



Pressure–voltage oscillations as a diagnostic tool for PEFC cathodes

Amir M. Niroumand^{a,*}, Walter Mérida^b, Michael Eikerling^c, Mehrdad Saif^a

^a Engineering Science Department, Simon Fraser University, Burnaby, BC, Canada

^b Department of Mechanical Engineering, University of British Columbia, Vancouver, BC, Canada

^c Department of Chemistry, Simon Fraser University, Burnaby, BC, Canada

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ABSTRACT

In this work, pressure-induced voltage oscillations are explored as a novel diagnostic tool for PEFC cathodes. In this method, a small signal oscillation is imposed on the cathode outlet pressure. As a response to this pressure perturbation, the fuel cell voltage exhibits oscillations with the same frequency. The amplitude ratio and phase difference between the voltage and pressure oscillations embody diagnostic information about the operating conditions and processes in the PEFC cathode.

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1. Introduction

Polymer electrolyte fuel cells (PEFCs) are electrochemical cells that combine hydrogen and oxygen to produce electricity. Diagnostic tools can be used at different stages of their life cycle to improve their performance, reliability, and lifetime [1]. During product development, diagnostic tools provide understanding of the dynamical processes, resulting in product optimization [2,3]. During operation, diagnostic tools are used for early detection and isolation of faults in the system, allowing the control system to take compensatory actions [4–8]. In Refs. [7,8], we reported a diagnostic algorithm that can isolate the voltage drop resulting from low flow rates at anode or cathode. The algorithm is based on the observation that reducing the anode stoichiometry to low values does not have any observable effect on the cell voltage, while reducing the cathode stoichiometry results in an increase of the amplitude of cell voltage fluctuations. In experiments, we observed that cell voltage fluctuations were periodic, with a frequency similar to that of the cathode outlet pressure [9]. We propose using the voltage to pressure amplitude ratio and the phase shift between voltage response and pressure perturbation signal to obtain diagnostic information about the fuel cell cathode.

In the rest of this letter, we first explain the experimental hardware used to obtain the data, followed by experimental results that establish the correlation between cathode output pressure and cell voltage oscillations. Finally, we propose a methodology to exploit

pressure–voltage spectroscopy as a diagnostic tool for PEFC, furnished with capabilities similar to impedance spectroscopy.

2. Experimental setup

Testing was performed on a single cell with an active area of 49 cm². A Nafion 112 membrane was used with an anode and cathode platinum loading of 0.1 and 0.4 mg Pt/cm², respectively. A 200 μm Toray carbon paper was used for both anode and cathode GDLs. Cross flow fields with a channel cross section of 1 × 1 mm were used with 36 passes on the anode and 38 passes on the cathode side.

The fuel cell temperature was controlled by circulating hot water into a separate pair of flow fields sandwiching the fuel cell. Anode and cathode input flow rates were controlled using mass flow controllers upstream of the fuel cell, and the output pressures were controlled using a pressure control valve downstream the fuel cell. Anode and cathode streams were humidified using bubbling humidifier and heated using tape heaters around the connector tubing between the humidifier and PEFC. The set points used for these parameters are shown in Table 1.

3. Results and discussion

To reproduce anode and cathode low flow regions, we operated the cell at a fixed current density of 500 mA/cm², and other operating conditions as in Table 1. In the first experiment, we fixed the anode stoichiometry at 1.7, and reduced the cathode stoichiometry from a high value of 2.4 with steps of 0.1, until the cell voltage reached zero volts. In the second experiment, we fixed the

* Corresponding author. Address: Engineering Science Department, Simon Fraser University, 8888 University Dr, Burnaby, BC, Canada V5A 1S6. Tel.: +1 604 782 4407. E-mail address: amniroum@sfu.ca (A.M. Niroumand).

Table 1
Fuel cell operating values.

Parameter	Value
Cell temp. (°C)	80
Anode temp. (°C)	50
Cathode temp. (°C)	50
Anode dew point temp. (°C)	40
Cathode dew point temp. (°C)	40
Anode pressure (psi)	30
Cathode pressure (psi)	30

cathode stoichiometry at 2.4, and reduced the anode stoichiometry from 1.7 with steps of 0.1, until the cell voltage reached zero volts. The results of these experiments are shown in Fig. 1.

We can see in Fig. 1a that the amplitude of fuel cell voltage oscillations grows in amplitude with the reduction in cathode stoichiometry. Fig. 1b reveals no correlation between the anode stoichiometry and the cell voltage oscillations, until very low anode stoichiometries are reached. At this point, the anode starves from low hydrogen concentrations, and the cell voltage drops to zero. We used these properties in Refs. [7,8] to design a diagnostic algorithm that isolates anode and cathode low flow rates during real time operation of fuel cell.

