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On-line Impedance Monitoring of Direct Methanol Fuel Cell

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Abstract

In this study, a research technique – Dynamic Electrochemical Impedance Spectroscopy for fuel cell research is presented. The direct methanol fuel cell was the object of the study. The changes of operational conditions such as temperature, oxidant flow intensity and load on the cell global impedance were examined. The results of these changes on the performance of the cell were observed.

Keywords: AC- Impedance Spectroscopy; DEIS; Direct Methanol Fuel Cell; DMFC; On-line monitoring.

1. Introduction

We live in times of constant development of the technical sciences, as more and more devices are driven by electric power. The demand for ever lighter and smaller portable devices with extended life span and higher efficiency is rising. Simultaneously, new sources of energy are being sought, which is why there is growing interest in direct methanol fuel cells (DMCFs), with respect to both scientific and technological applications which promise great opportunities for portable power sources [1, 2].

Due to complex chemical reactions occurring both on the anode [3] and cathode [4] and the crossover phenomenon [5], DMFC is currently characterized by low power intensity. To improve the DMFC efficiency, the conditions of the cell operation are being studied, amongst other things. Electrochemical Impedance Spectroscopy [EIS] is a frequently applied technique, and it was used to study fuel cell impedance both experimentally and by means of equivalent circuits with varying intensity of methanol [6-8, 10] or oxidant [6-8, 10, 13] flow. Characteristics of the impedance of a fuel cell operating in various temperatures [6-12] and under various loads were established.

On the basis of the aforementioned studies, it was found that the impedance of the entire cell decreases, coupled with increases in temperature, oxidant flow intensity and power

consumption. Research on the influence of methanol flow on the cell impedance has shown that there exists an optimal methanol flow at which fuel cell impedance reaches its lowest value. However, this research was conducted using the method of classical electrochemical impedance spectroscopy, where it is necessary to maintain system stationarity. The use of Dynamic Electrochemical Impedance Spectroscopy (DEIS) makes it possible to obtain impedance in non-stationary systems. However, in the time range in which it is obtained a single spectrum, the system should retain the quasi-stationarity. In DEIS method, the frequency characteristic is obtained by Fourier transformation which is averaging in character [14]. This technique has been successfully used in the new field of research on the occurrence of excursion's peaks on lead [15]. The aim of the study is to verify the DEIS technique as a method enabling on-line monitoring of the cell operation under changeable conditions.

2. Experimental

The single fuel cell tested in this study had an active area of 1 cm^2. The membrane electrolyte assembly consisted of Nafion 115 (thickness 125μm) loading Pt-Ru of 2.5 mg/cm^2 at the anode, Pt of 2.5 mg/cm^2 at the cathode. Gas Diffusion Layer was hydrophobized substrate with a 5wt% PTFE loading at the anode and 10wt% PTFE loading at the cathode. Which – according to producers - assures an open pore structure, good mechanical strength and high electrical conductivity, and is targeted for use in moderate-to-high humidity and higher current density operating environments. Processing steps to the substrate consist of a bulk impregnation of the standard carbon fiber matrix with Polytetrafluoro-Etylene (PTFE). There were channels with parallel geometry in the graphite plates, 1mm flow field depth and 1mm width. The fuel used at the anode was 3%wt. methanol solution. The solution was supplied to the fuel cell via a pump (KNF, Stepdos FEM03_18/RC). Air was used as an oxidant with its flow controlled by a mass flow controller (Brooks MFC 5850E). The measurements were performed in galvanostatic mode using multiple sinusoidal excitation. The measurements were conducted using the two-electrode system. Which means that both the potential and current were measured between two gold current collectors connected to the electrodes. Combined time and frequency analysis was used. The excitation signal consisted of a set of elementary sinusoidal signals within the range from 4.5KHz to 30mHz. The ac excitation amplitudes were selected in a manner which ensured that the amplitude of voltage response did not exceed 5mV. Signals were acquired and recorded using the National Instruments PXI6120 measurement card and the Autolab PGSTAT30 was used as galvanostat.

3. Results and Discussion

3. 1. Effect of cell temperature

During the measurement via the use of the DEIS research technique, the temperature was changed in a linear manner at a rate of 0.0075^oC per second. The values of air flow and the flow of methanol amounted to 16mL/min and 0.11mL/min, respectively. The cell load was 30mA. The change of temperature and its influence on the impedance value were measured on-line.

