



Short communication

Gas crossover leakage in high temperature polymer electrolyte fuel cells: In situ quantification and effect on performance

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ABSTRACT

Here we report an experimental in situ analysis of internal gas crossover leakage in single high-temperature polymer electrolyte membrane fuel cells. The study is based on the analysis of the exhausts from the anode and the cathode of the fuel cell during operation. An abnormal crossover rate across the membrane of the investigated fuel cell was detected, indicating the presence of an internal leakage. The internal flux shows linear dependence on the pressure difference between fuel cell compartments, attesting for permeation as the driving force. When the average cathode pressure is higher than the anode pressure, air crossover is measured. Conversely, hydrogen crossover is measured when the anode pressure is higher than the cathode. The effects on fuel cell performance are evaluated under air or hydrogen crossover conditions. Under both conditions, crossover leakage causes a significant increase in hydrogen consumption that reduces fuel recovery from anode exhaust.

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1. Introduction

Polymer electrolyte membrane fuel cells (PEMFC) are particularly attractive due to their modularity, low environmental pollution and high energy conversion efficiency. Improved reliability is essential for the wide-spread use of fuel cells, especially for automotive applications. Failure modes, which have recently been reviewed [1–3], are several and are generally classified according to the component involved. Among the many failure modes, great importance is covered by gas transfer leaks which are divided into two categories: external or “overboard” transfer leaks and internal leaks. External leaks occur when gas leaks from reactant streams to the external environment. Internal leaks occur when gas leaks from one reactant stream to the other one, as defined in [4,5]. Internal leaks, also known as “crossover leakage,” can occur when separation of reactants is not maintained, due to the presence of defects in the electrolyte membrane or in the gaskets. If fuel and oxidant mix, they can directly react on the electrodes to generate hot spots and aggressive radicals, which can compromise fuel cell integrity and reduce durability [1–3,5–7]. For these reasons, there are many studies that evaluate crossover detection and analysis methods [4,5,8–15]. The majority of these works focus on low temperature polymer electrolyte membrane fuel cell stacks and report leakage detection techniques that cannot be performed when the fuel cell

is normally operating. A work that describes a continuous in-line monitoring method is [9], but such technique is based on the analysis of the CO₂ concentration in the oxidant stream and requires complex and sometimes very expensive gas analysis systems. In the case of high temperature polymer electrolyte membrane fuel cells (HT-PEMFC), crossover leakage could be enhanced due to the harsher operating conditions, which may reduce the integrity of the components [3,16]. Throughout our experimental activities using HT-PEMFC, this problem was detected on some single cells. The present work describes the experimental characterization of such internal crossover leakage and proposes a new in situ method to detect and quantify the leaks. The reported investigation of fuel cell exhausts is based on the analysis of water molar flow rate and dry molar flow rate using simple instruments. This method can be continuously applied during fuel cell operation; therefore, it is also suitable for long-time degradation testing.

2. Experimental

2.1. Methodology

A single phosphoric acid-doped polybenzimidazole-based HT-PEMFC was operated with dry hydrogen as a fuel and dry air as an oxidant, fed in co-flow configuration at ambient temperature. Polarization measurements were consecutively performed by applying a current across the fuel cell, and flow rates were automatically regulated to keep constant stoichiometry. The conditions that were investigated are reported in Table 1. The voltage was

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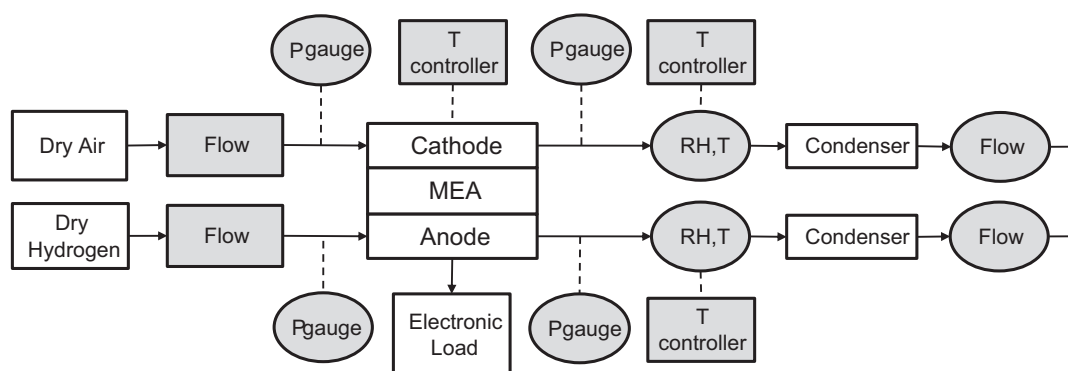


