

Practical Considerations Regarding the Measurement of Ionic Conductivity by EIS in Conductive Polymers

D.I. Vaireanu, A. Cojocaru, I. Maior, S. Caprarescu

* Faculty of Applied Chemistry and Materials Science University "Politehnica" of Bucharest, OP 39, CP C10, Bucharest, 021711, Bucharest, Romania, tel.: +40214023939; email: di_vaireanu@chim.upb.ro

Abstract: Electrochemical Impedance Spectroscopy (EIS) is a powerful technique for the evaluation of ionic conductivity in conductive polymers used for PEM electrolyzers/fuel cells or for other purposes. Although this technique is a very well established one, the determination includes compulsory the thickness of the membrane (this varies with the relative humidity, water uptake, membrane batch etc.), and hence a series of errors, often incurred due to a crude determination of membrane thickness or due to various factors that determines the modification of membrane thickness during the experimental determination of EIS spectra. The paper discusses various measures that may contribute to enhance the precision of thickness determination, presents a novel cell (used in a two-electrode or three-electrode configuration) that has the advantage of allowing a precise determination of the membrane thickness (at micrometer resolution) during the determination of the electrochemical impedance spectra and discusses the effect of various parameters on EIS measurements.

Keywords: conductive polymers, ionic conductivity, electrochemical impedance spectroscopy

1. Introduction

Electrochemical cells used for the determination of ionic conductivity in PEM are based either on modified classical membrane electrodes and the evaluation is carried out in sulphuric acid solution or on various other designs which involve applying a certain degree of pressure - gravitational using metallic weights of mechanical caused by a vice or screws and nuts systems - on the membrane subjected to the evaluation, which is placed between two platinum electrodes and acts now as a solid electrolyte [1-6].

The applied pressure leads to a change in membrane thickness due to the increased compression and membrane squeezing, and the membrane thickness, taken either from the supplier's/manufacture's technical datasheets or measured before/after the experiment does not reflect the actual value of the membrane thickness during the experimental evaluation. As the determination of the impedance is done with a high degree of precision from EIS spectra, the determination of the ionic conductivity will be as precise as the determination of the membrane thickness is.

2. Materials and methods

The proposed cell is based on two platinum 1.1 cm disk electrodes, embedded in Pertinax, which acts as an insulating material (see fig.1). This newly obtained arrangement is placed between the vice of a precision digital micrometer (Mitutoyo) that is able to measure the membrane thickness at micrometer resolution. This two electrodes cell configuration (see fig. 2) can be easily changed in a three electrodes cell configuration by

attaching a golden plated flatten clamp direct onto membrane, clamp that acts as a reference electrode (see fig. 3).

The setting up procedure consists in establishing firstly the origin on the digital micrometer (in the absence of the membrane) and then, by inserting the membrane, the value indicated on the display is the actual membrane thickness.



Figure 1. Platinum disk electrodes

The micrometer dynamometric screw ensures a constant pressure on any membrane, regardless the membrane type, maintaining identical conditions for any evaluation.

In order to evaluate a homogenous membrane from the thickness point of view, a contour map is plotted representing the distribution of membrane thickness depending on the membrane surface coordinates (fig. 4.); the required part of membrane is then cut from an evenly distributed area and subjected to the evaluation.



