier understanding information than some other early method. Measurements of impedance spectra for the MFC at different cell voltages allow the determination of the internal resistance R_{int} of the MFC. In recent years, the research on EIS used in microbial fuel cell has gradually increased. For instance, EIS was used to compare the transfer resistance of two kinds of microbial fuel cell with carbon cloth electrode and three-dimensional graphene electrode [31]; EIS was used to detect the operating performance of the microbial fuel cell in different mediators [32]; EIS was used to test the changes in the anode, cathode, and solution/membrane impedances during enrichment of an anode microbial consortium [33]; EIS was used to study the biological capacitance of anodes in microbial fuel cells [34]. Manohar's research show that measurements of impedance spectra for the MFC at different cell voltages resulted in determining the internal resistance of the MFC and it was found that the internal resistance is a function of cell voltage [35].

EIS can be used in the actual operating conditions of the fuel cell. The results of the impedance measurement using EIS can be presented in two common ways: the Nyquist plot and the Bode plot. The Nyquist plot expresses the impedance with a real part and an imaginary part as a

semicircle. Each point on the complex plane plot represents the impedance at a certain frequency. The impedance at the high frequency limit is the ohmic resistance $R_Ω$ and the diameter of the semicircle is the polarization resistance R_{ct} . The Bode plot, on the other hand, shows the information of impedance, frequency and phase angle. EIS is regarded as a useful method for separating out and identifying the different loss mechanisms of a fuel cell, due to the association of certain loss mechanisms with particular frequency ranges. For instance, at very high frequencies, the impedance is due to ohmic losses, predominantly the membrane ionic resistance. At intermediate frequencies, charge transfer resistance coupled with the double layer capacitor, also contributes to the impedance. Finally, at low frequencies, diffusion/mass-transport losses add to the measured fuel cell impedance [36]. Accurate results are obtained by fitting the impedance data to the appropriate equivalent circuit, for example the simplified equivalent circuit shown in Fig. 1. The structure of the equivalent circuit and the values of its components can be determined by an experiment. Using the electrochemical implication of these elements, the structure and the properties of the electrode process can be analyzed.

Compared with current interruption method, EIS can determine the parameters of the more detailed model. Fig. 3 shows a more detailed model of the MFC, where $R_Ω$ is the solution resistance (ohmic resistance), R_a and R_c are the anodic and cathodic polarization resistances respectively, The capacitors C_1 and C_2 represent the double layer capacitor present at the anode and cathode electrode-electrolyte interfaces. By fitting the impedance data to the equivalent circuit, the equivalent circuit was defined using the best fit for the EIS data [37], [38]. The sum of R_a , R_c and $R_Ω$ will be the internal resistance R_i of the MFC.

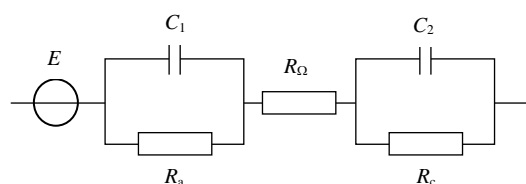


Fig. 3 A common equivalent circuit of MFC

The advantages of EIS is that the measurement accuracy is high, which can avoid the large effect of the disturbance on the system, so that the linear relationship between the disturbance and the response of the system is maintained. The disadvantage of EIS is that such an approach can be time consuming and in some cases even inappropriate for on-line monitoring of operational fuel cell system.

D. Phase Locked Amplifier

The internal resistance of a fuel cell is generally a few hundred micro ohm to several ohm. Because the internal resistance is very small, the interference and noise will have great effects on the measurement precision. So it is very important to suppress the interference and noise for improving the measurement accuracy.

The phase locked amplifier technique can suppress the interference and noise effectively, which can make the measurement of internal resistance tend precise. Meanwhile, the phase locked amplifier technique is fast in speed and low in cost, and it needs no discharge, which can avoid imposing harmful impact on the fuel cell [39], [40].

