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Study of Direct Methanol Fuel Cell Process Dynamics Using Dynamic Electrochemical Impedance Spectroscopy

Kazimierz Darowicki, Ewa Janicka, Pawel Slepski*

Gdansk University of Technology, Department of Electrochemistry, Corrosion & Materials Engineering, PL-80-233 Gdansk, Poland
*E-mail: ewa.janicka@hotmail.com

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A new technique, which was developed to characterize the direct methanol fuel cell under work conditions, has been presented in this paper. The impedance measurements were made using dynamic electrochemical impedance spectroscopy research technique in the galvanostatic mode, using multiple sinusoidal excitation. Obtained results show, that together with an increase of the temperature and working load, the global impedance of the cell decreases. However the value of methanol flow rate does not have any influence on the impedance value. Current-voltage characteristics were also obtained.

Keywords: Direct Methanol Fuel Cell; Impedance Spectroscopy; Online Monitoring; Direct Methanol Fuel Cell; Dynamic Electrochemical Impedance Spectroscopy

1. INTRODUCTION

Direct methanol fuel cells (DMFC) are promising energy conversion devices due to their great opportunities for applications as stationary or portable power sources. The DMFC generate electricity through the direct oxidation of the liquid aqueous methanol enters the anode in conjunction with the reduction of oxygen feeds cathode. The both electrodes are separately by the membranes. The typically electrolyte are Nafion, it provides thermal and chemical stability and also high proton conductivity. The DMFC are characterized by high efficiency, and they are environment friendly.

Due to broader applications of fuel cell, there is a growing demand for techniques for on-line monitoring of the DMFC. Diagnostic methods for fuel cells investigation, which have been used so far did not give its complete characterization, still leaving unresolved the question of dynamics. Liu et al.

[1] described a method of the on-line measurement of the ohmic resistance by the current interruption method. However, in this method it is necessary to temporarily take the load off the cell. Polarization curve method and the cyclic voltammetry are also widely used to characterize performance of fuel cells [2]. However, up to this date, the electrochemical impedance spectroscopy (EIS) was, and still is, the most frequently applied technique for examination of the fuel cells under working conditions. Using this technique, the dependence of the impedance of the DMFC on a variety of operating conditions, such as temperature [3-8], cell load [5], methanol [3-5,7] or oxidant [3-5,7,9] flow rate can be determined. Classical EIS assumes stationarity of the system under examination, so it is necessary to wait for an equilibrium each time working conditions are changed. It is possible to obtain impedance of the non-stationary systems, with use of the dynamic electrochemical impedance spectroscopy (DEIS) [10]. It is a versatile technique with a high potential for research and providing reliable information to evaluate the analyzed electrochemical phenomena. This technique was successfully applied in the field of pitting [11] and intergranular corrosion [12,13], erosion-corrosion [14], inhibitors [15,16] or analysis of the electrode materials[17] and gave a new, groundbreaking information in the above mentioned fields.

The aim of this study is to present the DEIS technique as an excellent tool for on-line monitoring of fuel cells during operation in order to ensure safe operation.

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 of 2.5 mg/cm^2 at the cathode and Pt-Ru of 2.5 mg/cm^2 at the anode. Gas diffusion layer was hydrophobized substrate with a 10wt% polytetrafluoroethylene (PTFE) loading at the cathode and 5wt% PTFE loading at the anode. These were enclosed between two parallel graphite plates with 1mm depth and 1mm width channels distributing reagents evenly to whole active area. The fuel used at the anode was 3%wt. methanol solution. The solution was supplied 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 multisinusoidal excitation. The measurements were conducted using the bi-electrode configuration. Combined time and frequency analysis was used, that means stimulation is a multisinusoidal signal and for analysis signals using a of-line Fourier transformation, the result allows it to obtain a characteristic impedance of the fuel cell. The excitation signal consisted of a set of elementary sinusoidal signals of frequency ranging from 4.5kHz to 30mHz. The AC excitation amplitudes were selected in a manner which ensured that the amplitude of the voltage response did not exceed 5mV. The signals were acquired and recorded using a PXI6120 card, the Autolab PGSTAT30 was used as a galvanostat. The cell voltage versus current density response was measured galvanostaticly, by progressively increasing the current load from open circuit, after stabilization of the working conditions of DMFC.