Figure 2. Two electrodes cell configuration



Figure 3. Three electrodes cell configuration

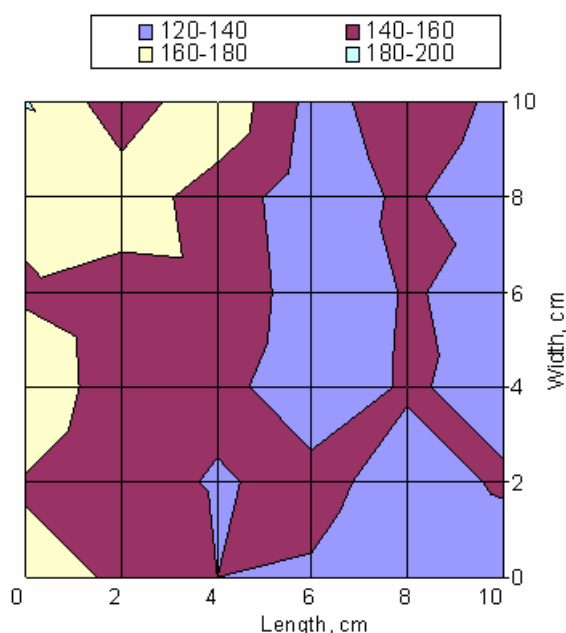


Figure 4. Contour map distribution of a PESA membrane thickness, micrometers

The cell is connected to a Voltalab 40 potentiostat and the EIS procedure is applied using the potentiostatic single sine mode - a sinusoidal potential perturbation of 10 mV amplitude within the frequency range of 100 kHz – 100 mHz.

By using a circular regression procedure, the ionic conductivity is calculated from the value of normalised impedance, R_1 , ($\text{ohm}\cdot\text{cm}^2$), obtained from intersection with the real impedance axis in the high frequency (see fig. 5) area of Nyquist plot and from the actual value of the membrane thickness displayed on the digital micrometer during the determination (see equation 1).

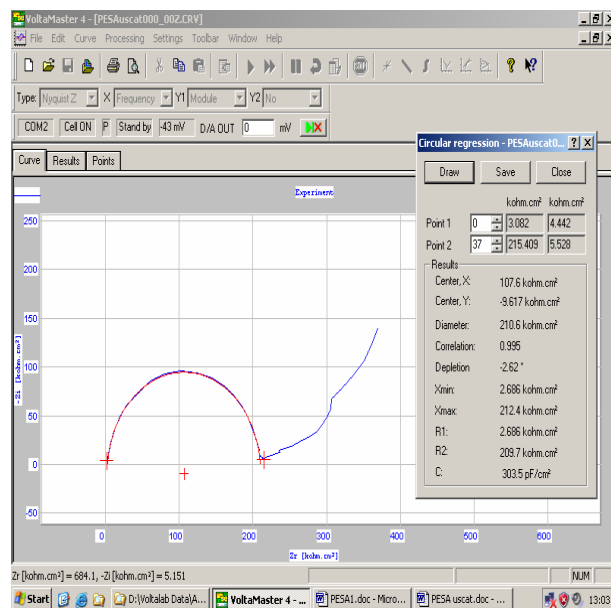


Figure 5. Nyquist plot of a PESA membrane

$$\sigma = \frac{d}{R_1} \quad (1)$$

where:

σ is the ionic conductivity, S/cm
 d , actual membrane thickness, cm
 R_1 , the intersection of experimental curve with the real impedance axis, $\text{ohm}\cdot\text{cm}^2$

The effect of various parameters on EIS measurement

The establishment of a particular set of experimental conditions is of a paramount importance on the success of the experiment. Although most of the potentiostat manufacturers are offering a set of guidelines regarding the experimental setups [7-8], one should test beforehand the behaviour of the equipment and decide on a particular set of conditions and parameters that will suit best its experiment. Although some of the conclusions arisen from these considerations may be extended to various types of equipment, they are fully applicable with respect to the above said potentiostat. In order to ensure highly reproducible conditions, the tests are carried out with the dummy cells that will maintain the very same conditions and ensures that no unwanted perturbations take place.

Measurement linearity

The EIS determination will be as accurate as the impedance response of that system is linear, namely it is independent of the perturbation amplitude [7-8]. Normally, this is done for most electrochemical systems by imposing a very small amplitude perturbation, e.g. 10 mV. The drawback is that this small value will yield a small poor signal-to-noise ratio. The question is how high can one go until one reaches a value that will break the linearity

condition. The determination of the linearity range was carried out by performing replicated experiments with increased perturbation amplitude. The results are presented in table I and figure 6. The linearity range, where the impedance was independent of the perturbation amplitude was found between 5 mV and 50 mV with a boundary at 100 mV.