The visible change of the impedance value together with an increase in the operational temperature presented in Fig. 1 may indicate an improvement of the kinetics of electrochemical reactions. Impedance spectra, together with an increase in the temperature change their shape. At temperatures of up to 70 ^oC, impedance diagrams are arcs with greater diameters and at temperatures higher than 70 ^oC Nyquist diagrams form arcs with smaller diameters. Probably temperature has a positive influence

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on the mobility of the charge carriers. On the other hand, the temperature increase has a negative influence, because it may lead to mechanical damage to the membrane. Additionally, together with a rise in the temperature the phenomenon of methanol crossover increases and overly high operational temperatures may result in a considerable reduction in water content in the membrane, which leads to disappearance of ionic conductivity [16].

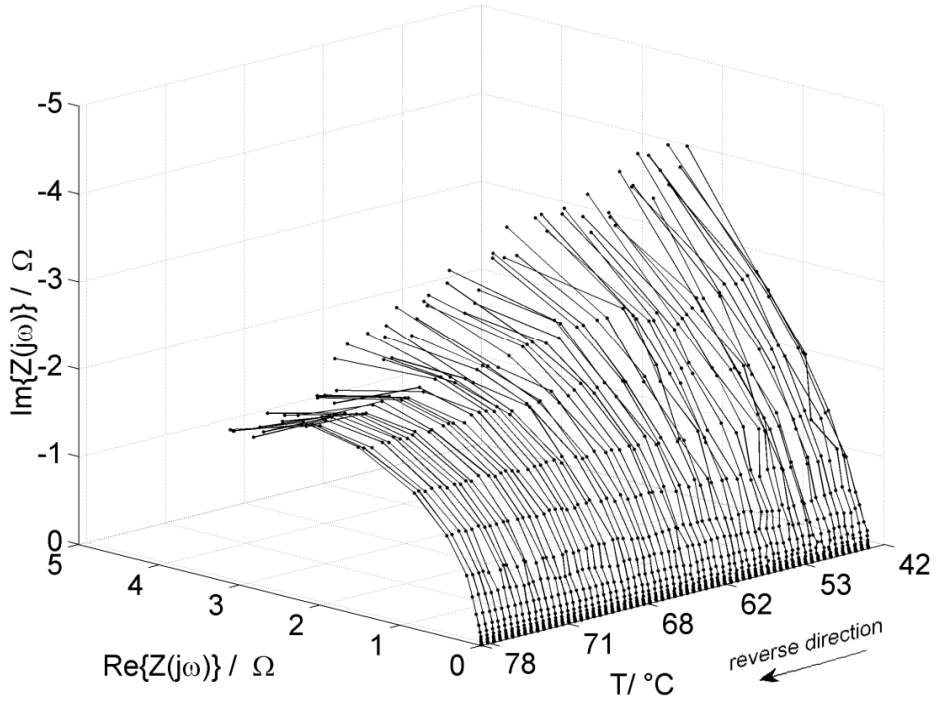

Fig. 1. Change in global cell impedance during a change in the operational temperature.

3. 2. Effect of air flow rate

Using the DEIS research technique, the measurements were conducted at a temperature of 78 ^{o}C, with the power consumption at 30mA and the reducer flow speed registered at 0.11 mL/min. The flow of air was linearly changed at a speed equal to 0.0033 mL/min per second.

Fig. 2 presents the results of the experiment conducted via the use of the DEIS technique, owing to which the influence of the intensity of air flow on the global cell impedance can be observed. In the Nyquist diagram, the lowest impedance values were obtained for 30 mL/min with the value of impedance increasing consistently along with a decrease in the flow value up to a value equal around 17 mL/min. However at the lowest values of the airflow the magnitude of impedance is lower than at the intermediate values. Charge transfer resistance is not only a function of potential but also depends on the activity of oxygen on the surface of the catalytic layer [17]. Therefore it may be the reason for obtaining the lowest impedance value when air flow rate equals 30 mL/min.

3. 3. Effect of operating-current density

The experiment was conducted at a constant temperature amounting to 78 ^{o}C and at a constant methanol flow equal to 0.11 mL/min, with an air flow of 16 mL/min. The measurements were performed in a galvanodynamic manner with a linear load change at a velocity equal to 0.004 mA/s.