3. RESULTS AND DISCUSSION

3.1.Effect of cell temperature

During the measurement with the DEIS research technique, the temperature was changed linearly at a rate of 0.015^{o}C per second, from 70^{o}C to 80^{o}C. The methanol flow rate was 0.11ml/min and value of the air flow was 13.5ml/min. The cell load was set to 150mA. The change of temperature and its influence on the impedance value were measured on-line.

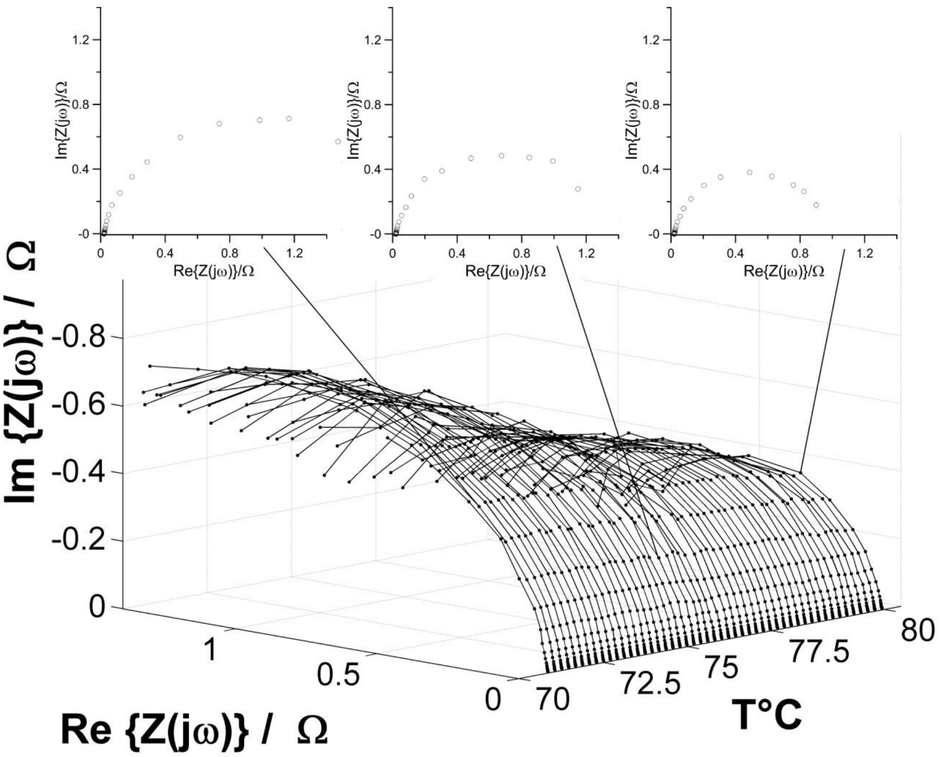

Figure 1. Effect of operating temperature on global DMFC impedance

Fig.1 presents the change of the impedance value together with the increase of the operational temperature. At temperatures of up to 75^{o}C, the impedance diagrams are bow-shaped and at temperatures higher than 75^{o}C Nyquist diagrams form nearly closed semicircles. This may indicate an improvement of the kinetics of electrochemical reactions. The electrochemical process on the anode is complicated owing to the multi-steps mechanism of the methanol oxidation reactions (MOR). The rate of the MOR is severely limited by poor reaction kinetics and also oxidation rate of the methanol strongly increases with temperature. The process taking place on the cathode is the reaction oxygen reduction. Individual impedance spectra in figure 1 show that the value of the diameter of semi-circles on spectra decreased nearly by the factor of two with the increase of the temperature. Temperature influences on the activation energy of the processes occurring on the electrodes and has a positive effect on the mobility of the charge carriers [18].

While measuring current-voltage characteristics, the values of air and methanol flow rate were the same as in the case of the DEIS measurement. For every current-voltage characteristic the temperature was different as follows 38, 48, 58, 68 and 78°C.