Fig. 1. Experimental setup scheme: gray squares represent the controlled parameters, while gray circles represent the measured parameters.

recorded in response to imposed currents, and the mass balance was investigated by measuring water molar flux and dry gas molar flux at anode and cathode outlets. Every polarization curve was randomly repeated three times on three different days to assure for measurements repeatability. Representative values of each experimental condition are reported as an average of three tests. More details on the experimental methods can be found in [17].

2.2. Experimental setup

A 20 cm² polybenzimidazole-based MEA was placed between two graphite distributors where serpentine flow fields are machined (single and triple serpentine on anode and cathode side, respectively, both with the same square section: depth 0.8 mm, width 0.8 mm, length 700 mm). Graphite distributors are held together between two stainless steel plates by 8 screws and tightened with a controlled torque of 12(±0.5) Nm. The temperature of the plates was measured by a calibrated thermocouple (±1 °C) and was set by a temperature controller. Air and hydrogen flow rates were controlled and measured by two calibrated flow controllers (uncertainty: 0.7% of setpoint + 0.004 Nl min⁻¹ for air flow controller and 0.7% of setpoint + 0.0004 Nl min⁻¹ for hydrogen flow controller). Pressure at the fuel cell inlets and outlets was measured by four transducers (pressure range: 4 bar relative, uncertainty: 10 mbar). Relative humidity at both anode and cathode outlets was measured by temperature and relative humidity transmitters based on a capacitive sensor (temperature range: 0–120 °C, uncertainty: 0.3 °C; relative humidity range: 0–100%, uncertainty: 1.5% RH + 1.5% of reading). The sensors were housed in two heated metal cases in which temperature is adjusted to prevent vapor condensation. Water was then separated by two condensers operating at 20 °C so that dry volumetric fluxes could be measured using two graded cylinders (estimated uncertainty: 2%), taking into account for the presence of residual water. The power produced by the fuel cell during operation was dissipated by an electronic load working in constant current mode (uncertainty: 0.25%). A simplified scheme of the experimental setup is reported in Fig. 1. More details about the hardware are reported in [17]. The combined uncertainty of the analyzed parameters is evaluated according to [18] and is reported in Table 2.

Table 1
Investigated experimental conditions.

T_{cell} [°C]	λ_{H_2}	λ_{air}
140	1.3	2/4/6
160	1.3	2/4/6
180	1.3	2/4/6

Table 2
Uncertainty of measured parameters.

Parameter	Estimated uncertainty
Fuel cell voltage	7 mV
Cathode exhaust dry flow	2%
Anode exhaust dry flow	5%
Cathode exhaust water flow	6%
Anode exhaust water flow	10%

3. Results and discussion

3.1. Crossover leakage analysis

The overall mass balance in a PEMFC must take into account for the consumption of the reactants and for the production of the water due to the electrochemical reaction. A distinction is made here between water flows and dry flows, with the latter including any species different from water. Throughout our experimental activities on HT-PEMFCs, the global mass balance was closed within measurement uncertainty, and consistency between expected and measured exhaust flows could be verified [17]. However, in this work, measured dry molar flow is less than expected at the cathode outlet and dramatically higher at the anode outlet (Fig. 2). This difference increases at high current density and cathode stoichiometry. An anomalous behavior is also observed for the water mass balance. Because dry reactants are fed to the fuel cell and the current production is controlled, the total fuel cell water output is normally expected to be equal to the internal electrochemical water generation. In the reported case, considering total water

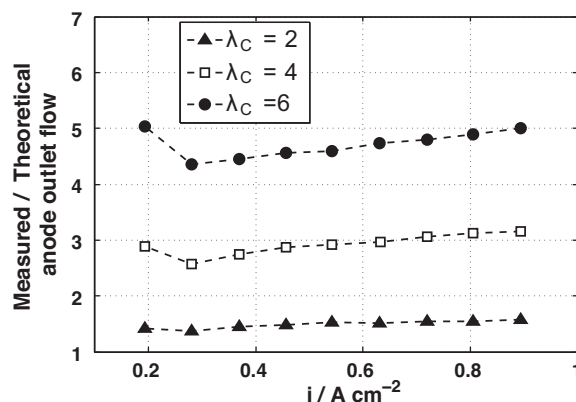


Fig. 2. Measured to theoretical dry flow ratio in anode exhaust versus current density at different air stoichiometry; $T_{\text{cell}} = 160$ °C, $\lambda_{\text{H}_2} = 1.3$.

