



# An electrochemical method for high accuracy measurements of water transfer in fuel cells

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## ABSTRACT

A novel method for the high accuracy measurement of water transfer in differential polymer electrolyte fuel cells (PEFCs) is proposed. This method is based on the potential difference forming in a H<sub>2</sub>/H<sub>2</sub> concentration cell in the presence of humidity differences between the electrodes. In the present work, the relation between the partial pressures of hydrogen and water vapor and the potential difference over the concentration cell are verified. Furthermore, a validation experiment allowed to confirm that the targeted accuracy of 0.25% for the differential humidity can be obtained with our method, making it suitable for the measurement of water transfer in small-scale differential cells.

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## 1. Introduction

Due to the importance of water management, many researchers have studied the water transfer in operating PEFCs (e.g. [1–3]). A common characteristic of the reported studies is the fact that they were conducted with relatively low gas flow stoichiometries (cf., overview by Colinart et al. [4]) implying large humidity gradients over the cell area. To get a direct insight on the effect of materials or operating parameters on the water transfer on the local scale, studies performed on *differential cells* (small cells using high stoichiometries) are highly desired. However, the measurement of water transfer in such conditions is very challenging. This was pointed out by Sauriol et al. [5] who evaluated the theoretical accuracy of water transfer for cells of full technical size, and for cells with a reduced size, but with the same gas flow as technical cells. In general, the accuracy is expected to be worse for small cells: in these cells, the change of water flow between the cell inlet and outlet is small compared to the total water flow transiting through the cell.

We propose here a method for the accurate measurement of water transfer in differential cells, based on the measurement of the *differential humidity* between the anode inlet and outlet. For this purpose, we use a hydrogen concentration cell with a polymer electrolyte as separator. Our proposed measurement principle involves 2 cells, as illustrated in Fig. 1a: the operating fuel cell whose water transfer is to be measured, and the concentration cell acting as a sensor. However, the present work focuses on the validation of the concentration cell as a differential

humidity sensor, using the setup described in Fig. 1b. As developed by Fuller and Newman [6], differences of water partial pressure between the electrodes of a H<sub>2</sub>/H<sub>2</sub> cell result in a non-zero open cell voltage, which they related to the *electroosmotic drag* effect in the membrane. Such an effect can be used for measuring humidity differences if the *electroosmotic drag coefficient* (number of transferred water molecules per proton) of the polymer electrolyte is known. In our work, this coefficient is extracted from the measured cell voltage dependency on pressure changes, so that no a priori knowledge of it is necessary. Our target is to measure the water transfer in differential cells with a 5% change of water partial pressure between inlet and outlet, with an accuracy of 5%. Therefore, the targeted accuracy of the differential humidity measurement is set to 0.25%.

## 2. Theory

In a concentration cell, the reacting species are the same on both electrodes and the open cell voltage is zero if the activities of the concerned species are equal on both sides. When there is a difference of activities between the electrodes, a voltage appears according to the Nernst equation. For a hydrogen concentration cell with a polymer electrolyte membrane, both water and hydrogen are considered reacting species. The equivalent electrochemical reaction corresponding to the transfer of one electron can be written as:



where  $k_{\text{drag}}$  represents the *electro-osmotic drag* coefficient and the subscripts (r) and (w) represent the reference and working electrodes,

