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Application Note

Characterization of fuel cells using Electrochemical Impedance Spectroscopy

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Application Guide: ANML03

Introduction

The following text illustrates some of the recent work using electrochemical impedance spectroscopy (EIS) to characterize cells. Particular emphasis is placed upon Proton Exchange Membrane (PEM) cell technology including hydrogen and direct methanol cells.

A significant proportion of scientists engaged in this research have little or no formal training in EIS. There are numerous papers on the subject and it is the intention of this note to give examples of the analysis of the most common sets of impedance data. A comprehensive review of the literature regarding EIS analysis of fuel cells is beyond the scope of this note. However, it is hoped this will be of value to those who are new to this field.

It is strongly recommended that the reader consult the recommended reading list at the end for a more detailed understanding of EIS.

Fuel cell voltage and voltage losses

Whilst the thermodynamic potential for the oxygen-hydrogen couple is 1.23 V, this is never achieved in a real cell and that results from four major effects;

i) Ohmic losses: the voltage loss associated with electronic conduction through the various interconnects and the material of the electrode in addition to the resistance to the flow of ions in solution. The voltage drop is linear and increases proportionally with current density.

ii) Activation losses: the voltage loss associated with the kinetics of the charge transfer step. For the reaction to proceed at an appreciable rate, significant departures from the equilibrium potential are required.

iii) Mass Transport (or concentration losses): the voltage loss associated with the depletion of reactant at the electrode surface.

iv) Fuel Crossover: fuel sometimes diffuses across the membrane without reacting at either the anode or cathode. For example, methanol can diffuse across the anode and react directly with oxygen on the cathode producing no net current.

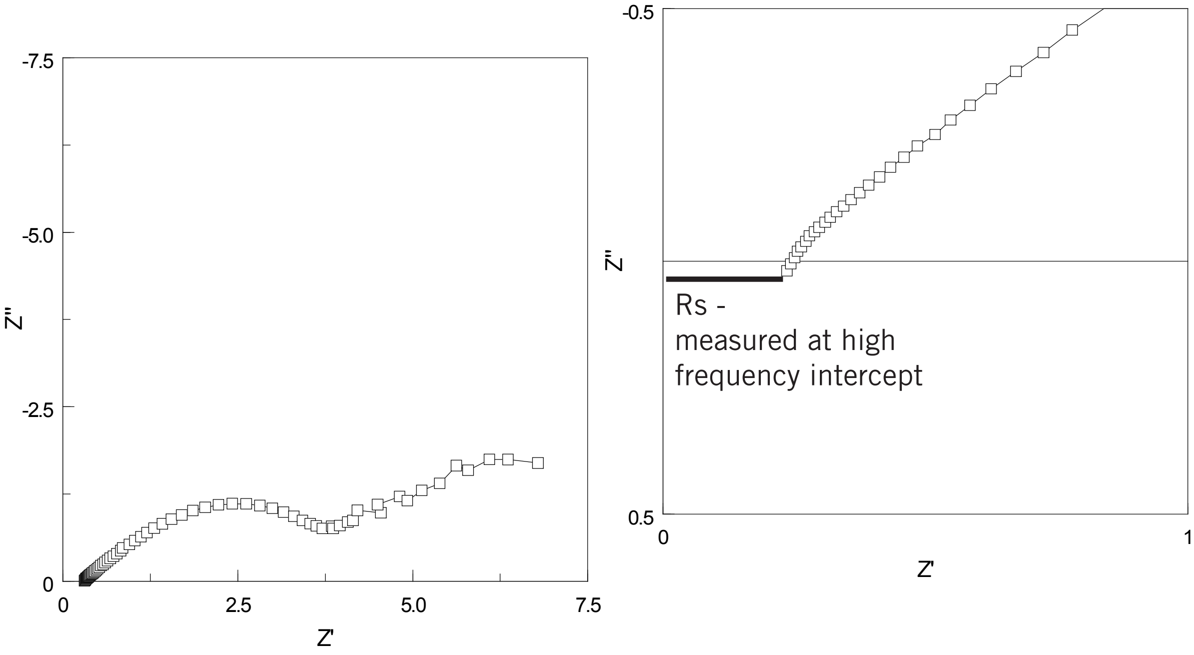
Impedance spectroscopy has been used to examine each of these problems and the following examples are typical of the results found in the literature. The following sections will concentrate on the first three mechanisms since they are common to all PEM cells.