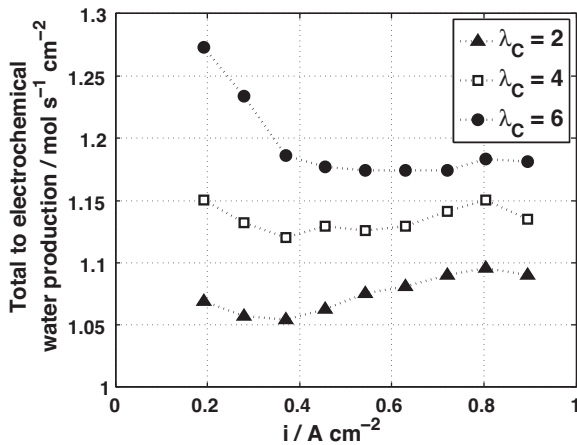


Fig. 3. Ratio of total water production over electrochemical water production versus current density at different air stoichiometry; $T_{\text{cell}} = 160^\circ\text{C}$, $\lambda_{\text{H}_2} = 1.3$.

molar flow in anode and cathode exhausts, the measured water output is considerably higher than would be generated from the electrochemical reaction. The water excess is represented in Fig. 3 as a ratio between the total water exiting the fuel cell and electrochemical water production. As can be observed, the extra water production increases with cathode stoichiometry and can be up to 30% of the electrochemical water at low current densities. The previous findings indicate the presence of an internal gas leak from the cathode to the anode. Such a leak is responsible for the high dry molar flow at the anode exhaust and for the excess water production. Assuming that the additional water production is due to a direct reaction of hydrogen with oxygen coming from the cathode compartment, this reacting component of crossover $\dot{n}_{\text{reacting}}^{\text{cross}}$ can be estimated with the following relation:

$$\dot{n}_{\text{reacting}}^{\text{cross}} = \frac{\dot{n}_{\text{H}_2\text{O}}^{\text{c,out}} + \dot{n}_{\text{H}_2\text{O}}^{\text{a,out}} - I/2F}{2} \quad (1)$$

where $\dot{n}_{\text{H}_2\text{O}}^{\text{c,out}}$ is the water flow measured at the cathode outlet, $\dot{n}_{\text{H}_2\text{O}}^{\text{a,out}}$ is the water flow measured at the anode outlet and $I/2F$ is the electrochemical water production. High dry flow rates exiting the anode exhaust indicate the presence of a nonreacting component of crossover. This component can be evaluated as the difference between the total dry flow $\dot{n}_{\text{dry}}^{\text{a,out}}$ and dry hydrogen flow in the anode exhaust, according to the following relation:

$$\dot{n}_{\text{non-reacting}}^{\text{cross}} = \dot{n}_{\text{dry}}^{\text{a,out}} - \left[\dot{n}_{\text{H}_2}^{\text{a,in}} \times \frac{\lambda_{\text{H}_2} - 1}{\lambda_{\text{H}_2}} - 2 \times \dot{n}_{\text{reacting}}^{\text{cross}} \right] \quad (2)$$

where $\dot{n}_{\text{H}_2}^{\text{a,in}}$ is the hydrogen molar flow at the anode inlet, λ_{H_2} is the hydrogen stoichiometry and $2 \times \dot{n}_{\text{reacting}}^{\text{cross}}$ is the hydrogen consumption related to reacting oxygen crossover. In Fig. 4, the total crossover flux $\dot{n}_{\text{reacting}}^{\text{cross}} + \dot{n}_{\text{non-reacting}}^{\text{cross}}$ is graphed as a function of the pressure difference between the cathode and anode inlets. The pressure difference between the reactants has been reported to play a role on crossover leakage rates [3,15], but no characterization of such relation is available yet. The calculated crossover flux shows a linear trend, indicating that air crossover is due to gas permeation with linear proportionality to the pressure difference between the fuel cell inlets. This value grows with cathode flow rate, due to pressure drops, as the current density and stoichiometry are increased. Crossover leakage can increase to as much as 10% of the air feed stream, which is more than that reported in literature, in the case of hydrogen crossover in non-defected HT-PEMFC [19–23]. Crossover leakage rates measured at fuel cell temperatures of 140°C and 180°C (data not shown) are consistent