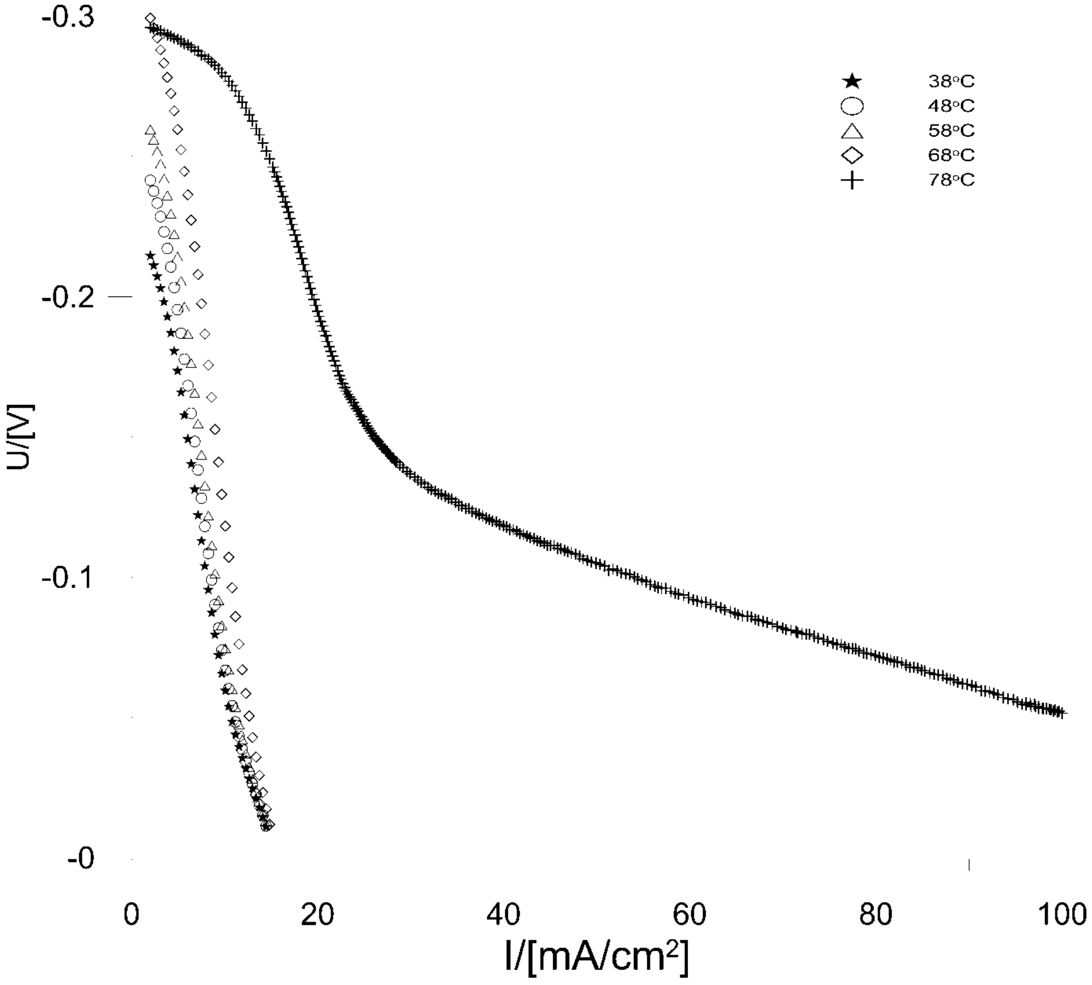

Figure 2. Effect of operating temperature on DMFC voltage output

The visible change of the electromotive force value of a fuel cell in a wide range of the operational temperature is presented in fig. 2. Cell voltage is lower at lower temperatures as the result of slower kinetics of electrochemical reactions. The optimal current-voltage characteristic of the DMFC can be observed at a temperature of 78°C. If the value of the operating temperature is too low it does not allow for effective operation of the fuel cell.

3.2. Effect of the methanol flow rate

The DEIS experiment was conducted at a constant temperature of 75°C and at the constant air flow rate equal to 13.5ml/min, with the cell load of 100mA. The methanol flow was linearly changed at a rate equal to 0.001ml/min per second.