The basic principle of measuring the internal resistance of the fuel cell by a lock-in amplifier is that, when an AC signal is injected to the fuel cell, the voltage and current of the fuel cell caused by this signal are measured, and then the internal resistance of the fuel cell can be calculated by

$$R_i = \frac{U_{\text{rms}}}{I_{\text{rms}}} \quad (5)$$

where U_{rms} is the effective value of the AC voltage at the both ends of the fuel cell; I_{rms} is the effective value of the current in the input circuit of the fuel cell.

The functional block diagram of a phase locked amplifier is shown in Fig. 4. Through the phase locked amplifier, the noise signal is suppressed and the effective signal is amplified, which improves the measurement accuracy.

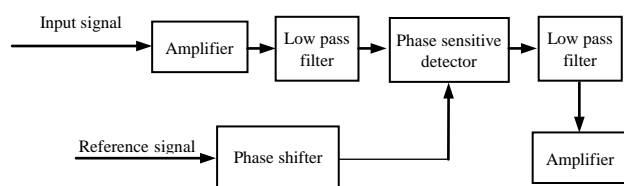


Fig. 4 Functional block diagram of a phase locked amplifier

E. High frequency resistance method

High frequency resistance (HFR) method is also one of the generally used method for internal resistance measurement. In the HFR method to determine the internal resistance of a MFC, a small AC signal is applied to the electronic load to modulate the DC load current. The resulting magnitude and phase of the AC voltage and current response are measured by a frequency response analyzer. This method is actually a subset of the EIS method. The method for choosing the HFR frequency requires that the test system also have EIS capability. a test system capable of true HFR measurement will also be capable of performing EIS measurements.

HFR measurement minimally disturbs the cell from its operating condition, both in magnitude and duration, and therefore it is suitable for routine, periodic application during normal fuel cell operation [41].

F. Soft Sensing Method

Due to it is difficult to measure the internal resistance of the MFC, some soft sensing methods are considered to use in predicting or estimating the internal resistance. Researches on using soft sensing method to estimate the internal resistance of polymer electrolyte membrane or proton exchange membrane fuel cell (PEMFC) can be found in some references. A practical method of estimation for the internal-resistance of PEMFC stack was adopted based on radial basis function (RBF) neural networks by Li et al [42]; Chen et al, proposed an algorithm to estimate the internal resistance when the system works under transient state [43]; Kazmi et al presented a estimation method based on sliding mode observe to estimate the parameter of proton exchange membrane fuel cell system [44]; and also some method is proposed to estimate the contact resistance in proton exchange membrane fuel cells [45]; Chang proposes an equivalent circuit parameters measurement and estimation method for fuel cell based on current loading technique, and then a hybrid method that combines a radial basis function

(RBF) neural network and enhanced particle swarm optimization (EPSO) algorithm is further employed for the equivalent circuit parameters estimation [46].

Reports on using soft sensing method in MFC is now still few. It is worth making some efforts on using soft sensing methods in detecting the internal resistance of MFC so as to realize convenient and swift measurement.

II. CONCLUSIONS

The commonly used methods for determining the internal resistance of a microbial fuel cell contains polarization curve method, current interruption method, electrochemical impedance spectroscopy and high frequency resistance method, et al. The internal resistance value determined by different measurement method may be different, users of these techniques should be cognizant of differences in these methods so as to properly apply and interpret the results if accurate and useful measurement of cell resistance is to be obtained. In practical application, the appropriate measurement method should be selected according to the test purpose.

In the future, our work will focus on using electrochemical impedance spectroscopy (EIS) to make up some accurate measurement scheme for MFC. Further, a suitable MFC equivalent circuit for our experimental system will be built up and determined, and some soft sensing methods for estimating the internal resistance of MFC will be questioned and compared based on neural network, support vector machine, pattern recognition, correlation analysis, and some other alternative methods.

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