Ohmic Loss

It is easy to demonstrate that even small resistances associated with electronic and ionic conduction can result in a significant drop in the performance of the cell. Therefore, it is critical that the engineer measures this property accurately and identifies the major cause of ohmic loss.

Historically, this property has been characterized using the current-interrupt technique (1) and is a simple experiment to perform. However, many researchers believe that the current interrupt method should not be applied to power devices such as fuel cells. It is not the intention of this note to cover this particular topic any further, however, many advocate impedance analysis to determine this property.

Figure 1 shows the impedance spectrum of a 1 W Direct Methanol Fuel Cell (DMFC) operated at 10 mA constant discharge for 20 mins. To simplify the analysis, we will assume that all electronic impedances can be represented as a simple resistor, Rs. According to AC theory, both the current and voltage are in phase, therefore the ohmic loss is simply derived from the point at which the high frequency arc bisects the ordinate axis. In this particular example, the measured impedance was in the order of 250 mW. One can calculate the cell voltage loss at a particular current density by applying Ohm's law. In this example, at a constant 10 mA load, the cell voltage loss for this mechanism was 2.5 mV.



Rs -
measured at high
frequency intercept

Figure 1: Complex plane diagrams of a 1 W DMFC operated at open circuit. Figure B shows an expanded view of A in the high frequency region. Impedance measurements were recorded from 65 kHz to 10 mHz using a Solartron ModuLab system with a 10 mA AC stimulus. The ohmic loss Rs, was determined from the point at which the curve bisected the real (Z) axis. At this point the current and voltage are in-phase; the phase angle = 0.

Poor catalyst utilization due to inefficient proton transport through the catalyst layer determines that all reaction occurs on the catalyst particles near the membrane surface. Attempts have been made to improve the conductivity of the system with particular emphasis placed upon impregnated catalyst layers. The work by Pickup (2) and co-workers discussed in detail the measurement of the ionic conductivity of proton exchange membranes. They focused on the impregnation of Nafion in the catalyst layer and were able to gain an understanding of the conductivity of the catalyst as a function of distance from the membrane. Figure 2 show a typical impedance plot of an impregnated catalyst layer in contact with a membrane. The ionic resistance is obtained by the length of the Warburg-like region projected onto the ordinate axis (as shown in Figure 2) and is derived from,

