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Hydrogen crossover and internal short-circuit currents experimental characterization and modelling in a proton exchange membrane fuel cell

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ABSTRACT

Open circuit losses encompass a set of phenomena that reduce PEM fuel cell (PEMFC) efficiency, especially at low current densities. Properly modelling these losses is crucial for obtaining PEMFC models that reproduce accurately the experimental behaviour of PEMFCs operating at low current densities. The open circuit losses can be disaggregated into three distinct contributions: mixed potential, hydrogen crossovers and internal short-circuits. The aim of this work is to obtain a model for the anodic and the cathodic pressure effects on the hydrogen crossovers and the internal short-circuits in a commercial PEMFC. In order to achieve this goal, the hydrogen crossovers and the internal short-circuit were measured experimentally on a commercial PEMFC by linear voltammetry. The measurements were performed at a given temperature and gas inlet humidification level, for different anodic and cathodic pressures.

Introduction

Fuel cells (FCs) are electrochemical devices that are able to transform the energy of a chemical reaction directly into electrical energy [1]. PEM fuel cells (PEMFCs) have attracted a great attention in the last decades as very promising alternatives for power generation devices for automotive, portable and distributed applications; due to their high power density, compactness, light weight and low cost [1]. Great research efforts have been made in recent years in order to increase the power density and the reliability of such fuel cells, and to decrease their cost [2].

One approach to increase the power density is to increase the performance of a single cell, by tackling the different irreversibilities that reduce its power density performance [3]. These irreversibilities are commonly known as voltage drops or over-potentials. The Nernst potential of an individual PEMFC is the theoretical thermodynamic open circuit cell potential that would appear between the terminals of a PEMFC working under certain conditions, and supplying no current (in thermodynamic equilibrium). However, the experimental open circuit cell voltage is lower than the Nernst theoretical potential. This voltage difference is known as open circuit voltage loss. These open circuit losses significantly affect the efficiency of the cell, particularly for cells working at low

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current densities, where these losses have a more significant effect [4].

The open circuit losses involve three different phenomena: the mixed potential; the gas crossover from the anodic to the cathodic compartment; and the internal short-circuit currents [5].

On the one hand, for potentials above 0.8 V (which occur in cells working at low current densities) the platinum of the catalyst layer is not stable and is oxidised, creating a PtO layer that partially covers the catalyst surface. This leads to the appearance of a mixed potential, composed by the potential of the cathodic half reaction O_2/H_2O and the potential of the anodic half reaction Pt/PtO. This causes a potential drop compared to the pure platinum catalyst layer situation. This phenomenon is known as mixed potential [4].

On the other hand, the polymer membrane is substantially impermeable to the reactant gases. However, small amounts of gases diffuse from one compartment to the other. These diffusive fluxes of gases are called gas crossovers [6]. In principle, all gases in a PEMFC system crossover: hydrogen from the anodic compartment to the cathodic one; and oxygen and nitrogen from the cathodic compartment to the anodic one. However, in practice, the only relevant gas crossover is the hydrogen crossover, since due to its small molecular size the hydrogen crossover flux is several orders of magnitude higher than the other gases crossovers [1]. Therefore it is usually assumed that the only gas crossover that exists in a PEMFC is the hydrogen crossover from the anodic compartment to the cathodic one.

Finally, even though the PEM membrane is an electron nonconductive membrane, some electrons can pass through the membrane, creating internal short-circuit currents [5].

Both, the hydrogen crossover and the internal short-circuit currents have equivalent effects on the PEMFC performance: a smaller number of electrons flow through the external circuit. In the internal short-circuit currents case, the electrons that cross directly through the membrane do not flow through the external circuit; whereas in the hydrogen crossover case, the hydrogen diffuses to the cathodic compartment, where it reacts directly, and therefore two electrons that would have flowed through the external circuit if the hydrogen had been oxidised in the anodic compartment, do not circulate through the external electrical circuit [1]. These losses are negligible at high current densities, since the hydrogen permeation rate and the electrical internal short-circuit currents are several orders of magnitude lower than the hydrogen consumption rate and the electric current respectively [2]. Furthermore, an increase in the current leads to a decrease of the hydrogen concentration on the electrode. Therefore the diffusion driving force decreases, and makes even smaller the hydrogen crossover [7].

In brief, these open circuit losses are not significant at high current densities; but they have a substantial effect on the performance at low current densities. The proper modelling of these open circuit losses is critical in order to achieve a model that fits suitably the experimental behaviour of the PEMFC at low current densities.

The general approach used in literature to model the open circuit losses consists in using a black-box model that encompasses all three open circuit losses phenomenons [8]. This kind of model does not allow the discrimination of the individual contributions of each one of the open circuit losses phenomenons; and just quantifies the open circuit losses as a whole. However, the split of the open circuit losses in the different individual contributions can allow a better understanding of the processes involved, which can be used to minimize these open circuit losses thereby increasing the performance of PEMFC at low current densities.

No such open circuit losses splitted models have been found in literature. Zhang measured the different contributions to the open circuit losses [4], but did not establish a model for them. Other works characterised the hydrogen crossovers independently [5–6], but did not deal with the other two phenomenons.

The present work intends to partially fill this gap in literature, by obtaining a model that discriminates between the different contributions to the open circuit losses. Therefore, the aim of this work is to experimentally characterize and model the effect of the compartment internal pressures on the hydrogen crossovers and the internal short-circuit currents of an individual cell of a commercial PEMFC stack.

Crossover and short-circuit model

The hydrogen crossover rate strongly depends on the operating conditions of the PEMFC membrane [9]. Therefore, in order to get more realistic results, it is important to perform the measurements in conditions as similar as possible to the real operation conditions during normal operation of the PEMFC system. This can only be achieved by in-situ measurement methods [5].

The crossover phenomenon is simply a gas permeation phenomenon through a membrane. Numerous techniques have been developed for in situ measurement of gas permeation rates through polymeric membranes, in various fields of application [5]. The most relevant in-situ gas permeation rate measurement techniques, mentioned in literature, are the volumetric method [10–11]; the lag time method [12–13]; the gas chromatography method [14]; and the electrochemical methods [6,15].

The only in-situ gas permeation rate measurement methods that can measure in parallel the PEMFC internal short-circuit currents are the electrochemical methods [5]. Since the goal of this work is to characterize both, the hydrogen crossovers and the internal short-circuit currents, this type of methods was selected to perform the measurements of this study.

From all the available electrochemical methods for gas permeation rate measurement, the linear sweep voltammetry is the most simple and straight-forward one [15]. Because of this, it was the selected method for the present study. Fig. 1 shows the setup of the in-situ linear sweep voltammetry method. The PEMFC is fed with humidified hydrogen to the anodic compartment; and with humidified nitrogen to the cathodic compartment. A known potential difference is applied to the terminals of the PEMFC using a potentiostat. The polarity of the connection is selected properly in order to oxidize the hydrogen crossovers, when they arrive to the PEMFC cathodic compartment. Therefore during the in-situ