TABLE 1. The dependence of circular regression correlation coefficient on the applied amplitude perturbation (100 kHz - 1Hz)

Amplitude perturbation, mV	Correlation Coefficient, 25 points
5	0.998
10	0.999
20	0.997
50	0.994
100	0.990
500	0.985
1000	0.820

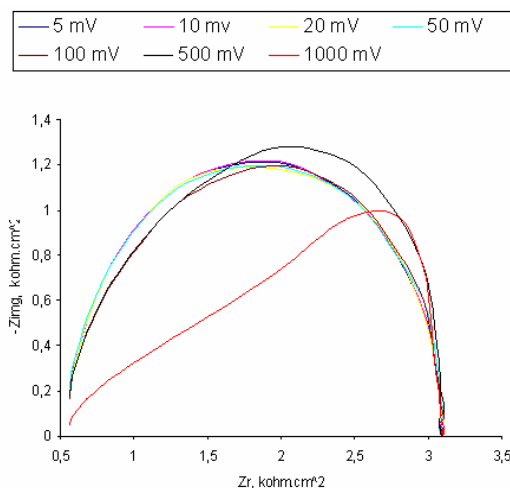


Figure 6. Overlaid Nyquist diagrams plotted for increased single sine potential amplitude perturbations

Twisted or untwisted cables?

Although the manufacturers will recommend avoidance of coupling effects between current-feeding and potential-sensing lines by twisting the leads of the working (WE) and counter (CE) electrodes together and keeping them separate from the twisted leads of the reference electrode (RE) and sense (S) of the working electrode [7-8], no significant effect was found in the case of twisted wire configuration in comparison with the normal, untwisted wire configuration (see table II). This is probably due to the fact that the leads of the above said equipment are of a coaxial type, properly shielded and the earthing connections are fully functional.

TABLE 2. Comparison data between twisted and untwisted wires configurations (100 kHz - 10 mHz; 10 mV)

EIS output parameter	Twisted wire configuration	Untwisted wire configuration
R1	550.4 ohm.cm ²	553.5 ohm.cm ²
R2	2.541 kohm.cm ²	2.540 kohm.cm ²
C	9.892 nF/cm ²	9.899 nF/cm ²
r, out of 30 points	0.999	0.999

Number of measurements per decade

The higher the number of measurements per decade, the higher the precision, but also the higher the experiment duration. The problem is to see what parameter is really affected by decreasing the number of measurements per decade. It was found that, within the given experimental conditions, the strongest affected output parameter is the capacitive one, with an error larger than 10% (see table 3).

TABLE 3. The effect of decreasing the number of measurements per decade on the output parameters (100 kHz - 10 mHz; 10 mV)

EIS output parameter	20 meas/decade	10 meas/decade	5 meas/decade
R1	551.2 ohm.cm ²	550.5 ohm.cm ²	549.4 ohm.cm ²
R2	2.541 kohm.cm ²	2.541 kohm.cm ²	2.544 kohm.cm ²
C	8.766 nF/cm ²	9.893 nF/cm ²	9.881 nF/cm ²

Experiment duration

One of the drawbacks when conducting experiments at low frequencies is that they take a lot of time - the lower the frequency, the longer it takes. In the case of the determination of ionic conductivities, as the areas of interest are located at high frequency, a compromise solution would be to reduce the frequency range and to increase the number of measurements per decade, ensuring in this way that one obtains enough experimental points for regression equations of for constructing various equivalent models. The results of the experimental investigations are presented in Table 4.

