Impedance spectroscopy as a tool in the evaluation of MEA's

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Abstract

Impedance spectroscopy is a very useful technique as a testing method in analysis of electrochemical systems, material studies, corrosion systems, batteries, etc. However its use in fuel cells has been relatively limited. This work presents impedance results during MEA's evaluation, when testing conditions are varied in single cells. Contributions of different processes effects on complex plane results are discussed.
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1. Introduction

PEM fuel cells have had a great development in the lasts few years, due to their great versatility in generating electrical energy in a clean way, providing an invaluable solution for the degradation of the environment. These systems allow users to provide energy everywhere in an easy way, for mobile or stationary applications. However, the best performance of these systems depends on a complex group of features which interact internally to provide the optimum situation for the entire process. Therefore, it is of much interest to analyze performance losses in the different processes inside the cell, such as the specific gas diffusion phenomena in both, anode and cathode, mass and charge transport mechanisms in the membrane, the liquid water produced in the cathode, and all the operation parameters that influence the function of the entire cell. For all the previous reasons, it is important to examine the operation of a PEM fuel cell with a suitable technique, which allows a separation of the effects, in order to determine the influence of every one on the overall response.

Impedance spectroscopy is a powerful method for investigating the electrical behavior of interfaces [1]. Due to the complexity in electrode's behavior inside the fuel cell and the influence of several factors, EIS has demonstrated to be a useful and powerful technique to study the different processes that take place in fuel cells and in many cases, also allows us to evaluate them in a separate way in order to determine the influence of each on the global fuel cell performance.

Some papers mention the use of this method for measuring fuel cell performance [2,3] and finding the performance losses in the different process stages.

At the beginning of the 1980s the EIS began to be utilized for studies in porous gas diffusion electrodes, generating impedance functions based on models of the electrode's structure simulating a real fuel cell electrode [4]. The increasing utilization of EIS as a powerful technique to analyze the origin of the performance losses in the fuel cell, has originated a varied R&D, aiming at the identification and individualize problems in accordance with all the different fuel cell components and phenomena involved.

The aim of this work, is to determine the characteristic impedance behavior of a monocell cathode. Because of the importance of the oxygen reduction reaction (ORR) in the global reaction rate in the fuel cell, in this work we concentrate the attention on it, in order to demonstrate that the main characteristics in the fuel cell impedance spectra, are determined by the cathode.

It is known that ORR is the determining step in the global electrochemical process of the fuel cell and the cell performance is controlled by this reaction (at low loads), even the fuel cell performance has already been described as the electrolyte resistance in series with the cathode impedance [3].

When working with a fuel cell under ideal operating conditions, no performance limitations will appear. Thus, it is important to analyze what would happen if the cell works far from the ideal. In this work, it will be presented the PEMFC operation, at room temperature (30 °C), with pure oxygen feeding in the cathode inlet and pure hydrogen for anode side and keeping a constant symmetric gas flow supply on both sides. It was possible to accomplish polar-

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ization and impedance measurements at different potential values, using a reference electrode.

2. Experimental

EIS experiments were carried out in a single cell of 5 cm^2 of active area with commercial MEAs from Electrochem$^®$ with Pt loading of 1 mg/cm^2 supported on carbon paper. A Pt wire reference electrode was connected to the cell and symmetric gas flow supply was fed into the cell using pre-humidified H$_2$ and O$_2$, passing them through a water bottle, at room temperature. The cell was operated with a back-pressure of 20 kPa in the cathode side and 62 kPa for the anode. As mentioned above the experiment was carried out at room temperature (30 °C at the time).

The electrochemical characterization of the fuel cell was performed by measuring a polarization curve and carrying out impedance measurements, using a Solartron 1287 electrochemical interface and a Solartron 1260 frequency response analyzer. The frequency range swept was from 100 mHz to 100 kHz, with an ac signal amplitude of 10 mV. Impedance spectra were obtained under cathodic potentiostatic conditions at values of open circuit to 0.5 V versus reference electrode.

3. Results and discussion

A typical cathodic polarization curve is shown in Fig. 1, where a low density current reflects the low temperature at which the monocell was tested. The cathodic open circuit potential measured was 0.95 V versus reference. On that curve arrows point at the potential values for the carried out EIS measurements.