$$Z' = \frac{R_{ionic}}{3}$$

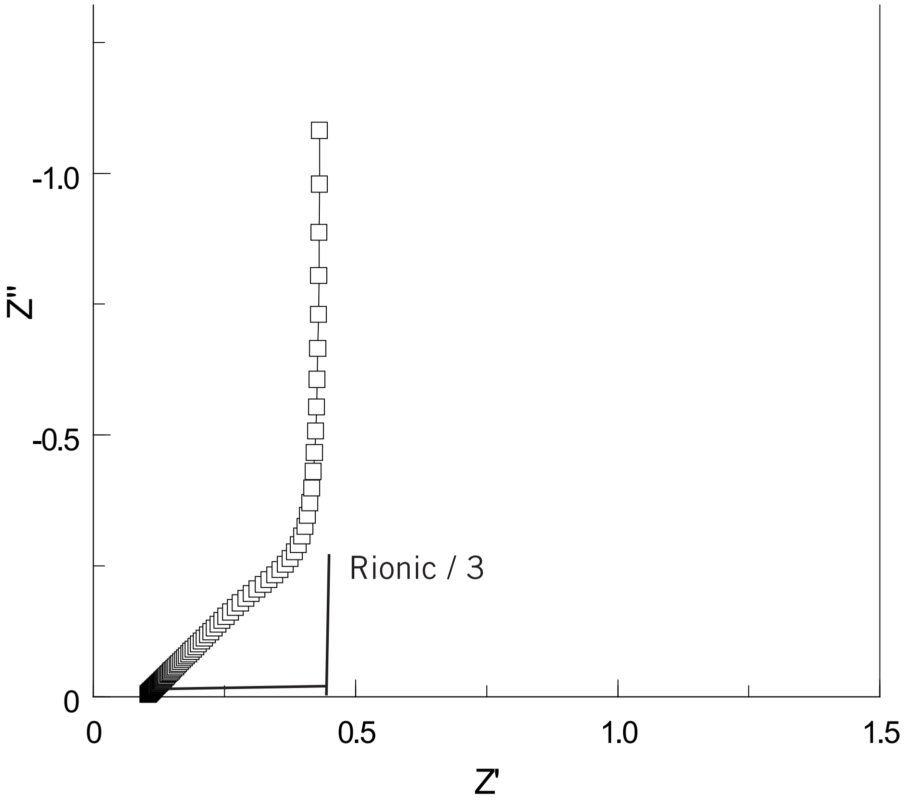


Figure 2: Simulated complex plane diagram for a finite transmission line model (see 5 for details). Simulation was performed using ZView software in the frequency range 10 kHz to 1 Hz.

Their data showed that by impregnating the catalyst layer, the utilization of the catalyst increased and therefore improved the performance of the fuel cell.

Zawodzinski et al. (3) examined the contribution of ionic and electronic impedances in the catalyst layer. By using a combination of impedance analysis and steady-state polarisation techniques they were able to determine these impedances independently from,

$$1/R_i = 1/Z_{DC} - 1/R_e$$

where ZDC is the overall DC resistance calculated from the low frequency intercept, Re is the electronic resistance calculated from the steady state polarisation curve and Ri is the computed ionic resistance. Such measurements can also be performed on entire cells and individual cells within the stack.

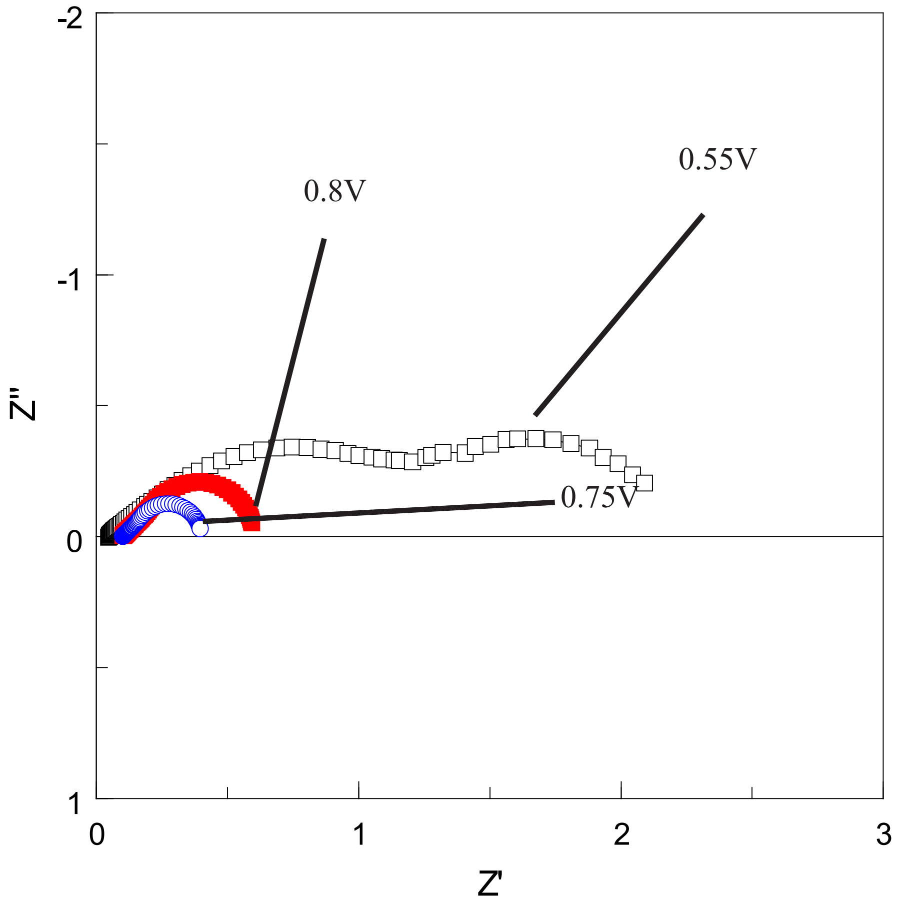


Figure 3: Simulated complex plane diagrams of a PEM cell (Hydrogen anode, Oxygen cathode). Each spectrum was recorded at the voltages shown in the diagram.

