LOCALISED ELECTROCHEMICAL IMPEDANCE MEASUREMENTS ON A SINGLE CHANNEL OF A SOLID POLYMER FUEL CELL

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ABSTRACT

A novel method of acquiring localised electrochemical impedance measurements (LEIS) in a solid polymer fuel cell (SPFC) is presented. Measurements were made at a constant reactant flow rate at a potential of 0.8 V and 0.6 V, each representing a different regime of operation as determined by localised dc measurements. The fuel cell on which the measurements were performed is a highly idealised one composed of a single linear flow channel. A distribution of impedance characteristics is seen along the channel with evidence of mass transport effects that are not evident from localised dc measurements. Localised membrane conductivity measurements did not show any variation along the channel at either of the potentials studied, as is expected from the fully humidified mode that the fuel cell was operated in. Simulation of reactant distribution has been achieved by using the known current distribution as an input into a simple flow model.

INTRODUCTION

The progress of Solid Polymer Fuel Cells (SPFC) from a promising alternative energy device to a commercially successful product depends on the solution of certain problems. These problems include lowering capital cost and increasing the fuel cell's efficiency. The best way to address these challenges is to gain a comprehensive understanding of how fuel cells function. The most direct way to achieve this understanding is by making detailed measurements of the parameters that affect fuel cell performance. This insight provides a means of determining which alterations to a fuel cell's design and operating conditions are most beneficial. As well as this empirical approach, data obtained will

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allow more sophisticated mathematical models to be constructed that realise a predictive pathway to system design. The purpose of our work is to ascertain how a SPFC is functioning by making these internal measurements. Presented here is the first report of localised impedance measurement in a fuel cell.

Various efforts to map the current distribution within both electrolysis cells (1) and inside SPFCs have been reported (2,3,4,5). Recently we have published results on a new approach which provides unparalleled time and distance resolution (6,7). Results show that there can be a dramatic variation in the current density at different parts of a fuel cell depending on the operating conditions. This spatial variation is influenced by factors such as reactant composition and humidity; operating temperature and pressure; pore flooding; hardware issues such as bipolar plate design and manufacturing inconsistencies; edge effects; moisture content of the membrane; orientation of the fuel cell and the load requirements. In addition, these factors are not all discrete variables since a complex interplay can exist between each of them. This makes it difficult to accurately control the conditions within the fuel cell that result in optimal performance. This emphasises the need to make internal measurements in real time.

One of the most insightful ways that fuel cells can be analysed is by making Electrochemical Impedance Spectroscopy (EIS) measurements. This technique has been applied to all varieties of fuel cells (8), as well as studies aimed specifically at the SPFC (9,10,11,12,13,14,15). This alternating current technique complements direct current measurements by providing a new dimension of information. Impedance measurements furnish values of membrane resistance, kinetic and mass transport information as well as giving an insight into the overall mechanism of operation. Since these factors are expected to change depending on the load, it is important that these measurements can be made at different operation potentials. One limitation to the application of EIS to larger fuel cells is that the bandwidth of most commercial loads operating at large current densities is not large enough to encompass the high frequency (ca. 10 kHz) features.

Localised impedance measurements will aid system design and performance optimisation but will also address a problem associated with using EIS with fuel cells. A fundamental limitation of conventional EIS when applied to fuel cells is that the measurement is performed on the entire cell i.e. the fuel cell is treated as a two-terminal device and a bulk measurement is made. This is only reasonable if the fuel cell is being operated under a mode in which local conditions are invariant within the fuel cell i.e. that there is an even distribution of reactant and current generation. In reality, such a mode of operation will rarely be encountered. One way in which this leads to inaccurate interpretation of EIS results is in the choice of the equivalent circuit with which the data is analysed. Various equivalent circuits have been proposed to mimic SPFC operation ranging from simple 4 component circuits to more complicated transmission line representations (16). The problem when choosing an equivalent circuit is that it must suit the bulk EIS result; when in actual fact different parts of the fuel cell may be fit to the equivalent circuit with very different parameters or may require a different equivalent circuit altogether. Thus knowledge of the way in which impedance characteristics vary should in itself lead to improved generic equivalent circuit design.