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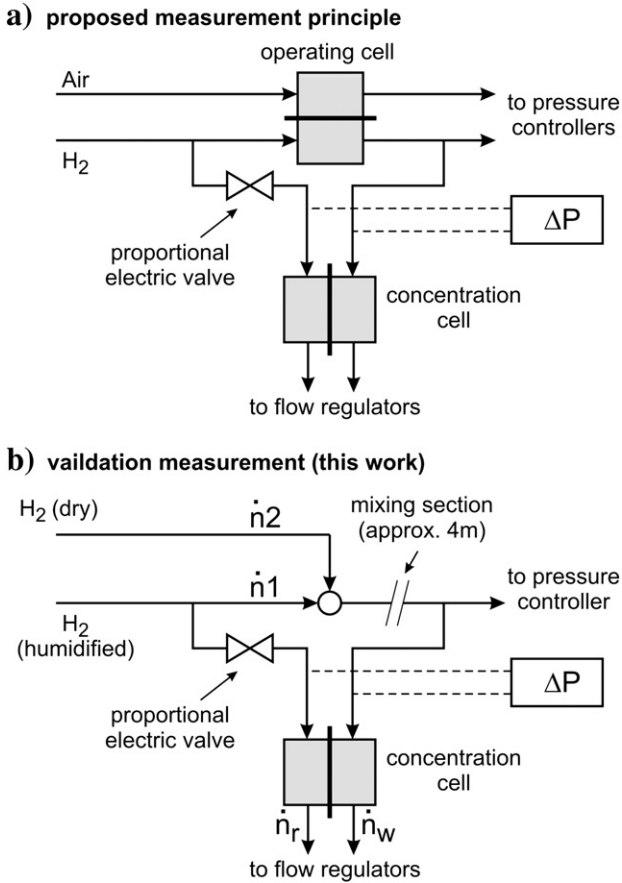


Fig. 1. Illustration of the proposed water transfer measurement setup (a) and of the validation setup used in this work (b).

respectively. Assimilating the activities to the corresponding partial pressures  $p(\text{H}_2, r)$ ,  $p(\text{H}_2, w)$ ,  $p(\text{H}_2\text{O}, r)$  and  $p(\text{H}_2\text{O}, w)$ , the theoretical open cell voltage is given by the Nernst equation:

$$U = -\frac{RT}{2F} \cdot \ln \left[ \frac{p(\text{H}_2, w)}{p(\text{H}_2, r)} \right] - k_{\text{drag}} \cdot \frac{RT}{F} \cdot \ln \left[ \frac{p(\text{H}_2\text{O}, w)}{p(\text{H}_2\text{O}, r)} \right]. \quad (2)$$

We introduce the absolute pressure  $P_{\text{ref}}$  and the water vapor molar fraction  $x_{\text{ref}}$  on the reference side. For these parameters, the differences between working and reference sides are noted  $\Delta P$ , respectively  $\Delta x$ . Eq. (2) becomes:

$$U = -\frac{RT}{2F} \cdot \ln \left[ \frac{1-x_{\text{ref}}-\Delta x}{1-x_{\text{ref}}} \right] - k_{\text{drag}} \cdot \frac{RT}{F} \cdot \ln \left[ \frac{x_{\text{ref}}+\Delta x}{x_{\text{ref}}} \right] - \frac{RT}{F} \cdot \left( \frac{1}{2} + k_{\text{drag}} \right) \cdot \ln \left[ \frac{P_{\text{ref}}+\Delta P}{P_{\text{ref}}} \right]. \quad (3)$$

Eq. (3) relates the cell voltage  $U$  to  $\Delta x$ , but requires the value of  $k_{\text{drag}}$  which is not a priori known. To solve this issue, a “calibration period” is defined, during which a constant composition of the gas flows (defined by  $x_{\text{ref}}$  and  $\Delta x$ ) and a constant value of  $k_{\text{drag}}$  is assumed. During this period, two measurements called “C−” and “C+” are performed, between which the pressure at one of the electrodes is changed. The values of  $U$ ,  $P_{\text{ref}}$  and  $\Delta P$  during these periods are called  $U^{C-}$ ,  $P_{\text{ref}}^{C-}$ ,  $\Delta P^{C-}$ ,  $U^{C+}$ ,  $P_{\text{ref}}^{C+}$  and  $\Delta P^{C+}$ . The voltage response to pressure changes is defined as:

$$U_{\text{CAL}} = \frac{U^{C+} - U^{C-}}{\ln \left[ \frac{(P_{\text{ref}}^{C+} + \Delta P^{C+}) \cdot P_{\text{ref}}^{C-}}{(P_{\text{ref}}^{C-} + \Delta P^{C-}) \cdot P_{\text{ref}}^{C+}} \right]}. \quad (4)$$