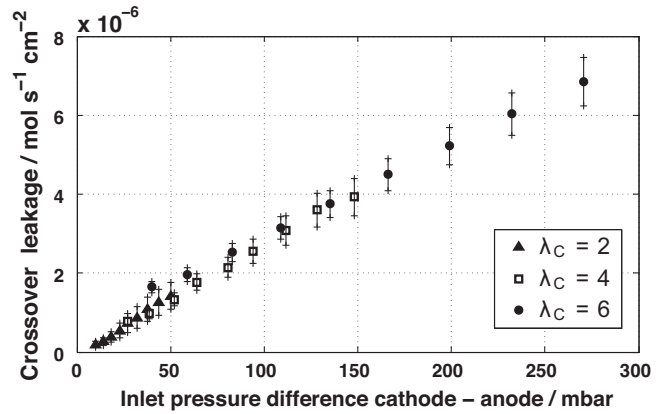


Fig. 4. Total molar crossover flux versus the pressure difference between the cathode and anode inlets; $T_{\text{cell}} = 160^\circ\text{C}$, $\lambda_{\text{H}_2} = 1.3$.

with those shown here. This finding indicates that temperature has no significant influence on the measured leakage rates, thus the crossover occurs as a result of a pressure difference only. A possible reduction in air crossover was investigated by manually setting the reactant flow rates (values not reported in Table 1). During this test, the fuel cell temperature and current were set at 160°C and 0.2 A cm^{-2} , respectively, and the automatic regulation of reactants flow rates was interrupted to achieve independent control of the air and hydrogen streams. Hydrogen stoichiometry was gradually increased from $\lambda_{\text{H}_2} = 1.3$ (equivalent to 0.036 NI min^{-1}) to $\lambda_{\text{H}_2} = 7.6$ (equivalent to 0.2 NI min^{-1}), while air stoichiometry was kept constant at $\lambda_{\text{air}} = 2$ (equivalent to 0.133 NI min^{-1}). Under these conditions, the anode compartment mean pressure rose above that of the cathode. This finding was due to different pressure drops at the anode and cathode sides related to different fluid properties and flow field geometry. As a result, the dry flux at the anode outlet was always lower than expected. This mismatch increased with an increasing pressure difference between the anode and cathode. These observations highlight the presence of hydrogen crossover leakage due to higher anode pressure. This finding further upholds the proposed interpretation that pressure difference is the driving force of crossover leakage. By reversing the pressure difference between fuel cell compartments, the crossover flux direction is also reversed.

3.2. Fuel cell performance

Performance of the previously mentioned fuel cell and of a similar non-defected fuel cell was compared. Lower voltages were expected in the first case due to the presence of mixed potentials as reported in [3] for a leaking cell within a stack. Conversely, the polarization curve of the damaged cell did not show a lower voltage, as can be observed by Fig. 5. This finding indicates that, in the investigated case, crossover leakage does not affect performance considerably. Thus, such a defect cannot be detected by simply evaluating the fuel cell voltage but only through performing a mass balance analysis. A definitive explanation for this behavior is not available. A post mortem analysis, using an optical microscope, did not reveal any evidence of holes or defects in the membrane. Micro-cracking, pinholes and gasket detachment could all be possible origins of the leakage [1,2]. Unaltered voltage could be motivated if crossover leakage occurs at the end of the fuel cell active area. In this case, the variation in air and hydrogen partial pressure and the effect of their mixing do not greatly affect the fuel cell voltage. Even though no significant decrease is observed in fuel cell voltage and performance, the hydrogen content in the anode exhaust remarkably decreases. The presence of