In this paper we describe localised impedance measurements in a simplified SPFC comprising of one linear channel. Such a simplified geometry allows significant
information to be determined whilst still providing a system that can be modelled (17). Our measurement system divides the current generated between many separate loads, thus allowing access to the whole range of applicable frequencies. This study looks at the cathode side of the fuel cell since most operating limitations are associated with delivery and reaction of oxygen, especially when using air as oxidant.

EXPERIMENTAL

The fuel cell system used was the same as that described in a previous paper (6). In essence the anode is supplied with hydrogen gas (100% relative humidity) via a cross-flow configuration that is machined into a graphite plate. Air is supplied to the cathode (dry) via a single channel that is 110 mm long, 2 mm wide and 1 mm deep. This channel is machined out of a printed circuit board that has 10 segmented current collectors running adjacent and along the channel. The current flows from each contact is and routed through its own individual electronic load circuit. The carbon diffusion layer adjacent to each contact is driven to the same potential with dynamic compensation for all electronic iR losses (i.e. in cables and at the MEA/contact interface). The system does not require a segmented MEA, as each contact drives local region of the MEA to the same potential and thus there is no lateral flow of current due to potential gradients. The MEA used was composed of a Nafion 112 membrane with 0.6 mg cm\(^{-2}\) PtRu on the anode and 0.6 mg cm\(^{-2}\) Pt on the cathode, and was supplied by Johnson Matthey. The catalysed area of the MEA was 120 mm \(\times\) 15 mm, although a significant part of the catalysed area away from the channel is not utilised on the cathode to produce current, as the only way that reactant can get to those regions is by lateral diffusion through the gas diffusion backing material.

The distinction between this and our previous work - in which DC current distribution was measured along the channel - is that all loads apply a potential on which is superimposed a small ac modulation from an impedance analyser (Solartron 1260). Measuring the local modulated current and potential at each load provides the impedance spectrum for that local region of the fuel cell. Figure 1 shows a simplified diagram of the system configuration.

In order to make measurements with non-segmented MEAs it is necessary to operate the fuel cell in constant cell potential mode - otherwise differences in cell potential at the gas diffuser would result in lateral current flow. Thus it is not possible to run the system at precise stoichiometries, and instead these must be determined after the experiment. In this paper the stoichiometry on the anode is approximately 10-20, and on the cathode in the range 1.1-2. Thus operation of the fuel cell is always governed by the cathode.
Localised impedance measurements can be made with this system since every contact is associated with its own load. This allows an ac signal to modulate all of the loads and the current measurement to be made on each load individually. This process ensures that there is no lateral current flow between contacts at different potentials, since each load is modulated in unison.

The modulation frequency ranged from 10 kHz to 0.1 Hz at an amplitude of 10 mV rms (as recommended by Parthasarathy et al. (9)). An air-flow rate of 20 cm$^3$ min$^{-1}$ and a hydrogen flow rate of 40 cm$^3$ min$^{-1}$ were used. The exhaust end of both the anode and cathode was at atmospheric pressure. The fuel cell temperature was under PID control and set to 30 ± 0.5°C. The large stoichiometric excess of hydrogen was used to minimise loses on the anode side and to ensure that the membrane was well hydrated. One hundred frequency points were collected (20 / decade) and an entire frequency scan took 450 seconds. All measurements were made with the system under steady-state conditions and the current profile along the channel did not change over the time required to collect all 10 spectra.
DC and EIS measurements were made at 0.8 V and 0.6 V. Figure 2(a) shows the current distribution along the length of the cathode flow channel at each potential. These two potentials represent two different operation regimes for this particular reactant flow rate. At 0.8 V the current is relatively evenly distributed along the channel (a standard deviation of only 42 mA cm\(^{-2}\) – i.e., 15% of the average current of 0.28 A cm\(^{-2}\)), whereas at 0.6 V after an initial plateau there is a significant loss of current density along the channel. This behaviour has been described before (6,7) and is attributed to a starvation effect, whereby the oxygen content of the air is depleted as the flow moves down the channel. This effect is confirmed by plots of oxygen utilisation as a function of position along the channel, also displayed in Figure 2(a). Operation at the higher potential means that the air flow rate has the capacity to satisfy the entire length of the channel, and at the end of the channel about half the oxygen in the air has been consumed. In comparison, at the lower potential the larger current at the start of the channel leaves the downstream channel depleted of reactant, and about 90% of the oxygen is utilised in the gas when it reaches the end of the channel.