In order to estimate the possible errors during the experimentation, KK transforms were calculated for each set
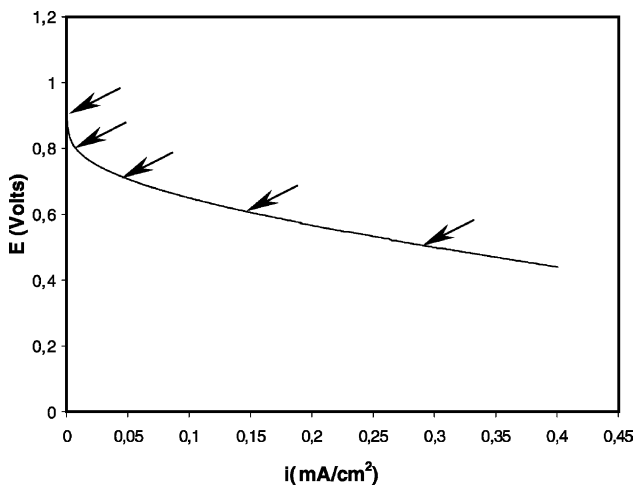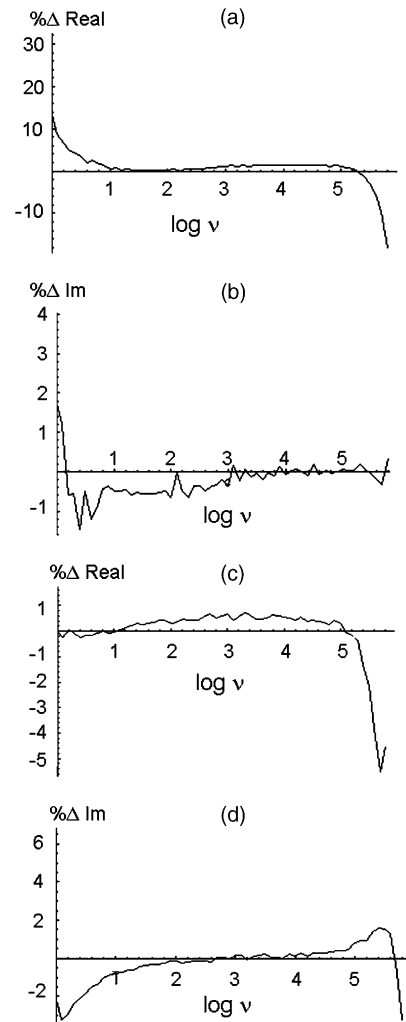

Fig. 2. KK transform error percentage calculated for experimental results: (a) E_{oc}, real part, (b) E_{oc}, imaginary part, (c) 0.5 V real and (d) 0.5 imaginary part.

of data.[1] These estimates are shown in Fig. 2 for the two extreme conditions, E_{oc} and 0.5 V. Other results lie in between and are not plotted for simplicity. As it can be seen from that figure error estimates are minimal in the range of 10 Hz to 100 kHz, giving enough confidence for the use of these results. Figs. 3 and 4 are complex plane representations of EIS, where a decrease in the low frequency semicircle diameter with potential is clearly shown. In Fig. 3, the E_{oc} spectrum did not produce the *RC* component associated to the cathodic reaction at low frequencies. If we have a closer look at the high frequency region of the Nyquist plots (Fig. 5), a second incomplete semicircle can be detected at all potentials tested including E_{oc}. This high frequency component does not vary with potential nor at the E_{oc} condition.

Fig. 1. Current–voltage curve of 5 cm^2 active area fuel cell with symmetrical supply of H$_2$ and O$_2$, working at 30 °C.

