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Hydration and dehydration cycles in polymer electrolyte fuel cells operated with wet anode and dry cathode feed: A neutron imaging and modeling study

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HIGHLIGHTS

- Hydration-dehydration cycles are found in PEFCs with wet anode and dry cathode feed.
- The current alternates between low/high levels due to changes in anode humidification.
- The cycles and performance states are analyzed by neutron imaging and modeling.
- The condensation and shedding of water at the anode inlet fully humidifies the channel.
- The humidification offsets the membrane dry-out induced by the cathode stream.

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ABSTRACT

Proper water management plays an essential role in the performance and durability of Polymer Electrolyte Fuel Cells (PEFCs), but it is challenged by the variety of water transport phenomena that take place in these devices. Previous experimental work has shown the existence of fluctuations between low and high current density levels in PEFCs operated with wet hydrogen and dry air feed. The alternation between both performance states is accompanied by strong changes in the high frequency resistance, suggesting a cyclic hydration and dehydration of the membrane. This peculiar scenario is examined here considering liquid water distributions from neutron imaging and predictions from a 3D two-phase non-isothermal model. The results show that the hydration-dehydration cycles are triggered by the periodic condensation and shedding of liquid water at the anode inlet. The input of liquid water humidifies the anode channel and offsets the membrane dry-out induced by the dry air stream, thus leading to the high-performance state. When liquid water is flushed out of the anode channel, the dehydration process takes over, and the cell comes back to the low-performance state. The predicted amplitude of the current oscillations grows with decreasing hydrogen and increasing air flow rates, in agreement with previous experimental data.

1. Introduction

Adequate water and thermal management is of vital importance to achieving improved performance and extended durability in Polymer Electrolyte Fuel Cells (PEFCs) [1–10]. Two opposite effects of the presence of water on PEFC operation can be distinguished. On one hand, a good hydration of the Proton Exchange Membrane (PEM) is necessary to maintain a low ionic resistance, and therefore a high cell performance [11,12]. A strong increase of the ionic conductivity of Perfluorosulfonic Acid (PFSA) membranes, such as Nafion®, with water content has been widely reported in the literature (see, e.g., [11–14]). On the other hand, accumulation of liquid water should be avoided, because water flooding blocks reactant pathways towards the active catalyst sites, thus limiting

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the maximum power output [15–17]. Hence, a careful control of the Relative Humidity (RH) of the feed streams and of the operating temperature of the cell is crucial to find an optimal balance [18–20]. This endeavor is further complicated by the wide variety of water transport phenomena that occur in PEFCs, including among others: i) diffusion, electro-osmotic drag, thermo-osmotic transport and convection of liquid water in the membrane [12,21–23]; ii) water production by the oxygen reduction reaction [24,25]; iii) water sorption and desorption in the Catalyst Layers (CLs) [23,26,27]; iv) two-phase flow in the mini-channels grooved on the Bipolar Plates (BPPs) [28]; v) capillary transport, and evaporation/condensation of liquid water in the Membrane Electrode Assembly (MEA) [29–31]; vi) two-phase interactions at the interface between the Gas Diffusion Layers (GDLs) and the flow channels [32–35]; and vii) convection and diffusion of water vapor under multiphase conditions, the latter governed by Fick's law or Maxwell-Stefan's equations and with a significant effect of Knudsen diffusion in the nanopores of the Microporous Layers (MPLs) and catalyst layers [15,16,36–40].

A thorough understanding of the complex transport and electrochemical processes that occur in PEFCs from a combination of experimental and numerical research is therefore necessary to fully understand and optimize fuel cell performance [41]. Multiple diagnostic and visualization tools are currently available to explore cell operation [42,43], such as electrochemical impedance spectroscopy, cyclic voltammetry, segmented cells, neutron imaging and X-ray tomography (see, e.g., [15–19,31,44–47]). Significant advances have also been achieved in the characterization of the physicochemical properties of fuel cell components by both experimental and numerical methods [15–17,35,48,49]. As a complement to experimentation, numerical modeling is an essential tool to optimize cell design, and plays an important role for the study of multiphysics, multiphase and multiscale phenomena, which are difficult to explore experimentally due to the small characteristic dimensions of PEFCs [15–17,50–56].