![Figure 2](image)

**Figure 2:** Plot as a function of position down the channel the current density and cumulative utilisation, (a); and the high frequency real resistance, (b), (extracted from the results in Fig. 3) at cell potentials of 0.8 V and 0.6 V. Conditions described in the experimental section.
Figure 3a and 3b show the complex plane plots at different positions along the channel for operation at 0.8 V and 0.6 V respectively. It is immediately clear that the EIS response contains much more information than the dc measurements. In this paper we only make qualitative assessments of the Impedance data and concentrate on the lower frequency features.

**Figure 3:** Complex plane EIS plots as a function of distance along the channel at cell potentials of 0.8 V, (a); and 0.6 V, (b). Conditions as for Fig. 2. Square points represent decadic frequencies (0.1, 1, 10, 100, 1000, and 10,000 Hz).
At 0.8 V, Figure 3a, a clear trend is observed as the arc radius increases with distance along the channel. The dc response shows no sign of a decrease in current density along the channel so the reaction is not being limited by reactant consumption. However, reactant is being consumed along the channel so there will be a depletion of oxygen in the channel and diffuser. This increase in the arc radius at low frequencies has been attributed to oxygen diffusion limitation in the diffuser of the electrode (10,11,15). It has been proposed that this limitation is due to the impediment of oxygen diffusion through nitrogen in the pores of the diffuser. Evidence to support this comes from the fact that no low frequency arc is observed for operation with pure oxygen and the arc radius is seen to increase when the thickness of the backing layer is increased (18,19).

The same work also shows that the characteristic frequency of the low frequency arc (corresponding to the maximum imaginary component of the semicircle) is a measure of the thickness and tortuosity of the backing layer. The characteristic frequency for all of the arcs in the 0.8 V case share a similar frequency (1.3 ± 0.7 Hz). This consistency is indicative of a diffuser with an even thickness and tortuosity distribution. The EIS profile for the contact at the exit end of the channel does not follow the trend; we believe that these smaller arcs are due to edge effects, or due to the open-ended operation.

The EIS plot at 0.6 V shows a different trend as a function of position down the channel. The first four contacts exhibit the same opening of the arc as seen at 0.8 V, but the subsequent plots show a distinct direction change away from the closing of the semicircle. The deviation initially approximates to a vertical profile before bending back, with the later contacts showing a transfer of the impedance into the negative real resistance quadrant. Higher flow rates in the channel (i.e. greater flux of reactants) delay this transition (results not shown). This means that a situation exists in which an increase in reactant consumption, with a corresponding current increase, at one point in the fuel cell (brought about by a decrease in cell voltage) can cause a decrease in current at another point of the fuel cell. We have already shown how reactant starvation in a channel can result in a decrease in local current when the cell voltage decreases, leading to negative polarisation plot gradients (6). The impedance feature seen here, where the plot curves backward into the negative real resistance quadrant, is a manifestation of operation under conditions of reactant starvation.