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[1] The software used was developed at the Universidad Autonoma Metropolitana (UAM-I), Mexico.
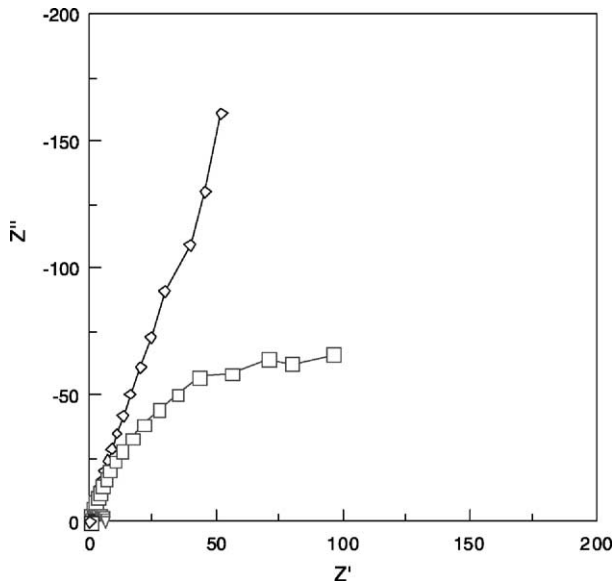
Fig. 3. Impedance spectra for ($\diamond$) E_{oc} and ($\square$) 0.9 V in cathode PEM fuel cell, with humidified H_2/O_2 supply, at room temperature.
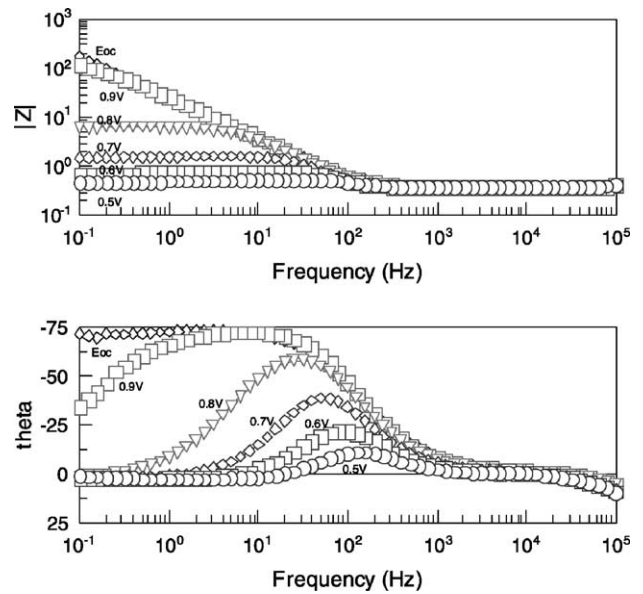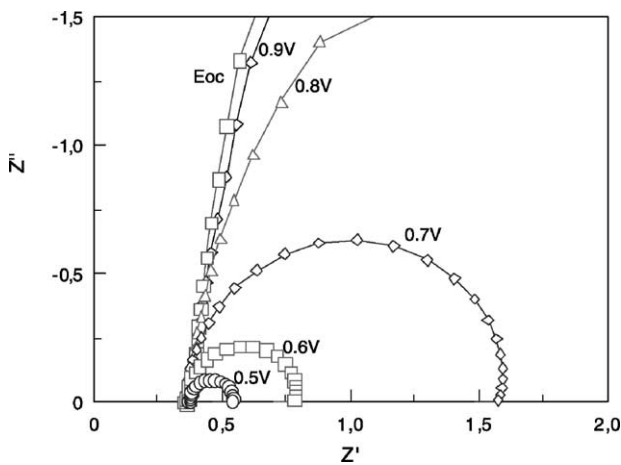

Fig. 4. Impedance spectra at several potentials for H_2/O_2 PEMFC: E_{oc}; 0.9, 0.8, 0.7, 0.6 and 0.5 V.
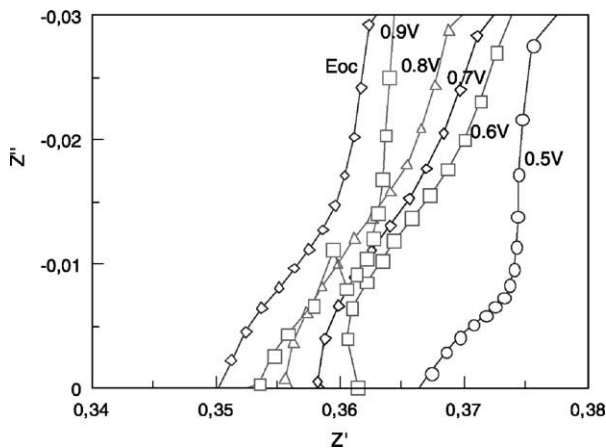
Fig. 5. High frequency view of the ac impedance spectra for several cathode potentials.

Fig. 6. Bode diagram of the measured impedance spectra: E_{oc}; 0.9, 0.8, 0.7, 0.6 and 0.5 V.

