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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 a loudspeaker arrangement and the resulting voltage perturbation is monitored. 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.

1. Introduction

The polymer electrolyte fuel cell (PEFC) has shown great promise as a power source for a range of applications [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. 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. 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 [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 [13]. Grübl et al. [14] verified the work with a mathematical model of the cell and Niroumand et al. [15] demonstrated the voltage response under cathode pressure perturbation at a single frequency.

In this work, the reactant gas pressure is perturbed and the electrical response monitored.

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

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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 5 cm^2 fuel cell with double-serpentine flow-fields was used with MEAs produced in-house using HP Nafion electrolyte (Nafion Store Europe, Germany) and Johnson Matthey 0237 platinum electrodes (Johnson Matthey Fuel Cells, UK, Pt loading 0.4 mg cm^{-2}).

A 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).

2.2. Pressure modulation

The experimental system used to illustrated in Fig. 1. For fixed cathode pressure measurements, a manual backpressure valve (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) in a Perspex jig.

The cathode backpressure was modulated by applying a sinusoidal current to the speaker using an 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. 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 Eq. 1:

$$P, V\ (\mathrm{Pa, V}) = A_{P,V}\ \sin(2\pi ft + B_{P,V}) + C_{P,V} \tag{1}$$

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.

$$\mathrm{AR}\left(\mathrm{V\ Pa^{-1}}\right) = \frac{A_V}{A_P} \tag{2}$$

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

$$\varnothing(\mathrm{degrees}) = (B_V - B_P)\frac{180}{\pi} \tag{3}$$

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 (Fig. 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

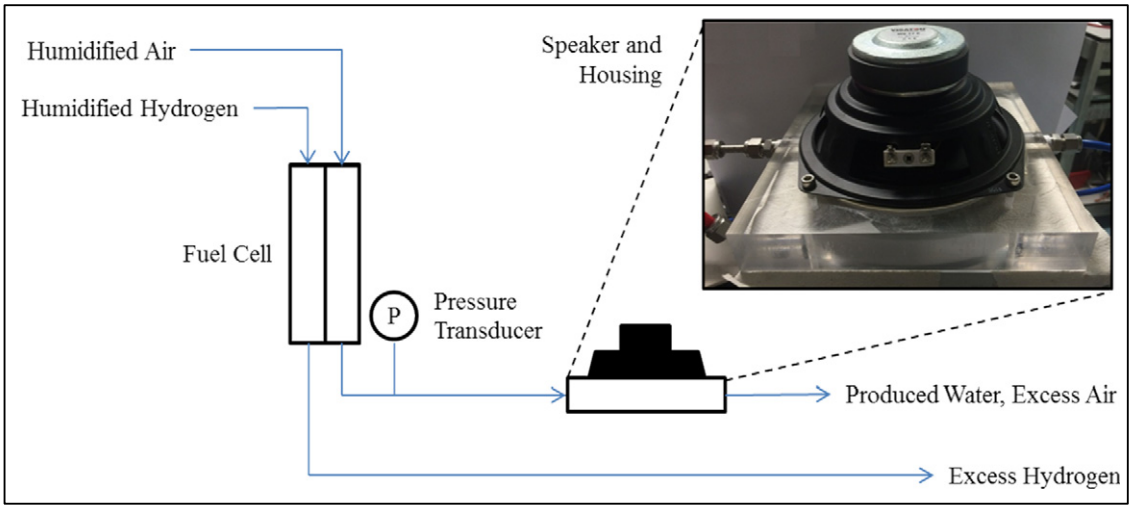

Fig. 1. Schematic diagram of the experimental rig (a) and inset photo of speaker and housing (b).