The transformation of the impedance plot into a negative resistance loop can be understood by considering the individual dc polarisation plots for each contact. Figure 4(a) shows a dc polarisation plot at a point 0.07 m from the start of the channel. The polarisation plot shows an initial increase in current with decreasing cell potential, this reaches a maximum at about a cell potential of 0.4 V after which the current decreases. The slope of the VI plot changes sign, and in the limit of very low frequencies the differential resistance thus also changes sign. The reason for this change in slope is that as the cell potential is decreased the cumulative utilisation of reactants at a given point along the channel increases. When the reaction occurring on the electrode is entirely under diffusion control, the decrease in partial pressure of the oxygen in the channel results in a decrease of local current density. This aspect of the VI response has been reported previously (6).
Thus we would expect that the EIS response at cell potentials above 0.4 V to appear normal, and for the low frequency response at potentials below 0.4 V to appear in the negative real quadrant. EIS plots at a point 0.07 m from the start of the channel as a function of cell potential are shown in Fig. 4(b). Because of the use of a wider channel (3 mm vs. the 1 mm wide channel used in Fig. 3), two arcs are seen in the EIS plots, resulting from the larger iR drop in the gas diffusion medium. For the potentials at which the VI curve has not folded back on itself, the EIS responses appear normal. For cell potentials below this value, the EIS responses at low frequency fall in the negative real impedance quadrant.

The impedance measurements taken at various polarisations show how operation in the regime after the maximum current point results in formation of a negative resistance loop. The impedance response at this potential contains high frequency information related to membrane conductivity and reaction kinetics but the low frequency range picks up the starvation effect and is manifest by the negative resistance loop which starts to form at ca. 0.5 Hz. This value is characteristic of reactant flow rate in the channel (5 cm s⁻¹ average gas flow rate).

If we now compare the localised EIS measurements with the total averaged response of the entire cell, the potentially misleading nature of a bulk EIS measurement can be appreciated. Figure 5 compares the localised response at 0.8 V and 0.6 V for the local measurements at the start and end of the channel, along with the average response of the entire cell.

Taking the 0.8 V case first, Fig. 5(a), we can see that the combined response is of the same general shape as that at the start and end of the channel. So in this case the global response is an accurate indicator of the local response, although any precise numerical
parameters determined from the analysis of the arc cannot be totally relied upon. However, the response at 0.6 V, Fig. 5(b), shows that there is a significant difference between the response at the start, the end and the average response. The EIS response at low frequency taken at the start of the channel exhibits no sign of reactant limitation; the response at the end shows that reactant starvation is occurring due to upstream consumption of reactant and the global response is that of an overall mass transport limitation i.e. the response is purely capacitive. In this case, a conventional global EIS measurement would be misleading if it were assumed that the fuel cell was reacting homogeneously.

![Figure 5: Comparison of the EIS response at 0.8 V, (a), and 0.6 V, (b) at the start, the end and for the global average of the channel. Conditions as for Fig. 3.](image)

**Figure 5:** Comparison of the EIS response at 0.8 V, (a), and 0.6 V, (b) at the start, the end and for the global average of the channel. Conditions as for Fig. 3.

Membrane Conductivity Profiles

Localised impedance measurements also allow membrane conductivity maps to be generated from the real impedance measured at high frequency (11). Figure 2(b) shows the membrane resistance distribution along the channel for the two set potentials. It can be seen that there is little variation in membrane resistance along the length of the channel or between the two set potentials. This result suggests that under the operating conditions used, external factors such as the drying effect of the reactant flow do not affect the membrane, or at most affect the membrane in a uniform manner along the channel.

The average resistance at 0.8 V is slightly higher than in the 0.6 V case although this difference is probably within experimental error. It has been reported that variation in the membrane resistance with current density, reactant humidification level and temperature is not significant for thin electrolyte layers. Since the solid electrolyte used in the MEA is Nafion® 112, no notable variation along the channel or between each operating
potential is expected. However, more extreme conditions, such as operation at higher
temperature or low stoichiometry and without external humidification are expected to
show such effects. We are currently examining these operation regimes.

These results are another demonstration of the need to fully understand how the fuel
cell operates in order to determine the optimal settings of operating parameters. It also
shows how conventional impedance measurements on the bulk fuel cell would not be
representative of how the system is actually performing, especially under low
stoichiometry conditions.