From a technical point of view, the operation of PEFCs with no external humidification is highly desirable in order to reduce the system complexity, weight, volume and cost, as well as to improve its efficiency and dynamical response [57–59]. Cells operated with low feed humidification rely on a delicate balance between water generated at the cathode and water removed by the gas streams to keep the membrane well hydrated. Multiple studies have addressed the operation of PEFCs with low humidification. One of the earliest works to consider the operation of a self-humidified PEFC was presented by Büchi and Srinivasan [57]. They showed stable operation of a dry-feed PEFC below 60 °C, with a 20–40% current density reduction at 0.6 V compared to a fully-humidified cell. Benziger et al. [59] studied the dynamics of an auto-humidified Stirred Tank Reactor (STR) PEFC, which was specially designed to ensure a uniform in-plane gas distribution. Different timescales were found in the cell dynamics due to sorption/desorption of water by the membrane, water transport through the membrane, and mechanical relaxation processes of the membrane. Kim et al. [60] reported an electrochemical analysis of a commercial PEFC operated at 60 °C with 80% anode RH considering various humidification levels at the cathode. They observed that the electrochemical active area and double-layer capacitance were weakly dependent on the cathode RH, and the catalyst layer and membrane ionic resistances were similar for dry-air feed. Adachi et al. [61] characterized ex-situ the water permeation flux through Nafion® NRE211 membranes exposed to either liquid and vapor phases of water, and examined in-situ the net water flux across the membrane in asymmetrically humidified cells. They found that the water flux in thin Nafion® membranes is larger when the membrane is exposed to liquid water on one side and water vapor on the other, and concluded that liquid-vapor permeation from cathode to anode can have a strong impact on the water balance of the MEA. Sánchez and García-Ybarra [62] studied the transients of a 25 cm^2 cell equipped with single-serpentine channels after a sudden change from fully-humidified to non-humidified operating conditions. They observed the propagation of a drying front from the cathode inlet, which eventually led to the deactivation of the entire active area.

The literature cited so far serves to illustrate the complexities of PEFC operation, and, in particular, of water management under low humidification. On top of that, several works have also reported intricate nonlinear PEFC dynamics, including multiple steady states and oscillations. These works, which initially appeared to be atypical studies scattered in the literature, are nowadays the focus of several investigations, as is the case of this work. A deeper knowledge of the interplay between mass, charge and heat transport coupled to electrochemical kinetics in unusual scenarios will contribute to a better understanding of PEFC technology. According to Hanke-Rauschenbach et al. [63], three main phenomena leading to nonlinear PEFC dynamics can be distinguished: i) coupled water and proton transport in the membrane, ii) electrochemical surface kinetics, and iii) interaction between reactant mass transport and water two-phase flow [18,19,64–75]. Below we review some relevant contributions that have addressed nonlinear PEFC dynamics induced by changes in membrane hydration under low feed humidification, i.e., belonging to point i) above.

Focusing first on steady-state multiplicity, Moxley et al. [76] showed that various steady states may arise in auto-humidified STR PEFCs owing to the strong dependence of membrane ionic resistance on water content. In analogy to auto-thermal reactors [77], current ignitions and extinctions were found when the initial hydration of the membrane was, respectively, above and below a threshold value (water content per sulfonic acid group, $\lambda \approx 1.8\ n_w/SO_3^-$). Current ignitions were caused by the good membrane hydration achieved from the positive (i.e., autocatalytic) feedback between water generation and membrane ionic conductivity. In contrast, current extinctions were caused by the dry-out of the membrane due to an insufficient initial water content. Hereafter, borrowing the terminology introduced by Benziger et al. [59] and Moxley et al. [76], the transitions from low to high and from high to low performance states will be referred to as ignition and extinction processes. In a second step, Benziger et al. [78] reported new findings on the bi-stable behavior found in Ref. [76] by examining the transients of the auto-humidified STR PEFC at different cell loads and temperatures. At temperatures above 70 °C and intermediate loads, they found the coexistence of two stable ignited states due to variations in the hydration level of the membrane, whereas a single steady state was present at either low or high loads. Chia et al. [79] developed a lumped isothermal single-phase steady-state model of an auto-humidified STR PEFC to study the effect of membrane ionic resistance, cell temperature, and hydrogen and air flow rates on the multiplicity of steady-state solutions. The bifurcation analysis showed the existence of up to five steady states for certain operating conditions. Nazarov and Promislow [80] presented a 2D isothermal single-phase transient model that captured the slow dynamics in an auto-humidified STR PEFC. They showed that the bi-stability observed by Benziger et al. [78] at intermediate loads could be explained by the effect of lateral water diffusion in the membrane.

Turning now the attention to oscillatory behavior, Benziger et al. [59,78] reported autonomous current oscillations with an extremely long period of up to 3 h after continuous operation of an auto-humidified STR PEFC for over 5000 h. They attributed this effect to the periodic relaxation of the membrane and the variation of the ohmic resistance at the membrane/electrode interface.

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