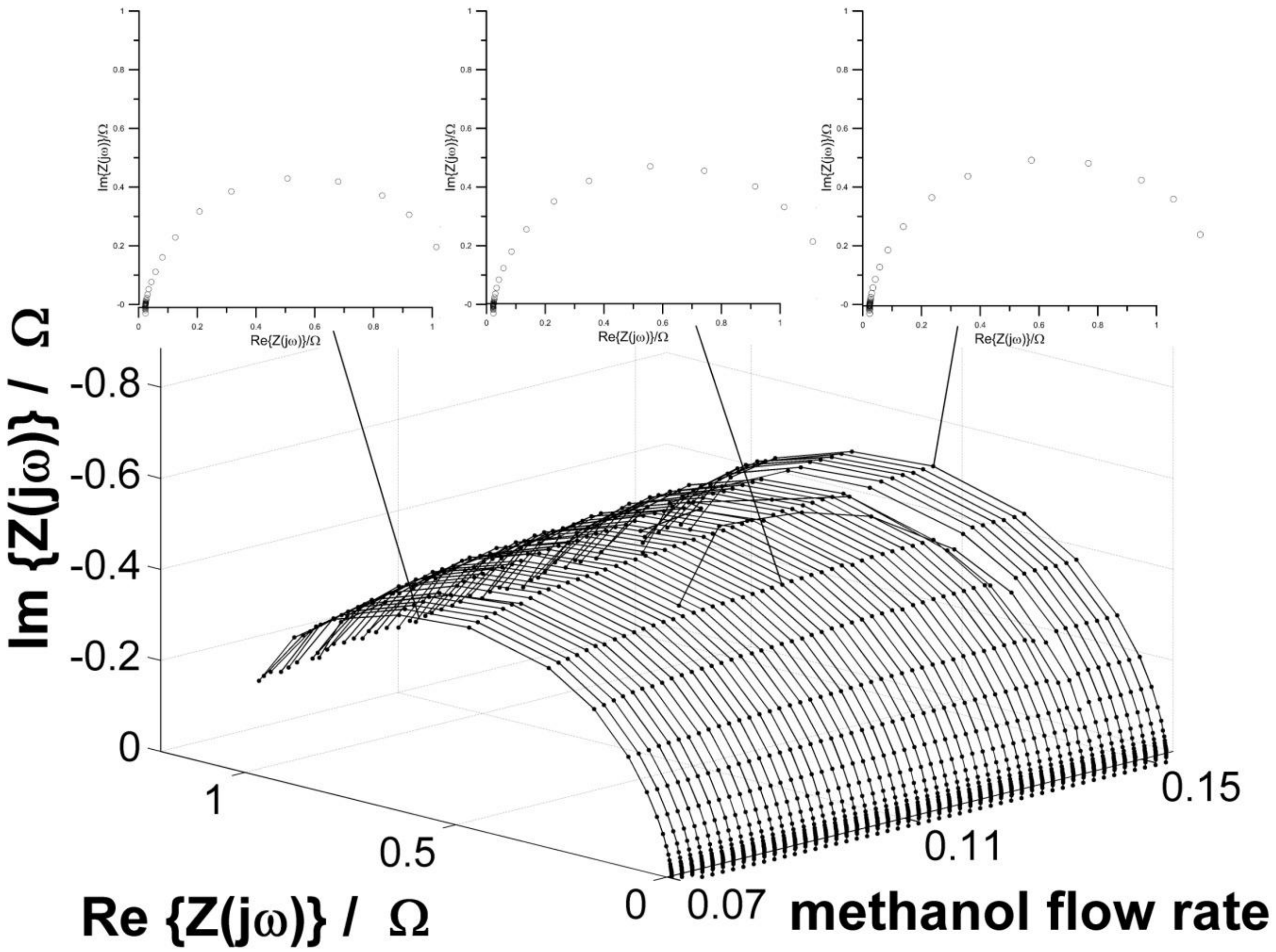

Figure 3. Effect of methanol flow rate on global DMFC impedance

Fig.3 illustrates the results of the DEIS experiment. It indicates that there is no significant change of the global impedance with the change of methanol solution flow rate within investigated range. However visible a slow increase of the diameter semi-circle with increase flow rate of the methanol. This probably steams from the methanol crossover. Oedegaard [3] also presented Nyquist plots of the fuel cell at 100 mA/cm^2 with the different methanol flow rates with use of the EIS method. The methanol flow rates as slow as half of the stoichiometric flow rate ensured minimal impedance of the process, with further increase of the flow rate having no significant effect.

Measurement of the electromotive force of the DMFC was conducted under the same conditions. For every current-voltage characteristic the methanol solution flow rate was different as follows: 0.09ml/min, 0.11ml/min, 0.13ml/min and 0.15ml/min.

The conclusions obtained by the DEIS technique can be supported by the current-voltage characteristics, shown in fig.4. After slight initial differences all obtained characteristics became similar at the load about 100mA. This may be a result of the methanol crossover, or the other hands needs to provide a rapid consumption of the methanol at higher load.