This result seems to indicate that for the conditions tested in this work, the high frequency region is not associated with any faradaic process nor with mass transport limitations on the cathode electrode side. A result of this is that the only condition unvaried associated to the construction of the MEAs, i.e. its structural features, is responsible for this behavior. Bode plots, such as those shown in Fig. 6 give additional information on the system under study. For example, the impedance module does not change for higher frequencies than 100 Hz. Also from the same plot we can see the potential effect, occurring at low frequencies, where at E_{oc} and at 0.9 V (i.e. very close to E_{oc}), the module changes more rapidly with frequency.

On the other hand, far away from E_{oc}, i.e. from activation control, the module remains with little variation up to a given frequency value. It is more or less clear that under the conditions studied during this experimentation, a three electrode configuration allows us to discriminate what happens on the other side of the monocell.

This results did not subtract *IR* effects for the approach of the study is to maintain manufacturing features, as well as to study regions away from activation control.

To further explore the dependence of the cathodic reaction characteristics on the potential, values of charge transfer resistance (R_{ct}) and cathode double layer capacitance (C_{dl}) were calculated and plotted. Such results are shown in Fig. 7, where the R_{ct} seems to decrease exponentially during the whole range of potential explored, probably up to a value determined by transport limitations. In the same figure, it is possible to see that the C_{dl} magnitude reaches a constant value of about 4.6 mF at a potential of 0.75 V. Although the order of magnitude of calculated values of C_{dl} correspond to those observed for porous electrodes, i.e. high effective area, further lowering the potential does not increment its value
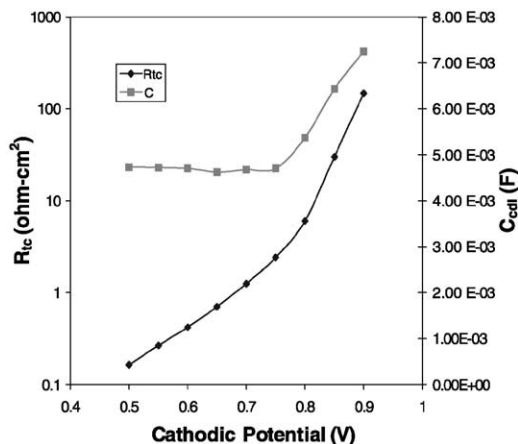
Fig. 7. Cathodic potential vs. double layer capacitance and charge transfer resistance.

due to faster double layer discharge, which in turn produces higher currents. From these values it is possible to differentiate both regions, one where values of capacitance vary near potentials with activation control. Once the reaction is controlled solely by ohmic effects, the capacitance reaches a constant value.

Other thought that we can elaborate on is, for example, the fact that the low temperature used might allow less water escape from the membrane. Although this is true, it might be critical to then increase gases temperature in order to maintain dragged water droplets far from condensing and blocking pores at the electrodes. In this case this did not seem to happen which allowed us isolate interfacial impedance changes along a potential range.

Although we do not present an electrical equivalent circuit for this cathode, it is tempting to propose a classical circuit considering pore impedance coupled to a faradaic impedance component. Finally, the potential range did not scan regions where mass transport could start to control current production (Fig. 1). The spectra obtained seemed to agree with the absence of these effects.

It has been previously reported the effect of several components on the impedance spectrum of a single cell, such as structure, membrane humidification (i.e. ionic conductivity), faradic impedance at both anode and cathode, mass transport limitations due, for example, to structural factors of the electrode or the flooding of porous at high currents [5,6]. Other effects depend on the structure of the cell such as the catalyst layer, the membrane thickness and their influence over the diffusion of oxygen, the number of active sites on the electrode and the water balance.

4. Conclusions

It has been possible to attain experimental conditions that allowed control on different contributions to the global impedance of a PEM monocell. In this way a clear faradaic contribution was shown to exist at the low frequency range measured and a structural component, with and in the absence of reaction currents at the high frequency range. The formation of the cathode capacitance was achieved after polarization of about 200 mV from E_{oc}. After that, the cathode capacitance reached a value that was kept constant for larger currents. The magnitude of the capacitance corresponds well with porous electrodes. Finally, as expected the charge transfer resistance diminishes as overpotential increases.

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