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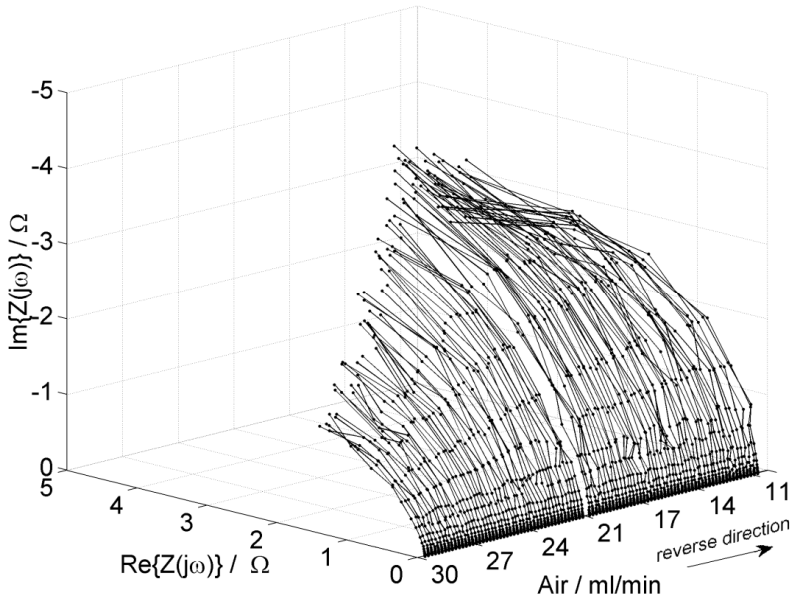

Fig. 2. Change in global cell impedance during a change in the oxidant flow rate during operation.

Fig. 3 presents a change of the cell impedance value during operation along with a changing power consumption value. The highest impedance values were observed for the lowest load of the fuel cell. By increasing the load the impedance values become reduced.

Because of such load range chosen (up to 30 mA) the decrease in impedance may be probably connected to the acceleration of methanol oxidation and oxygen reduction [17].

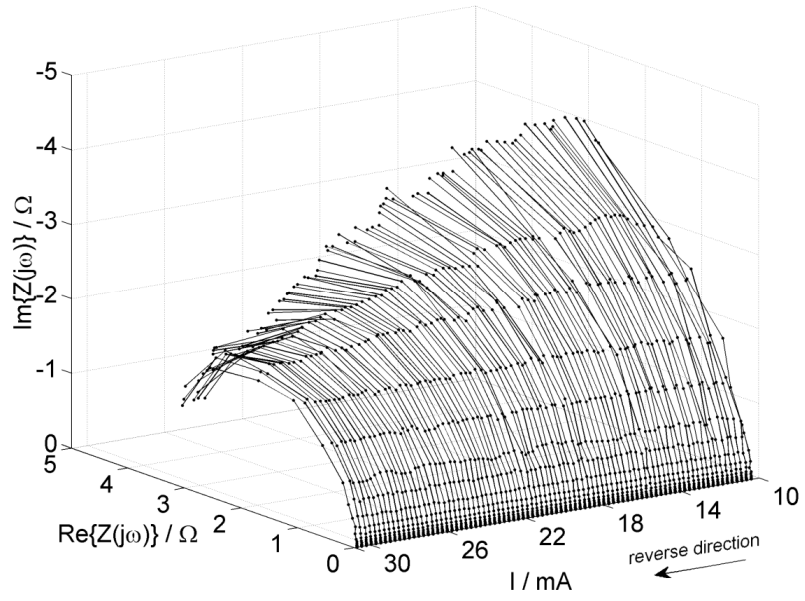

Fig. 3. Change in global cell impedance during a change in the cell load.

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4. Conclusion

The measurements conducted on-line ideally show the change in global impedance of a fuel cell during operation without simultaneous long-term stabilization. Together with an increase in the temperature, the global impedance of the cell decreases. An increase in the load and in the oxidant flow value also has an influence on the decrease in the impedance value. The monitoring technique presented here can be used during fuel cell operation, as it is possible to change the load, temperature, stream flow etc. A detailed analysis will be presented in subsequent studies.

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