Activation Losses

The activation overpotential and hence the voltage drop associated with any anodic and cathodic process should be kept to a minimum. Furthermore, the exchange current density for either process should be high. However, the anodic process is significantly faster than the oxygen reduction reaction. Therefore, it is often assumed that all of the activation losses are associated with the cathode (oxygen reduction). The chemical stability of oxygen and hence the difficulties associated with the reduction process requires the use of effective catalysts such as platinum. This is one of the most expensive metals on the market and therefore a significant proportion of work has focused on improving the utilization of the catalyst or seeking possible less expensive alternatives. The following section describes some of the work on evaluating catalysts using EIS as a tool.

Figure 3 shows generic impedance plots for a hydrogen-oxygen fuel cell operated at three overpotentials. Since the reaction kinetics at the anode was significantly greater than the anode, it is assumed that the major activation loss occurred at the cathode. At low overpotentials (see reference 3 for experimental details), a single arc was observed with a high frequency slope of 45° terminating on the real axis which is indicative of the coupling of the distributed ionic resistance and capacitance in the catalyst layer. This is similar to the observations of Pickup and co-workers. Increasing the applied overpotential resulted in the decrease of the high frequency arc and this was attributed to the increased driving force for the electrode kinetics. However, further increase in the overpotential resulted in an increase of the diameter of the high frequency arc suggesting that oxygen mass transfer limitations in the catalyst layer were dominant. This is a subject we shall return to in the next section.

When probing the fundamental mechanisms in a fuel cell such as those mentioned in the previous paragraphs, the fuel source is generally pure and in the case of hydrogen, the CO has been removed. The method of choice for hydrogen production at the present time utilizes the reformation of methane according to,

$$\mathbf{CH_4 + H_2O \longrightarrow 3H_2 + CO}$$

Whilst this is an attractive fuel source for high temperature cells, this is potentially disastrous for low and mid-temperature cells using proton exchange membrane technology. Carbon monoxide occupies platinum sites thus reducing the effective surface concentration of platinum sites for the oxidation of hydrogen. Indeed, concentrations as low as 10 ppm are deemed unacceptable

Much work has focused on the characterisation and effect of poisoning of the anode by CO. Figure 4 shows a typical response for a single cell exposed to 50 ppm CO for 2 mins. The high frequency arc was not present even after short periods of exposure to CO thus demonstrating that the kinetics for the oxidation reaction had significantly reduced.

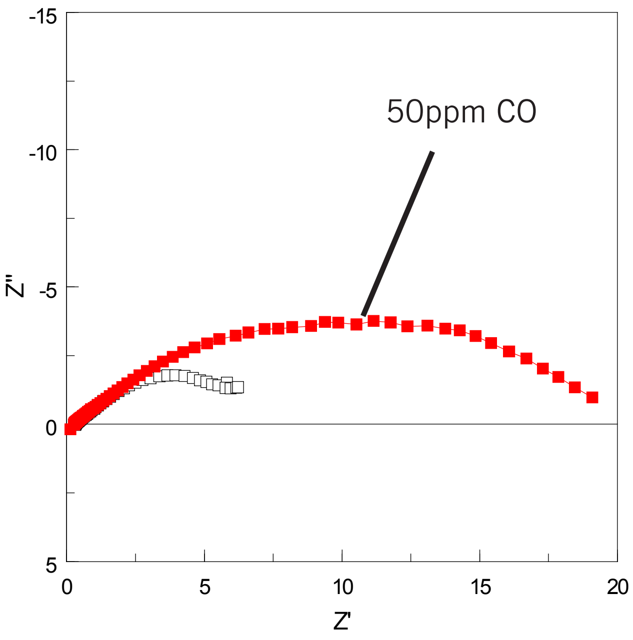


Figure 4: Nyquist diagrams of a 1 W DMFC operated at open circuit showing the effects of CO poisoning upon the kinetics of the electrode reactions.