Based on the measured  $U_{\text{CAL}}$  value, on Eq. (3) and on the assumption that  $\Delta x \ll x_{\text{ref}}$ , the differential humidity can be calculated without relying on the knowledge of  $k_{\text{drag}}$ :

$$\frac{\Delta x}{x_{\text{ref}}} = \frac{U - U_{\text{CAL}} \cdot \ln \left[ \frac{P_{\text{ref}} + \Delta P}{P_{\text{ref}}} \right]}{U_{\text{CAL}} - \frac{RT}{2F} \cdot \frac{1}{1-x_{\text{ref}}}}. \quad (5)$$

The value of  $x_{\text{ref}}$  needs to be known, but as there is no expression involving the difference of two molar fractions anymore, the accuracy of commercial dew point sensors (typ. 1–2%) is sufficient.

### 3. Experimental

#### 3.1. Cells design

Two different types of concentration cells were used for this work. *Cell type 1* is a fuel cell of usual design with a thin catalyst coated membrane (Primea 5710, Gore), carbon paper diffusion media and flow fields with 1 mm ribs and channels. *Cell type 2* has a thicker membrane (Nafion 117, Dupont) coated by catalyst layers (0.5 mgPt/cm<sup>2</sup>, Paxitech). A high permeability carbon paper and an interdigitated type flow field as described in [7] were used to minimize diffusion losses. The active areas of cell types 1 and 2 were 0.5 cm<sup>2</sup> and 1 cm<sup>2</sup> respectively.

#### 3.2. Performed experiments

A first series of experiments (Test 1) was performed to confirm the relation between the cell voltage and the hydrogen and water partial pressures. Fixed partial pressures of 1400 mbar (H<sub>2</sub>) and 100 mbar (H<sub>2</sub>O) were used at the reference electrode. The partial pressures at the working electrode were changed as follows. In Test 1A, a fixed H<sub>2</sub>O partial pressure (100 mbar) and a variable H<sub>2</sub> partial pressure (1100–1700 mbar) were used. In Test 1B, a fixed H<sub>2</sub> partial pressure (1400 mbar) and a variable H<sub>2</sub>O partial pressure (50–150 mbar) were used. These experiments were performed at 70 °C on both cell types.

In the second series of experiments (Test 2), a precise humidity difference was generated by mixing a humidified flow  $\dot{n}_1$  of hydrogen with a smaller flow  $\dot{n}_2$  of dry hydrogen representing 0–5% of the value of  $\dot{n}_1$  (setup illustrated in Fig. 1b). An electrical valve was introduced before the reference electrode to perform pressure pulses. The differential pressure was measured with a high accuracy sensor (MT210, Yokogawa, Japan). Additionally, the absolute pressure and dew point of the gas flows were measured. All experiments in Test 2 were performed with cell type 2 at an absolute pressure of 1.2 bar. The controllers used for regulating the gas flows  $\dot{n}_1$ ,  $\dot{n}_2$ ,  $\dot{n}$ , and  $\dot{n}_w$  were calibrated using a volume flow cell (Gilibator 2, Sensidyne, 1% quoted accuracy). The difference of molar fraction  $\Delta x$  between the working and reference electrode was calculated by:

$$\frac{\Delta x}{x_{\text{ref}}} = -\frac{\dot{n}_2}{\dot{n}_1 + \dot{n}_2} \cdot (1-x_{\text{ref}}) \quad (6)$$

where  $x_{\text{ref}}$  is the water vapor molar fraction in the reference flow. During all experiments performed with the setup described in Fig. 1b, regular pressure pulses (approx. 20 mbar) were applied to calculate the sensitivity as explained in paragraph 2. The validation experiments were performed at 26 °C with a dew point of 14 °C (Test 2A) and at 66 °C with dew points of 40–60 °C (Test 2B).

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