

# HYDROGEN CROSSOVER LEAK RATE ( $Q_{leak}$ )

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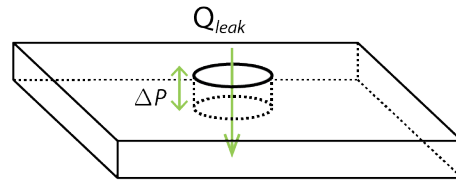
One of the key functions of a fuel cell membrane is to separate the anode and cathode gasses. However, a small amount of gas always permeates through the membrane and undergoes a chemical reaction at the opposite electrode, without providing useful energy. Furthermore, once pinholes develop in the membrane as a result of aging, the rate of gas crossover increases, reducing the fuel cell performance. Characterizing this phenomenon is useful for designing membranes and optimizing conditions that result in higher performance over the Membrane Electrodes Assembly (MEA) lifetime.

The pinhole size is difficult to observe and measure, especially in operational fuel cells. Therefore, pinholes are typically characterized by the rate of gas crossover at a given overpressure. The gas crossover flow rate is directly proportional to the overpressure, and inversely proportional to the viscosity of the gas:

$$Q_{leak} = S \frac{\Delta P}{\mu} \quad (1)$$

where  $Q_{leak}$  is the hydrogen flow,  $S$  is a proportional factor representing the leak size,  $\Delta P$  is the overpressure, and  $\mu$  is the gas viscosity. Note that when a pinhole is formed, a cathode overpressure would result in air crossover to the anode, which would react with the hydrogen in the anode and could result in anode starvation. On the other hand, an anode overpressure

would result in hydrogen crossover to the cathode, which would combine with oxygen and could result in cathode starvation. However, since anode starvation results in cell reversal and is more damaging than cathode starvation, a small overpressure is applied from the anode to the cathode, in order to ensure that once pinholes are developed, hydrogen would crossover to cathode, as opposed to air entering the anode and causing hydrogen starvation. Therefore, pinholes are quantified by hydrogen crossover leak rate at a given anode overpressure.



*Fig. 1. Schematic diagram of hydrogen crossover leak through membrane pinhole*

The following is a summary of different methods that can be used to quantify hydrogen crossover leak rate, along with an analysis of their pros and cons:

## 1. Direct Measurement

In this method, the rate of crossover leak between anode and cathode is measured directly. In order to conduct such measurement, the anode outlet and the cathode inlet ports are blocked, and the anode inlet is pressurized above the cathode outlet, which is at atmospheric pressure. Under these conditions, the rate of gas exiting the cathode outlet is measured via a mass flow meter, or by collecting the gas under a measuring cylinder over a known

period of time. This method is often performed using air instead of hydrogen for safety reasons, in which case the hydrogen transfer leak rate would be twice that measured by air, given the viscosity ratio of the two gasses [1]:

$$Q_{leak} = 2Q_{air} \quad (2)$$

This technique is simple and can be used to measure the crossover leak rate in an individual cell, as well as an entire stack. The downside of this method is that it cannot quantify the leak rate in individual cells of a fuel cell stack in-situ. Furthermore, if the stack is disassembled to measure the leak rate in each individual cell, changes in operating conditions and compression conditions highly affects the pinhole size, resulting in large measurement error [1].

## 2. Electrochemical Leak Detection

In this technique, hydrogen and air are supplied to the anode and cathode respectively, and the Open Circuit Voltage (OCV) is measured at different overpressures, induced by increasing the anode pressure [2]. In the presence of a leak, an increase in overpressure results in increases in the hydrogen crossover leak rate, which increases the leak current and therefore reduces the cell OCV:

$$\Delta i_{leak} = 2F\Delta Q_{leak} \quad (3)$$

$$\Delta E = -A \ln \left( \frac{\Delta i_{leak}}{i_0} \right) \quad (4)$$

where  $\Delta i_{leak}$  is the change in leak current due to different hydrogen crossover leak rates,  $F$  is the Faradaic constant,  $\Delta Q_{leak}$  is the change in

hydrogen crossover leak rate at different overpressures,  $\Delta E$  is the change in OCV at different pressures,  $A$  is the Tafel slope, and  $i_0$  is the exchange current density. This technique is very sensitive and can detect both small and large leaks in individual cells of a fuel cell stack. However, the downside of this method is that it is not accurate in terms of quantifying the leak rate, and can only provide qualitative information regarding pinhole formation and growth, due to the mixed potential caused by local hydrogen crossover leak across the MEA area.

