Electrochemical pressure impedance spectroscopy applied to the study of polymer electrolyte fuel cells

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Abstract

The development of novel *in-situ* diagnostic techniques allows new insight into the internal working of polymer electrolyte fuel cells (PEFCs) so that improved performance can be realised. Electrochemical impedance spectroscopy (EIS) is a widely used characterisation technique that takes advantage of the dynamic relationship between current and voltage to deconvolute critical mechanisms and sources of performance loss occurring with different time constants. Here, we apply electrochemical pressure impedance spectroscopy (EPIS) which examines the transfer function relating reactant gas pressure modulation to the electrical response of the fuel cell. A sinusoidally oscillating perturbation is applied to the cathode backpressure using an innovative loudspeaker arrangement and the resulting voltage perturbation is monitored across a frequency range while the fuel cell is operated in galvanostatic mode. It is shown that the technique can be used to separate the explicit effect of water management from reactant starvation when a PEFC is operated under different reactant humidification conditions.

Keywords

Electrochemical pressure impedance spectroscopy; polymer electrolyte fuel cell; backpressure; transfer function analysis; water management; mass transport limitation.

1 Introduction

The polymer electrolyte fuel cell (PEFC) has shown great promise as a power source for a range of applications due to its relatively high efficiency and low temperature operation [1, 2]. While ostensibly a simple electrochemical device, there are many complex and highly coupled processes that occur in PEFCs which determine the performance and durability [3]. Novel *in-situ* diagnostic techniques are required to develop a greater understanding of the processes occurring inside fuel cells so that improved operating conditions can be identified and the benefits of alternative components and materials realised. Electrochemical impedance spectroscopy (EIS) is a powerful and well-established diagnostic technique for electrochemical systems based on analysis of the transfer function between voltage and current [4, 5]. A periodic current (or voltage) stimulus is applied over a range of frequencies and compared to the voltage (or current) response. The relative amplitude and phase shift of the signals can be calculated at each frequency to decouple processes with different time constants. For example, EIS can be performed on PEFCs to identify kinetic, Ohmic, and mass transfer impedances.

There is the potential for the transfer function relationship between other parameters to be used to gain new insight into electrochemical systems. For example, the relationship between electrochemical performance and heat generation, using so-called electro-thermal impedance spectroscopy, has been reported [6-12].

The relationship between gas pressure and electrochemical performance, using electrochemical pressure impedance spectroscopy (EPIS), has been used to study the pressure dynamics in metal–air batteries under voltage and current cycling. Hartmann *et al.* [13] developed a system in which the pressure of an oxygen reservoir in a sodium-oxygen battery was varied and the electrochemical response was measured for selected frequencies. Grübl *et al.* [14] verified the work with a mathematical model of the cell. Niroumand *et al.* [15] demonstrated the voltage response under cathode pressure perturbation at a single frequency, noting that the pressure and voltage were counter-intuitively out of phase; as pressure increased, potential decreased. They identified this could have been because of dynamics of water at the catalyst layer.

In this work, the reactant gas pressure is perturbed and the electrical response monitored; the opposite of the cause-effect relationship is not investigated.

It is well known that the performance of a PEFC can be improved by applying a backpressure to the cathode [16-21]. The performance improvement becomes more pronounced at higher current density [17] but can also detrimentally increase gas crossover, cost, size, and weight of a PEFC system. Furthermore, the increased partial pressure of reactant gas has an influence on the Nernst potential and the current distribution due to the higher oxygen concentration at the cathode [22], with a consequent decrease in membrane resistance due to the increase in membrane water content [23].

By studying the relationship between reactant gas pressure and electrochemical response as a function of modulation frequency, it is possible to separate these different effects. In itself, this is a powerful diagnostic but it is also highly complementary to EIS, as processes that cannot be resolved due to similar time constants in the current/voltage regime may be determined by EPIS, e.g. mass transport effects associated with a hydration imbalance caused by water build-up or changes in reactant distribution.

2 Experimental

2.1 Rig and fuel cell design

A fuel cell test station (Scribner Associates, USA) was used to supply heated and humidified hydrogen gas to the fuel cell anode and air to the cathode. Hydrogen (99.995% purity, BOC plc, UK) was fed to the anode and zero grade air (21% O_2, BOC, UK) to the cathode at 60 °C and either 70% relative humidity (RH) or dry. Flow rates of gases were fixed at 100 mL min^{-1} and 250 mL min^{-1} to the anode and cathode, respectively. A commercially available fuel cell (Scribner, Alvatek, UK) was used with an active area of 5 cm^2 and double-serpentine flow-fields. MEAs were produced in-house using HP Nafion electrolyte (Nafion Store Europe, Germany) and Johnson Matthey 0237 platinum electrodes (Johnson Matthey Fuel Cells, UK). The Pt loading on both anode and cathode was 0.4 mg cm^{-2}.