Visualisation of Reactant Distribution in the Channel

Knowledge of the channel current distribution and utilisation of a simple flow model
allows for the visualisation of reactant concentration distribution along the length of the
channel and gas diffuser. The model is set-up with two separate regions, the flow
channel and the gas diffuser. A continuity boundary condition is set between these two
regions and the catalyst layer is assumed to be infinitely thin and therefore stated as a
boundary. In the solution domain we solve the Nernst-Plank equation:

\[-D_\text{O}_2 \cdot \left( \frac{\partial^2 \text{O}_2}{\partial x^2} + \frac{\partial^2 \text{O}_2}{\partial y^2} \right) + \mathbf{u} \cdot \left( \frac{\partial \text{O}_2}{\partial x} + \frac{\partial \text{O}_2}{\partial y} \right) = R_i\]

Where \(D_\text{O}_2\) is the diffusion coefficient, \(\mathbf{u}\) is the velocity vector, and \(R_i\) is the reaction
rate, which in our case is zero, as we treat the reaction layer as a boundary. The
independent variables \(x\) and \(y\) refer to the direction along and across the channel
respectively.

The gas velocity in the channel was set as for the experiment, but convection in the
diffuser is not considered since diffusion is the dominant mode of transfer. The effective
diffusion coefficient in the diffuser was corrected to account for the porosity of the
medium according to the equation (\(\varepsilon\) is the porosity, and in our case is equal to 0.75):

\[D_{\text{O}_2}^{\text{eff}} = D_{\text{O}_2} \cdot \varepsilon^{1.5}\]

To overcome the scaling problem rising from the significant difference between the
length of the channel and the width, the equation had to be rewritten in a dimensionless
form with the introduction of new dimensionless independent variables. The boundary at
the edge of the diffuser towards the membrane was segmented into ten individual regions
to conform to the experimental setup. The current, and therefore reactant flux, at each
contact was input as recorded in the experiment. The oxygen concentration at the
channel input was set to have a partial pressure of 0.21, with the exit concentration unspecified.

Since the finite element method was employed, there was no need to specify internal boundary conditions, all the other boundary conditions apart from the catalyst layer were set to:

\[ \frac{\partial c_{O_2}}{\partial x} + \frac{\partial c_{O_2}}{\partial y} = 0 \]  

[3]

The equations for this system were solved using FEMLAB\textsuperscript{®} for the two different operating conditions and the results are shown in Figure 6. The model shows how the higher overpotential (0.6 V case) results in greater utilization of reactant and subsequently more rapid decrease in the concentration of oxygen along the channel compared to the 0.8 V case. In the 0.6 V case it can be seen that there is significant depletion of reactant in the diffuser towards the end of the channel, whereas in the 0.8 V case the amount in the diffuser is ample enough to satisfy the current requirement along the length of the channel.

![Figure 6: Visualisation of reactant concentration in the cell operating at 0.8 V and 0.6 V. The air enters from the right hand side.](image)
This model, along with the data that our system generates combines to provide a useful visualization tool that can show how the reactant profile varies in the diffuser and into the depth of the channel. Such information may be useful in the interpretation of impedance results where mass transport limitation is a major feature of the response.

CONCLUSION

Localised electrochemical impedance measurements in an SPFC over a frequency range of 0.1 Hz to 10 kHz has been demonstrated for the first time. The technique illustrates how reactant starvation occurs along the flow channel and shows that dc measurements alone are not enough to properly characterise the operation of a fuel cell. These results also show that care should be taken when performing bulk EIS measurements, since there may be significant variations in the performance of the fuel cell that will not be appreciated unless localised measurements are performed. This system is ideal for monitoring fuel cell performance and is a valuable tool for system design. The impedance results emphasise the complex nature of making ac measurements on fuel cells.

Measured dc current distribution has been used as input to a simple flow model to provide a means of reactant distribution visualisation in the channel. Such information may be useful in the interpretation of impedance results where mass transport limitation is a major feature of the response. Future work will involve fitting results to equivalent circuits to obtain quantitative parameters; developing more sophisticated equivalent circuits and performing measurements on different flow field geometries and operating conditions.

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