



# Local impact of humidification on degradation in polymer electrolyte fuel cells



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## HIGHLIGHTS

- Locally resolved current density measurements reveal high localized degradation.
- Contaminants such as Ni and Si induce local degradation.
- Ni contamination leads to irreversible degradation, Si produces recoverable losses.
- Identification of Ni contamination as a RH dependent degradation agent.
- Defluorination of the ionomer is observed under full humidity conditions.

## ARTICLE INFO

### Article history:

Received 19 December 2016

Received in revised form

7 March 2017

Accepted 15 March 2017

### Keywords:

PEFC

Water management

Degradation

Local measurements

Current density distributions

## ABSTRACT

The water level in a polymer electrolyte membrane fuel cell (PEMFC) affects the durability as is seen from the degradation processes during operation a PEMFC with fully- and nonhumidified gas streams as analyzed using an in-situ segmented cell for local current density measurements during a 300 h test operating under constant conditions and using ex situ SEM/EDX and XPS post-test analysis of specific regions. The impact of the RH on spatial distribution of the degradation process results from different water distribution giving different chemical environments. Under nonhumidified gas streams, the cathode inlet region exhibits increased degradation, whereas with fully humidified gases the bottom of the cell had the higher performance losses. The degradation and the degree of reversibility produced by Pt dissolution, PTFE defluorination, and contaminants such as silicon (Si) and nickel (Ni) were locally evaluated.

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## 1. Introduction

Proton Exchange Membrane Fuel Cells (PEMFCs), can be considered as key technology to reduce greenhouse gas emissions. One of the main problems hindering the widespread commercialization of PEMFCs is the limited durability of membrane electrode assemblies (MEAs) caused by numerous chemical and physical degradation singularities. In recent years, significant progress has been made towards meeting the challenging cost, durability, and performance targets required for the use of PEMFCs in automotive applications announced by the U. S. Department of Energy. However, the currently achievable operation hours [1] are still 22%

under the 2020 target [2]. In order to reach the durability goals, degradation of cell components has to be understood and mitigated specifically the irreversible degradation [3]. To increase cell performance, activation losses, ohmic losses, and mass transfer losses have to be reduced. A factor that affects all of these aspects is the water content in the cell, which is governed by water formation, reactant humidification, and water transport.

The strong impact of the water on cell performance is caused by the water-dependent proton conductivity of perfluorosulfonic acid (PFSA) membranes, which is the state-of-the-art ionomer used as membranes and in electrodes of PEMFCs. Its proton conductivity increases with the hydration level of the ionomer. Most likely, this is also the reason why oxygen reduction reaction (ORR) kinetics are reduced at low relative humidification (RH) [4]. Performance is, however, not only diminished by insufficient humidification but

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also by excessive water in the cell components responsible for gas transport. Condensation of water within the PEMFC, is likely to produce accumulation of liquid water in the porous electrodes and gas diffusion media (effect known as flooding), thus hindering the transport of reactants.

Since the possibility of simplifying the system by avoiding additional components is of great importance in the design of fuel cell systems for automotive application, operation with less or without humidification is preferred. Numerous studies have investigated the operation of PEMFC under dry conditions. Early work by Büchi et al. demonstrates stable performance for PEMFC using non-humidified or slightly humidified gases [5]. Strategies for operating PEMFCs include also the reduction of humidification of both reactant gases [6–8] or the dry operation of cathode [9–14] or anode sides [15].

Besides performance, the water level influences also the durability of the cell. Generally, studies report an increase of reactant crossover rate and voltage loss rate, as well as accumulation of structural membrane defects as consequences of operation at low RH [16–22]. However, different dependencies of durability on RH level were reported. On the one hand, a correlation between degradation and RH level was observed [23], on the other hand degradation was highest at medium RH values [24]. The authors interpreted this non-linearity as the result of the interaction of different RH effects on chemical membrane degradation [24]. In this chemical degradation mechanism, the reaction of hydrogen and oxygen diffusing through the membrane can lead to the formation of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), and in further consequence to the formation of radicals ( $\text{OH}\cdot$ ), which decompose the membrane [25]. This mechanism is catalyzed by Pt [26–31] and metallic cations [25,32,33]. Thus, impurities from e.g. tubing or stack components such as  $\text{Cu}^{2+}$  or  $\text{Fe}^{2+}$ , and Pt precipitates in the membrane resulting from catalyst dissolution can aggravate membrane degradation.