An IviumStat potentiostat (Alvatek, UK) was used to apply constant currents to the fuel cell system while measuring the voltage. The cathode backpressure relative to atmosphere was measured directly downstream of the fuel cell with a pressure transducer (Honeywell 162PC01D, RS Components Ltd., UK).

2.2 Pressure Modulation

The experimental system used to apply the pressure modulation to the fuel cell is illustrated in Figure 1. For fixed cathode pressure measurements, a manual backpressure valve (Scribner Associates, Alvatek, UK) was used to apply pressure between 0 and 62 kPa gauge. For dynamic modulation (EPIS) measurements, the cathode backpressure was modulated using a loudspeaker (Visaton WS 17 E, RS Components Ltd., UK) in a Perspex jig.

The cathode backpressure was modulated by applying a sinusoidal current to the speaker using an IviumStat potentiostat (Alvatek, UK). The resultant amplitude of the pressure ‘front’ at the fuel cell was 60 Pa for the investigated frequency range.

3 Results and discussion

As previously reported [22], increased backpressure results in increased performance; the effect at OCV is relatively small but the performance enhancement becomes more pronounced with increasing current density [17, 18, 21]. While the reactant gas pressure affects the Nernst potential at all current densities, the effect of a higher pressure has a much more significant effect on the PEFC performance [18, 22]. In the system under study, between 62.1 and 0 kPa gauge there is an improvement of ~150 mV at 1600 mA cm^{-2}, as opposed to just 10 mV at OCV. As the effect is most significant at higher current densities, it is likely due to factors relating to water management and reactant access.

By analogy to EIS, the minimal modulation that can deliver a measurable response should be used in order to ensure a linear relationship between cause and effect and perturb the fuel cell as little as possible. The speaker system provided a peak amplitude pressure perturbation of 60 Pa across the measured frequency range. While this is several orders of magnitude lower than the pressures in Figure 1, it was large enough to elicit a transient voltage response. The maximum observed fuel cell voltage response to the pressure perturbation was 5 mV, which is comparable to the amplitude of a perturbation required to perform EIS on a system of a similar size [4].

The upper frequency limit of the cathode backpressure perturbation was determined by the magnitude of the fuel cell voltage response. The lower frequency limit was determined by the amplitude of the pressure perturbation; below 10 mHz the pressure perturbation began to drop below 60 Pa.

A sinusoidal fit over a minimum of 8 cycles was applied to the backpressure perturbation and voltage response signal at each frequency using Equation 1:

$$P, V\ (\mathrm{Pa}, \mathrm{V})\ = A_{P,V} \sin\left(2\pi f t + B_{P,V}\right) + C_{P,V}$$ **Equation 1**

Where *A* is the peak amplitude of the wave, *f* is the frequency, *t* is the time, *B* is the time offset, and *C* is the fixed backpressure (*P*) or voltage (*V*) offset. The amplitude ratio (AR) at each frequency is taken as the relative peak amplitude of the voltage response and backpressure perturbation.

$$\mathrm{AR}(\mathrm{V\ Pa}^{-1}\ ) = \frac{A_V}{A_P}$$ **Equation 2**

The phase shift is the difference in the time offsets between the voltage and the backpressure.

$$\emptyset(\mathrm{degrees}) = (B_V - B_P)\frac{180}{\pi}$$ **Equation 3**

By plotting the amplitude ratio and phase shift as a function of frequency, the EPIS Bode plots for the fuel cell could be generated for varying current densities (Figure 2).

At OCV (0 A cm^{-2}) the amplitude ratio is insensitive to modulation frequency and has an average value of 1.5 × 10^{-7} V Pa^{-1} across the range, consistent with a Nernstian response at 70 °C. The amplitude ratio at each of the other load levels reaches a steady state maximum value below 100 mHz, which increases with current density. Normalisation of the data in Figure 2 shows that at each current density above 0 A cm^{-2}, the characteristic corner frequency, the frequency at which the electrical response begins to reduce relative to the pressure perturbation, does not change. For each, the response tends to near 0 V Pa^{-1} above 70 Hz. It follows that the effect of pressure modulation is most significant at lower frequencies, associated with processes having a characteristic frequency below ~ 1 s.

It is clear that pressure modulation has an increasing effect on cell voltage with increasing current density. This is due to pressure having an increased effect on cell performance at higher polarisations and lower stoichiometries, where there are also water management issues. Moreover, the amplitude ratio increases more rapidly below 10 Hz at each current density, with increasing polarisation due to the cell operating nearer the limiting current density; the stoichiometric ratio decreases from greater than 7 at 0.4 A cm^{-2} to 2.5 at 1.2 A cm^{-2}.