TABLE 4. The effect of frequency range and number of measurements/decade on the experiment duration (10 mV)

Frequency range	20 meas/decade	10 meas/decade	5 meas/decade
100 kHz-10 mHz	2200 s	1230 s	660 s
100 kHz-1 Hz	311 s	183 s	110 s

Shielding the cell

Although the equipment has been designed with safety features regarding the shielding and earthing, and it has software filtering possibilities (either auto or manual), it is sometimes advisable to use a Faraday's cage, especially when using low potential/current perturbations and at low frequency. In order to notice anything, the filtering option was turned off in both cases - normal one and the one with the cell inserted in a Faraday's Cage. The results are presented in fig. 7.

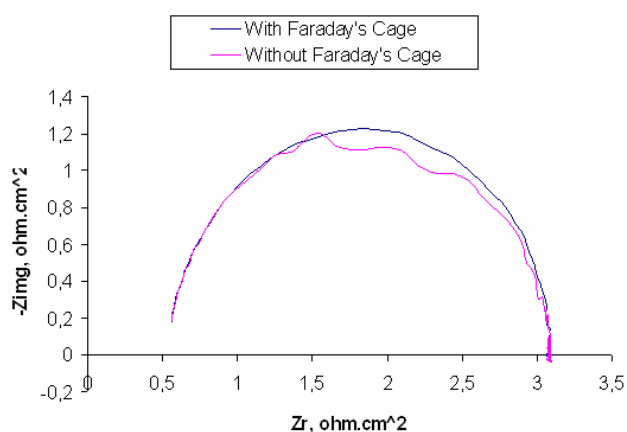


Figure 7. Nyquist diagram depicting the effect of a Faraday's Cage (100 kHz - 100 mHz; 5 mV)

3. Conclusions

A novel electrochemical cell that may be used for the determination of the ionic conductivities in polymer electrolyte membranes is proposed. The cell has the advantage of a precise determination, at micrometer resolution of the membrane thickness while the EIS experiment is carried out.

The effects of a series of parameters that may improve or worsen the performances of a particular experimental setup are also discussed.

It was found that the linearity range, where the impedance is independent of the perturbation amplitude is located between 5 mV and 50 mV with a boundary at 100 mV. Shielding the cell may be also useful when the filtering option is turned off or at low perturbation values. One may also optimise the experiment duration by reducing the frequency range, as in the case of the ionic conductivity, the area of interest is in the zone of high frequency, maintaining an acceptable number of experimental points by increasing the number of measurements per decade.

ACKNOWLEDGMENT

Financial support was provided by CEEEX 267/2006 AMCSIT and CEEEX X2C19/2006 AMTRANS Research Programmes. Special thanks go to the following people for their logistic support: Mr. Corneliu Andrei – PUB and Mrs. Mariana Andrei - PUB

REFERENCES

1. Freire, T.J.P., Gonzalez, E.R., Effect of membrane characteristics and humidification conditions on the impedance response of polymer electrolyte fuel cells, *Journal of Electroanalytical Chemistry*, **2001**, 503, pp. 57-68.
2. Wagner, N., Characterization of membrane electrode assemblies in polymerelectrolyte fuel cells using a.c. impedance spectroscopy, *Journal of Applied Electrochemistry*, **2002**, 32, pp. 859-863.
3. Mehta, V., Cooper, J.S., Review and analysis of PEM fuel cell design and manufacturing, *J. Power Sources*, **2002**, 5044, pp. 1-22.
4. Rikukawa, M., Sanui, K., Proton-conducting polymer electrolyte membranes based on hydrocarbon polymers, *Prog. Polym. Sci.*, **2000**, 25, pp. 1463-1502.
5. Guangehun, L., Pickup, P., Ionic Conductivity of PEMFC Electrodes, *Journal of The Electrochemical Society*, **2003**, 150, pp. C745-C752.
6. Parthasarathy, D., Srinivasan, A., Martin, J., The Platinum Microelectrode / Nafion Interface: An Electrochemical Impedance Spectroscopic Analysis of Oxygen Reduction Kinetics and Nafion Characteristics, *Journal of The Electrochemical Society*, **1992**, 139, pp. 134-140.
7. www.ecochemie.nl
8. www.radiometer-analytical.com