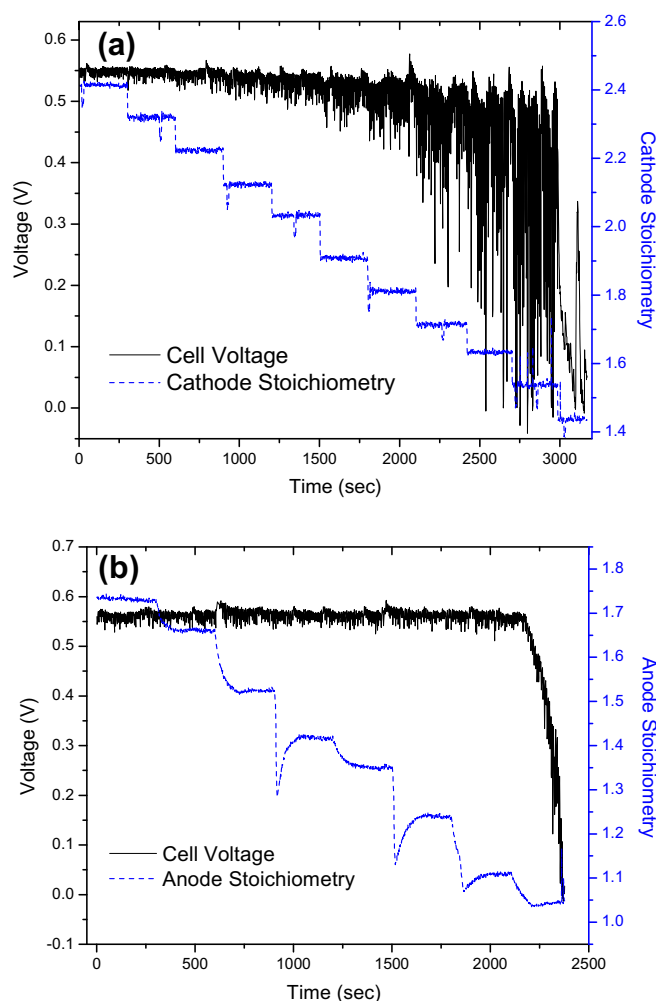


Fig. 1. Cell voltage at a fixed current density of 500 mA/cm². (a) Cell voltage and cathode stoichiometry versus time at a fixed anode stoichiometry of 1.7. (b) Cell voltage and anode stoichiometry versus time at a fixed cathode stoichiometry of 2.4. The slow settling time for anode stoichiometry is due to the PID parameters of the anode mass flow controller.

The dependence of the cell voltage oscillation amplitude on cathode stoichiometry suggests that the oscillations are primarily a cathode effect. Understanding the dynamical processes that result in these oscillations contribute to understanding structural effects on transport properties on the cathode side. This could be insightful in view of designing fuel cells with lower air flow requirements.

To understand the origin of cell voltage oscillations, Kulikovskiy et al. [10] operated a PEFC at a current density of 300 mA/cm², with cathode stoichiometries of 1.3 and 2.6. They reported voltage oscillations only at the lower stoichiometry. They showed that non-uniform oxygen concentration in the cathode flow field at low stoichiometry results in different possible voltages at a fixed current density (steady state multiplicity), hence voltage fluctuations.

Schneider et al. [11,12] showed that during impedance measurement, when an ac current is superimposed on the fuel cell load at frequencies below 10 Hz, it results in the oxygen concentration to oscillate in the cathode flow field channel. Using a segmented cell and mathematic modeling, they showed that this in turn affects the cell voltage oscillations downstream the cathode flow field. Note that the oscillations reported in Refs. [11,12] are forced by external excitation, while voltage fluctuation caused by low flow rates reported in Ref. [10] were self-sustained.

To understand the origin of cell voltage oscillations for our system, we have graphed 50 s of the cell voltage of Fig. 1a, along with the cathode output pressures in Fig. 2. We can see in Fig. 2 that the cell voltage oscillates at a frequency equal to that of the cathode output pressure, around 0.14 Hz. We can also see that the voltage oscillations phase is opposite the pressure oscillations phase, i.e., an increase in output pressure corresponds to a voltage drop. This is a counterintuitive result, as one expects that a high cathode output pressure results in higher cell voltage, due to better reaction kinetics. On the anode side, no correlation is observed between pressure oscillations and cell voltage. However, pressure oscillations applied on the cathode side result in voltage oscillations. This could be due to the dynamics of the liquid water that is produced at the cathode catalyst layer (CCL), the slower reaction kinetics in the cathode, or a combination of both. The liquid water produced at the CCL wets the catalyst layer, affecting the electrochemical surface area (ECSA). Liquid water, accumulating in pores of CCL via capillary condensation or condensing on GDL fibers, affects vaporization exchange and diffusion of vapor and oxygen. Cathode pressure oscillations would thus affect the concentration of reactants at reaction sites and hence cathode polarization. Since the overall polarization in PEFCs is dominated by the cathode side,