Interpretation of phase shift in EPIS is quite different from that in EIS. This is because the phase is a strong function of the cell geometry and the location of the pressure oscillation source relative to the cell. The phase shift does not vary significantly with polarisation and increases with increasing frequency. This can be attributed to the gas volume required for the pressure 'front' to affect the fuel cell voltage. As the frequency increases, the wavelength of each pressure perturbation decreases; thus more than one pressure perturbation may be required before a voltage response is observed in the PEFC and the phase shift can exceed -360°; given that the distance between the point of pressure measurement and the point at which the pressure 'front' first affects the fuel cell is fixed, the phase shift will tend to negative infinity. There is potential here to examine how flow is distributed in a fuel cell by examining the localised EPIS phase shift using a segmented current collector or reference electrode array, analogous to localised EIS [24-26]. Furthermore, diffusion of gas to the catalyst surface can be examined by comparing the phase shift of a system using air to one with helox, a mixture of helium and oxygen, in which diffusion will be an order of magnitude faster [18]. By a similar reasoning, the diffusion of oxidant to the catalyst layer through different gas diffusion and micro-porous layer materials can be examined, quantifying this effect.

Phase shift data at OCV is not included due to the relatively small amplitudes of the signals providing unreliable phase shift data.

In order to demonstrate the potential of EPIS to provide new information about PEFC operation, the effect of different reactant gas humidification conditions was examined. The effects of stoichiometry were normalised by fixing the flow rates and polarisation for each humidity condition. Figure 3(a) compares the polarisation curve performance when supplying gases with 70% relative humidity to both electrodes with that using a dry cathode/70% RH anode and a 70% RH cathode/dry anode. In accordance with previous studies, there is a significant drop in performance when inlet streams are not humidified [21, 23]. Moreover, fuel cell performance is particularly sensitive to anode humidity as water is generated at the cathode but not at the anode [23]. From the EIS Nyquist plot in Figure 3(b), the high frequency impedance at 800 mA cm^{-2} increases from 150 mΩ cm^{2} when both steams are humidified to 220 mΩ cm^{2} and 250 mΩ cm^{2} when the cathode and anode respectively are supplied with dry gases. Moreover, the low frequency impedance also increases when dry gases are supplied. This has been previously reported by Kim *et al.* [27] who attributed a higher ionic resistance to the increasing low frequency impedance.

When considering the EPIS response, it should be noted that the same current density and reactant flow rates were used in each case to eliminate the variables of stoichiometry and oxygen partial pressure in the cathode feed. Figure 3(c) shows that, below 1 Hz, the EPIS amplitude ratio when both inlet streams are humidified is near 10×10^{-6} V Pa^{-1}. This value increases to 15×10^{-6} V Pa^{-1} when the cathode is dry and 25×10^{-6} V Pa^{-1} when the anode is dry. Thus, the larger amplitude ratios observed when the anode or cathode were supplied with dry gas can be attributed to the fact that the humidification and thus water balance of the system is more sensitive compared to having both streams humidified. Furthermore, when comparing EIS to EPIS, it can be observed that below 1 Hz, there is little change in the magnitude of the EPIS response, which corresponds to the low-frequency intercept with the real axis in the EIS. Discounting the difference in the high frequency intercepts, it is observed that the frequency range over which the EIS responses diverge corresponds to ca. 100 Hz to 1 Hz, the same range over which the EPIS responses change and diverge. The two techniques are therefore complementary and can confirm that the difference in performance is a consequence of water management effects. Moreover, the equipment required to perform EPIS is cheaper than that for EIS and may lend a means to determine low frequency fuel cell behaviour at a lower capital cost.

4 Conclusion

EPIS has been developed and successfully applied to an operating PEFC for the first time to determine the frequency-dependent relationship between cell voltage and a periodic cathode backpressure perturbation. The amplitude ratio between the voltage response and pressure perturbation increased with increasing polarisation due to the more significant effects of altering partial pressure of oxygen and water management issues at higher current densities. In order to eliminate the effects of reactant partial pressure, the system was investigated under varying inlet gas humidity conditions. The amplitude ratio increases when dry rather than humid gases are supplied to the fuel cell, implying that water imbalances can be indirectly measured using EPIS, providing complementary information to EIS.

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Figure Captions

Figure 1 – Schematic diagram of the experimental rig (a) and inset photo of speaker and housing (b).

Figure 2 – EPIS Bode plots (amplitude ratio – top, and phase shift – bottom) at varying current densities. 60 Pa peak amplitude pressure stimulus. Both anode and cathode gases were humidified at 100 mL min^{-1} and 250 mL min^{-1}, respectively.

Figure 3 – Effects of supplying 70% RH and dried inlet gases on the polarisation curves (a), EIS Nyquist plots (b), and EPIS amplitude ratio Bode plots (c). In the case where the anode was dry, the cathode was humidified and vice-versa. Operated at 70 °C, hydrogen supplied at 100 mL min^{-1}, air at 250 mL min^{-1}. EIS between 100 kHz and 100 mHz at 800 mA cm^{-2}, peak amplitude of 20 mA cm^{-2}. EPIS between 100 Hz and 10 mHz with a peak amplitude of 60 Pa, operated galvanostatically at 800 mA cm^{-2}.