Concentration Overpotentials

At high overpotentials, voltage losses associated with mass transport become significant. There are a number of papers that review this overpotential, degree of hydration and temperature upon the losses associated with poor mass transport. Springer and co-workers found that mass transport limitations of a PEM cell operating under a variety of conditions could be measured using impedance. (3) In brief, it was shown that as the overpotential increased, the diameter of the low frequency arc increased. At the highest overpotential, the low frequency arc dominated the impedance spectrum (no high frequency arc present). This behaviour was not observed when the cells were operated in pure oxygen environments. Therefore, the growth of the low frequency arc in the cathode experiments clearly demonstrates the effect of poor mass transport in the gas diffusion and catalyst layers. Figure 5 shows a simulated spectrum demonstrating the effects of mass transport limitations upon the impedance response of a PEM cell cathode.

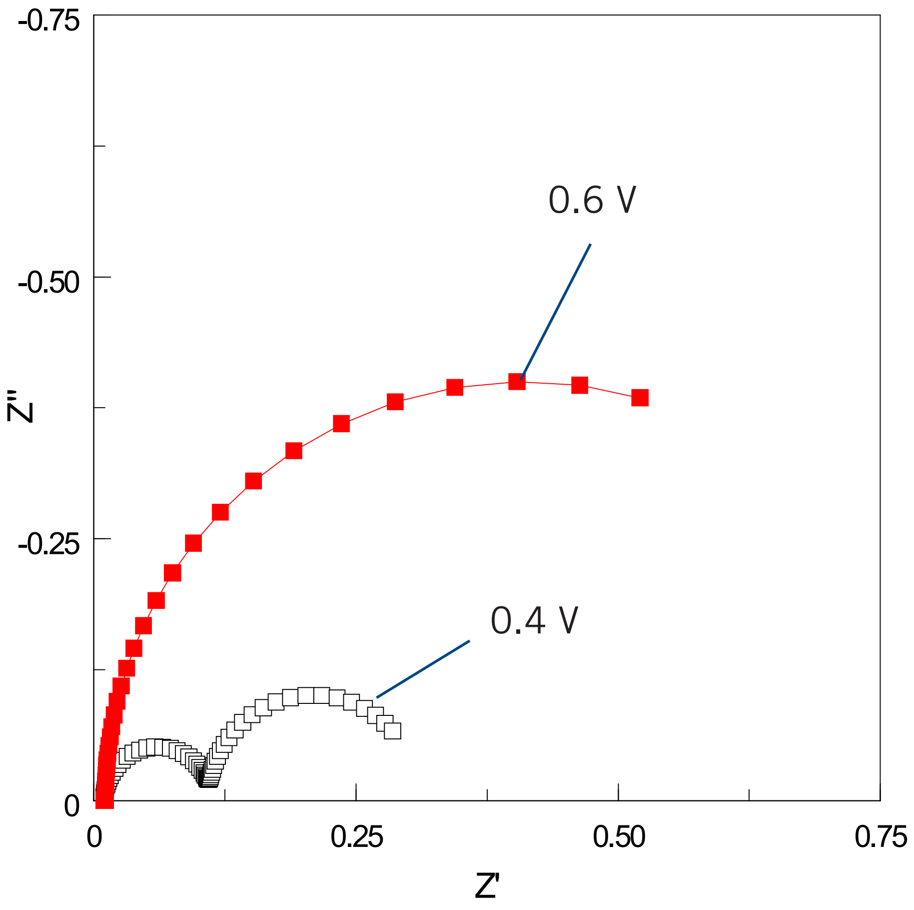


Figure 5: Simulated Nyquist diagrams of a Hydrogen-Oxygen cell operated at low and high overpotentials. Note the disappearance of the low frequency arc at high overpotentials indicating that diffusion of oxygen in the gas diffusion and catalyst layers dominates the impedance spectrum.

Conclusions

We have shown that EIS is a powerful tool for the determination of the cell losses and their source within a fuel cell. Such detailed investigations and analysis are often not possible with other DC electrochemical techniques.

References

1) **Fuel Cell Systems Explained, J. Larminie and A. Dicks, Wiley, 2003**

2) **M.C Lefebvre, R.B. Martin, P.G. Pickup, Electrochem & Solid State Letters, 2 (6), 1999, 259**

3) **T.E. Springer, T.A. Zawodsinki, M.S. Wilson and S. Gottesfeld, J. Electrochem. Soc., 143 (2) 1996, 587**

Recommended Reading

Solartron Analytical Technical Note 24, C. Gabrielli, 1984

Solartron Analytical ModuLab Technical Bulletin 1, C. B Sayers, 2008

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