The level of RH generally influences the chemical degradation mechanism in multiple aspects. First, it influences the reactant crossover through the membrane, since membrane permeability increases with water content [34–36]. Second, it influences the rates of decomposition of the membrane by enhancing Pt dissolution and precipitation in the membrane. Furthermore, also reaction rates at Pt/Nafion<sup>®</sup> interfaces are influenced because of its impact on the surface oxidation state of Pt, on the permeation of reactants to the active sites and on the proton activity of the ionomer phase. The influence of RH on Pt surface state arises out of the oxide layer formation on Pt from water (also possible from  $\text{O}_2$  gas) [37–39]. Because the oxide layer represents a protection from dissolution, RH affects the Pt stability [40–42]. The proton activity/conductivity of the ionomer phase influences the proton transfer in the ORR. Since the water content of the ionomer determines its proton activity, RH can affect the formation rate of water (four electrons ORR pathway) and  $\text{H}_2\text{O}_2$  (two electrons ORR pathway). Third, it influences (together with the gas flow rate) the water flux through the MEA and therefore the transport rate of contaminants, e.g.  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Pt}^{2+}$  [22].

The described effects differ in their dependence on RH as the maximum degradation at medium RH observed by Xu et al. indicates [24]. Following dependencies were observed: Pt dissolution was reported to decrease with increasing RH [43]. Nevertheless, the precipitation of Pt in the membrane was found to be higher at high RH [44]. In contrast, Inaba et al. noticed an increase of Fe ion ( $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$ ) concentration in the condensate water at high RH [22]. They concluded that impurities accumulate in the cell at low RH and are washed out at high level of humidification. Regarding the reactant crossover rate, the increase of RH should result in a higher degradation rate due to increased formation of  $\text{H}_2\text{O}_2$ /radicals.

However, the maximum rate of  $\text{H}_2\text{O}_2$  formation was observed at medium RH, dropping at higher and lower RH [45]. This might be related to the impact of water content on ORR activity. It was discovered that the intrinsic ORR kinetics is independent of humidification at  $\text{RH} > 50\text{--}60\%$  but decreases clearly with RH below this value [4,46].

Previous studies investigated the effect of humidification extensively and provided important insight. Some of them paid special attention to the fact that the effect of water in the cell is a highly local, which demands appropriate tools to determine the causes for performance loss [7,47,48]. Furthermore, the introduction of advanced membranes with improved mechanical properties, chemical resistance, and higher ionic conductivity at low RH by additives may change the reported dependencies. To our knowledge, the influence of RH on this kind of membrane has not been studied yet. To close these two gaps, we systematically investigated the impact of RH on performance, durability, and operational stability of MEAs equipped with a more recent membrane type. This work presents the comparative study of the local degradation caused by operation of a single cell at non-humidified and fully humidified gas supply.

## 2. Experimental details

The effect of relative humidification on the cell behavior was studied using  $142\text{ cm}^2$  MEAs consisting of a commercial Nafion<sup>®</sup> XL membrane coated with a Pt/C based catalyst layer, and with a Pt loading of  $0.3\text{ mg}_{\text{Pt}}\text{cm}^{-2}$  on both sides (Ion Power Inc.). The catalyst coated membrane was placed between the gas diffusion layers Sigracet 25 BCE (SGL Carbon SE). The end- and bipolar plates were provided with a multi-serpentine flow field (see Fig. 1). The end-plates were gold-coated and the bipolar plates were graphite-based. The gaskets used on anode and cathode side were manufactured from high temperature silicone with low Shore hardness (Eisenhuth GmbH & Co. KG). The operating conditions are summarized in Table 1. The cell was developed in-house to be used for in-stack testing at the German Aerospace Center (DLR) [49].

The test bench allowed automatic control of the operating cell conditions, such as cell pressure, cell temperature, gas flow rates, and humidity of reactants. The relative humidity of the inlet gases was controlled by mass evaporator mixers. The reactant pressure was measured and controlled at the cell reactant outlet.

To investigate the RH influence on the cell behavior, the MEAs were operated galvanostatically at 100 A for more than 275 h. The cell temperature was set to  $60\text{ }^\circ\text{C}$ . In the case of the MEA operated at wet conditions, water-saturated reactants were supplied to the cell; hence the RH was approx. 100%. For the MEA operated at non-humidified conditions, the reactant flows bypassed the humidifiers; in this case, the RH was approx. 5%, since the incoming gases from the pipeline are at ambient temperature, therefore a residual humidity is present. In both cases, the reactants were supplied to the cell with a flow rate of  $840\text{ ml min}^{-1}$  for hydrogen and  $3320\text{ ml min}^{-1}$  for air, both at a pressure of 1.5 bar. Before and after the test, the cells were electrochemically characterized using E-j curves and cyclic voltammograms (CVs). The measurement time is hereafter referred to as begin of test (BoT) and end of test (EoT), respectively. It has to be noted that, for both MEAs, during the BoT and EoT characterization the temperature was set to  $80\text{ }^\circ\text{C}$ , and the reactant humidification was kept at 100% RH for the cyclic voltammetry measurements and 50% RH for the E-j curves. The operating conditions are summarized in Table 1.

Performance losses were compared by means of current densities, E-j curves and ECSA (electrochemically active surface area) at the beginning and at the end of the test. In order to investigate degradation, the chemical composition of the MEA was locally

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