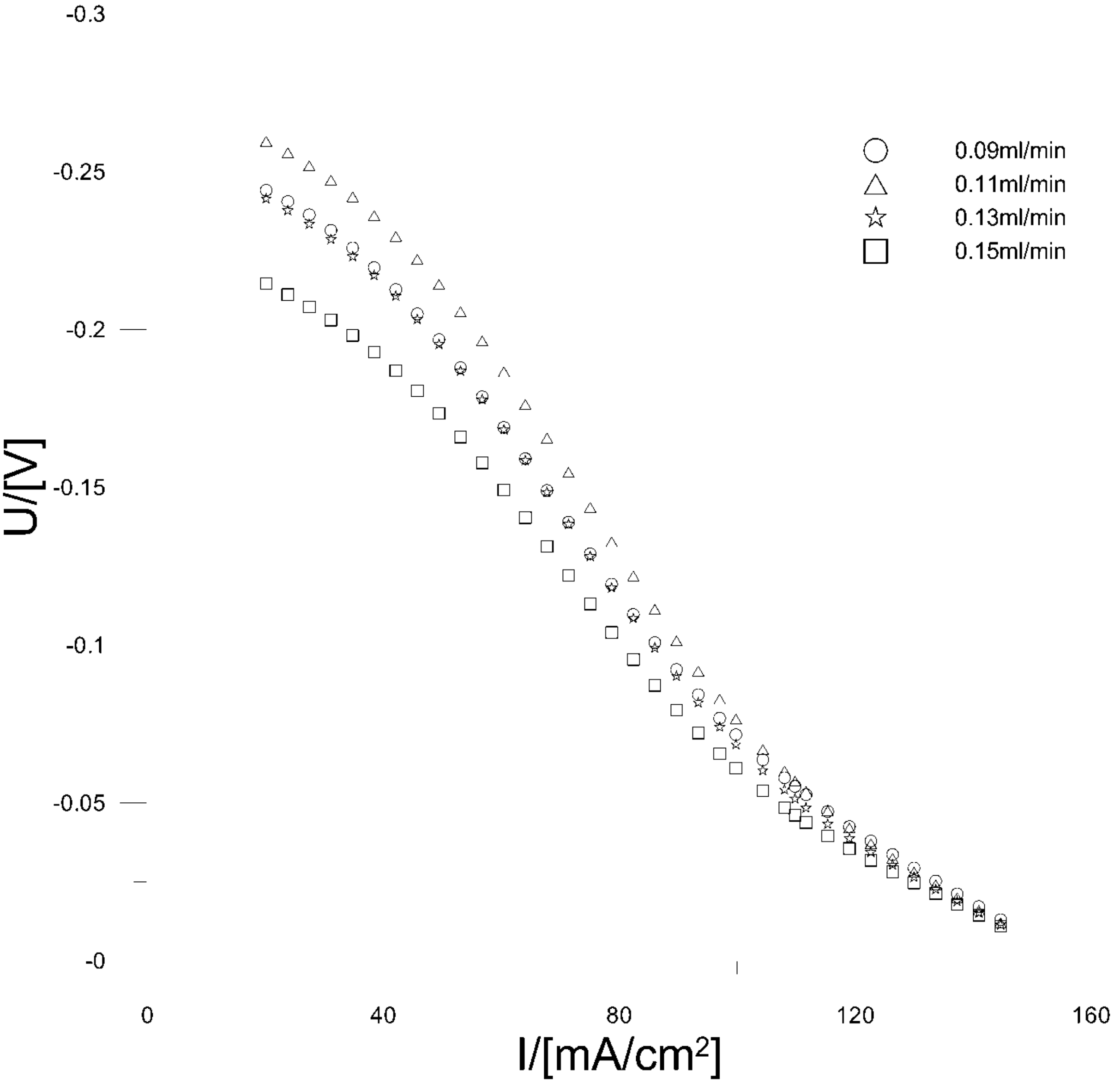

Figure 4. Effect of methanol flow rate on DMFC voltage output

3.3.Effect of the operating-current density.

The measurements were conducted at the temperature of 75^{o}C, with the air flow rate at 13.5ml/min and constant methanol flow rate equal to 0,11ml/min. The measurements were performed in galvanodynamic mode with a linear load change, at 0.03mA/s rate.