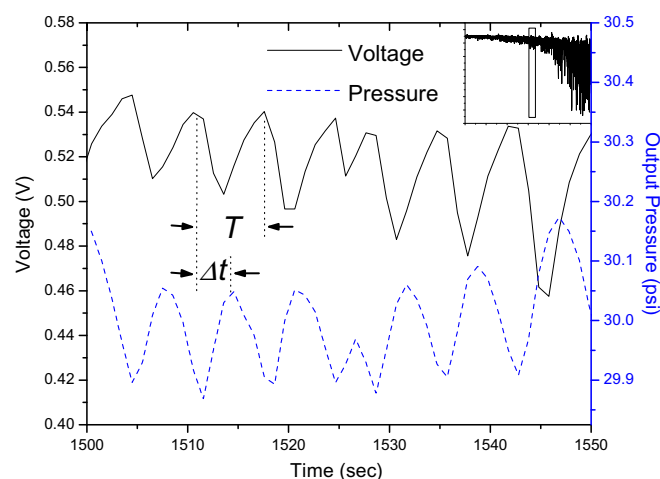


Fig. 2. Cell voltage and cathode output pressure for 50 s of cell voltage in Fig. 1a.

cathode pressure oscillations could therefore result in cell voltage oscillations.

One way to distinguish between liquid and gas phase effects is by changing the thickness, porosity and hydrophobicity of CCL and GDL. The effect of variations of these properties on cell voltage oscillations allows understanding their individual contribution.

An alternative method is to isolate the dynamical processes that result in the voltage oscillations by their characteristic frequency. Gradients in oxygen distribution across the GDL reach equilibrium in ~ 0.05 s, corresponding to a characteristic frequency of 20 Hz [13]. However, a liquid water saturation gradient across GDL reaches equilibrium in the order of 1 s (1 Hz) [13], while liquid water transport in the catalyst layer has a time constant in the order of 10 s (0.1 Hz) [14]. Therefore, the effect of changes in the cathode output pressure frequency in a range between 0.1 and 20 Hz on cell voltage would allow isolating liquid and gas phase transport dynamics. The current frequency of the cathode pressure at 0.14 Hz does not allow isolating these processes. The cathode output pressure is controlled using a PID controller as:

$$S = K_P e + K_I \int e dt + K_D \frac{de}{dt} \quad (1)$$

$$e = P_{out} - P_{ref} \quad (2)$$

with S being the output pressure control valve command signal, e the pressure error, calculated as the difference between the reference pressure, P_{ref} , and the measured cathode output pressure, P_{out} , and K_P , K_I , and K_D the PID controller proportional, integral, and derivative coefficients. The cathode output pressure oscillation depends on the system dynamics, as well as the PID control parameters. While changing the PID parameters affects oscillation amplitude and frequency, it is not possible to set the desired oscillation amplitude and frequency as input to the control system. We are developing a state space controller that has such capability.

By changing the cathode output pressure oscillation frequency, ω , we can then define the pressure–voltage ratio, Z_{VP} , as:

$$Z_{VP}(\omega) = V(\omega)/P(\omega) \quad (\text{V Pa}^{-1}) \quad (3)$$

with V being the cell voltage and P the cathode output pressure. We can then calculate the pressure–voltage oscillations amplitude, $|Z_{VP}|$, and phase angle, $\varphi(Z_{VP})$, using the following relationship:

$$|Z_{VP}| = \frac{|V|}{|P|} \quad (4)$$

$$\varphi(Z_{VP}) = \varphi(V) - \varphi(P) = 2\pi \frac{\Delta t}{T} \quad (5)$$

with φ being the phase, Δt the time delay between peaks, and T the oscillation period. As mentioned above, the amplitude ratio and phase difference of pressure–voltage oscillations at different frequencies can be used to understand dynamical processes in the fuel cell, similar to impedance spectroscopy that involves the analysis of the impedance response, viz. impedance amplitude and phase shift, in the frequency domain to small perturbation signals in voltage or current. During impedance measurements, oscillatory electrochemical reaction results in partial pressure oscillation along the flow

field channel, which adds to the complexity of interpreting the impedance results [11,12]. However, pressure–voltage oscillation would capture only the effect of partial pressure oscillations on electrochemical reaction; therefore, results should be more straightforward to interpret. These two methods would be most powerful when used as complimentary tools. Furthermore, pressure–voltage oscillations would be cheaper to integrate into applications compared to impedance spectroscopy, since it only requires changes in the pressure control algorithm without any additional hardware, while impedance spectroscopy requires addition of an active load.

The described pressure–voltage oscillation phenomenon is useful in failure mode detection [7,8] and could further lead to the development of a diagnostic tool of pressure–voltage spectroscopy. However, we could only speculate about underlying physicochemical effects and further detailed studies are required to rigorously establish such a tool.

4. Conclusions

We showed that when the cathode output pressure oscillates around 0.14 Hz, the cell exhibits voltage oscillations with identical frequency and negative phase. This is a counterintuitive result, since an increase in pressure is expected to result in a voltage drop due to an increased oxygen concentration at active catalyst sites. We proposed using the amplitude ratio and phase difference of pressure–voltage oscillations in the frequency range between 0.1–20 Hz as a diagnostic tool for understanding dynamical processes that involve water transport and accumulation in porous catalyst layers and gas diffusion layers. The pressure–voltage amplitude ratio can also be used for isolation of low anode and cathode flow rates in the PEFC during real time operation.

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