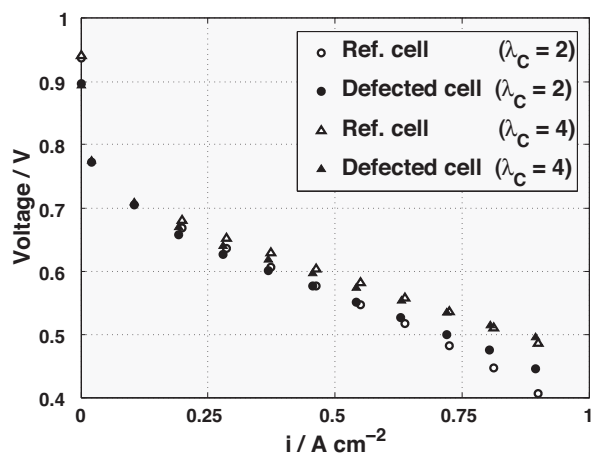


Fig. 5. Polarization curves of the defected cell compared to a similar non-defected cell at different air stoichiometry; $T_{\text{cell}} = 160^\circ\text{C}$, $\lambda_{\text{H}_2} = 1.3$.

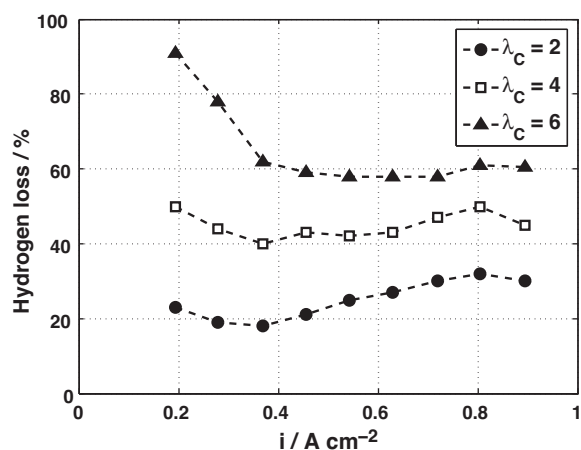


Fig. 6. Loss of hydrogen in the anode exhaust as a percentage of the expected amount at different air stoichiometry; $T_{\text{FC}} = 160^\circ\text{C}$, $\lambda_{\text{H}_2} = 1.3$.

crossover actually leads to further hydrogen consumption, which becomes no longer available for recovery, which strongly affects the overall energy efficiency. The extra consumption of hydrogen due to the crossover leakage is reported in Fig. 6 as a percentage of the expected hydrogen content of the anode exhaust when no leakage is present. This figure shows that the hydrogen loss in the anode exhaust significantly increases with growing cathode stoichiometry and consequently with crossover. As air stoichiometry increases from $\lambda_{\text{air}} = 2$ to $\lambda_{\text{air}} = 6$, the additional depletion of hydrogen increases from approximately 30% to as much as 60% at 0.9 A cm^{-2} . The energy loss becomes even greater at 0.2 A cm^{-2} , ranging from 20% to 90% of the total amount. This finding represents a significant problem when considering energy recovery from fuel cell anode exhaust, as done in co-generative systems where a fuel cell stack is coupled with a fuel reforming unit [24–26].

4. Conclusions

Our experimental analysis was effective in detecting and characterizing the crossover leakage in a defected single HT-PEMFC. The investigation is based on the analysis of fuel cell exhausts and can be

carried out using simple instruments without interrupting fuel cell operation. Observed trends indicate that crossover leakage depends with linear proportionality on the pressure difference between the fuel cell compartments and is not influenced by the fuel cell temperature. During normal working conditions, the cathode inlet pressure always exceeded the anode pressure, thus generating considerable air crossover. Hydrogen crossover is otherwise obtained by reverting the pressure difference through a remarkable increase in hydrogen stoichiometry. This finding confirms that crossover is driven by permeation, which is the cause of a dramatic gas transport when internal damage to the fuel cell is present. In this specific case, the crossover leakage does not affect voltage, which is comparable with the voltage of a non-defected fuel cell. Nevertheless, hydrogen consumption is remarkably increased, thus reducing the hydrogen availability in the anode exhaust and considerably compromising fuel cell energy recovery. The methodology and experimental setup employed in this study allowed for the analysis of fuel cell outlet streams using simple instruments and without interrupting fuel cell operation, thus making this a useful tool for crossover leakage detection during long-time degradation testing.

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