## 3. Linear Sweep Voltammetry

In this method, hydrogen and nitrogen are supplied to the anode and cathode of a fuel cell, respectively, and the cell voltage is swept from OCV to 500mV at a rate of 1mV/s [3]. Under these condition, the cell current at ~350mV represents the Hydrogen Oxidation Reaction (HOR) at the cathode. The hydrogen crossover flow rate can then be calculated from the HOR current,  $i_{leak}$ , using the Faraday law:

$$Q_{leak} = \frac{i_{leak}}{2F} \quad (5)$$

This technique is very accurate and suitable for measuring hydrogen crossover leak in single cells. However, the downside of this method is that it has limited application for quantifying leak in individual cells of a fuel cell stack, as the cells are in series and the current would be limited by the cell with the lowest leak. Note that hydrogen crossover leak rate measured using this methodology is a sum of hydrogen permeation through membrane and hydrogen convection through pinholes. For large leaks, the

permeation components is negligible. For smaller leaks, the two can be separated by measuring the crossover leak at different overpressures.

#### 4. H<sub>2</sub> Crossover (H2X)

An alternative methodology for quantifying hydrogen crossover leak is to supply anode and cathode with hydrogen and nitrogen respectively, at a fixed overpressure, and measuring the resulting cell OCV. Under these conditions, the OCV represents the ratio of hydrogen partial pressure in the anode and cathode, from which the rate of hydrogen crossover can be calculated using the following formula [1]:

$$Q_{leak} = \frac{Q_{N_2}}{\frac{P_c - P_{w,c}}{P_a - P_{w,a}} e^{\frac{2EF}{RT}} - 1} \quad (6)$$

where  $Q_{N_2}$  is flow rate of nitrogen in the cathode,  $P_c$  and  $P_a$  are the cathode and anode pressures,  $P_{w,c}$  and  $P_{w,a}$  are the partial pressure of water in the cathode and anode,  $E$  is the cell potential,  $R$  is the gas constant, and  $T$  is the cell temperature. The advantage of this technique is that it can be used to estimate the rate of hydrogen crossover leak in individual cells of a PEM fuel cell stack in-situ. This technique is specifically accurate for characterizing pinholes that are located close to the inlet. The methodology underestimates hydrogen crossover rate when pinholes are formed closer to the outlet. Greenlight's H2X module uses this methodology to estimate the rate of hydrogen crossover leak in individual cells of a PEM fuel

cell stack, as explained in Greenlight's [H2X white paper](#). Greenlight is currently optimizing this methodology to obtain a better estimate of outlet leaks, although in operational fuel cells, pinholes are typically formed closer to the inlet, due to lower humidity conditions. Note that the hydrogen crossover leak measured using this methodology is a sum of permeation and leak components. For large leak, the permeation components is negligible. For smaller leaks, the two can be separated by measuring the total leak at different overpressures.

#### References

- [1] [In-situ diagnostic tools for hydrogen transfer leak characterization in PEM fuel cell stacks Part I: R&D applications](#), A.M. Niroumand, O. Pooyanfar, N. Macauley, J. DeVaal, F. Golnaraghi, *Journal of Power Sources* 278 (2015) 652-659.
- [2] [Membrane degradation during combined chemical and mechanical accelerated stress testing of polymer electrolyte fuel cells](#), C. Lim, L. Ghassemzadeh, F. Van Hove, M. Lauritzen, J. Kolodziej, G.G. Wang, S. Holdcroft, E. Kjeang, *Journal of Power Sources* 257 (2014) 102-110.
- [3] [Gas crossover and membrane degradation in polymer electrolyte fuel cells](#), M. Inaba, T. Kinumoto, M. Kiriake, R. Umebayashi, A. Tasaka, Z. Ogumi, *Electrochimica Acta* 51 (2006) 5746-5753.

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