Fig.5 presents the change of the cell impedance value during operation along with the changing power consumption value. With the increase of the load, the impedance value becomes reduced. At the lowest load the impedance diagram was bow-shaped and for the highest load it almost forms a semicircle. The initial decrease in impedance values may be probably connected to the increase in the rate of the methanol oxidation and the oxygen reduction [19]. In the loads above 30mA, the characteristics of the impedance do not show changes, indicating stabilization of the process.

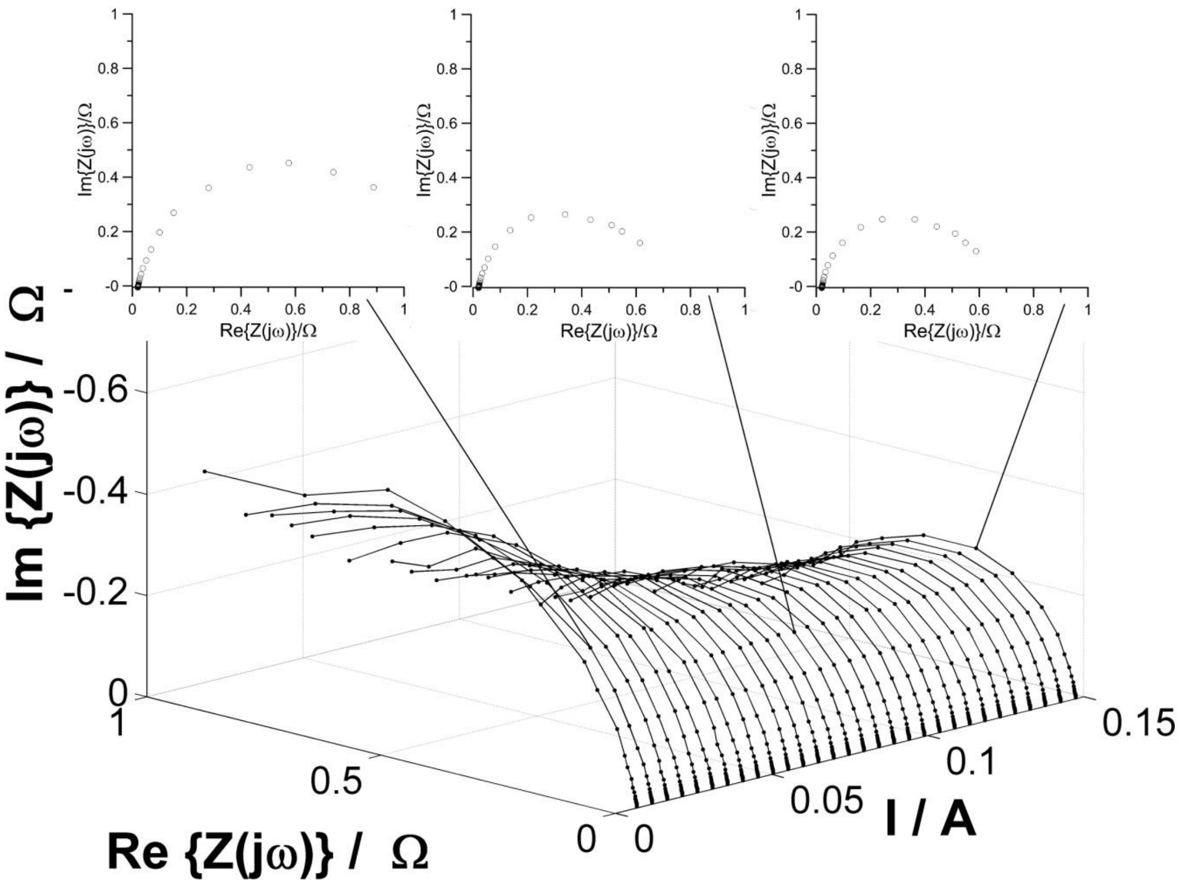

Figure 5. Variation of global DMFC impedance with current load

4.CONCLUSION

- This paper shows the results of the influence of temperature, load and methanol flow rate on the global impedance of the fuel cell using a new technique.
- Proposed method enables on-line measurements without the need of the long-term stabilization of the examined system.
- Confirmation of the accuracy of the results obtained by Dynamic Electrochemical Impedance Spectroscopy can be seen in the current-voltage characteristics of the Direct Methanol Fuel Cell.
- Described in the manuscript innovation technique can be used for monitoring the cell during the real operation and for optimizing the operating conditions of the fuel cells.

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