



Effect of pinhole location on degradation in polymer electrolyte fuel cells



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HIGHLIGHTS

- Degradation in a fuel cell with various pinholes was investigated.
- Mild defects may result in a temporarily improved performance.
- A correlation between carbon corrosion and hydrogen crossover was evident.
- Defects near the anode inlet have the strongest influence on degradation.
- Fuel starvation resulted in a more severe voltage drop with a perforated membrane.

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ABSTRACT

This work analyses the impact of the location of pinholes in polymer electrolyte fuel cells on the degradation of the electrodes. Defects with a diameter of 0.45 mm were created in a 25 cm² membrane electrode assembly (MEA) of a fuel cell. The MEA was operated and characterised using a segmented single cell. The effects of the pinholes on degradation were measured and evaluated. Defects affected the fuel cell behaviour during periods of hydrogen starvation, thus accelerating the degradation process of the carbon support as well as the loss of active platinum catalyst surface area. Furthermore, the effects of the induced pinholes on membrane degradation and performance decay were determined.

Pinholes close to the anode inlet in general have shown a more severe effect on the fuel cell operation parameters, such as open circuit voltage, performance, membrane resistance and hydrogen crossover, than pinholes at any other locations. Also, electrode degradation was accelerated. These effects were mainly due to locally increased temperatures.

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1. Introduction

The polymer electrolyte fuel cell produces power at high efficiencies and is, therefore, of interest both for use in automotive applications [1,2] and combined heat and power units in residential applications [3]. However, commercial systems do not fully live up to the expectations with regard to operational lifetime yet. The aim for mobile applications is 5.000 h and 40.000–80.000 h for stationary applications [4].

Limitations in lifetimes are mainly caused by the degradation of

the membrane electrode assembly (MEA). The degradation of the membrane has a different effect on the fuel cell operation than degradation of the electrodes. In order to improve durability, it is necessary to gain a profound understanding of each failure mode.

Pinholes and areas of membrane thinning both result in a localised increase in hydrogen crossover and are, therefore, expected to lead to further degradation in a similar way. Both defects may derive from membrane degradation under undesirable operation conditions, such as operation under conditions of open circuit potential (OCV) or low humidity. Pinholes and cracks can, furthermore, be introduced to the membrane by mechanical stressors either within the fuel cell, during membrane manufacturing, or during implementation in the fuel cell. Such defects, therefore, cannot be avoided completely and their effects should be investigated.

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Pinholes are the subject of intense research, which has mostly been conducted using accelerated stress tests that provoke specific defective modes [5–7]. However, only few studies have been conducted that evaluate the effects of pinholes on different operation parameters or further degradation processes [8–10], and none of the cited studies have taken the effects of pinhole locations on the observed results into account.

This research evaluates the effects of pre-existing defects at different locations in the membrane on the behaviour of the fuel cell during normal and critical operation modes and on further degradation processes of the electrodes and the membrane. Pinholes were created in the membrane electrode assembly at various locations. A single cell setup with a segmented cathode was used for in-situ characterisation.

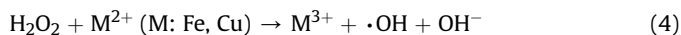
2. Degradation in polymer electrolyte fuel cells

Pinholes in the fuel cell membrane are formed by material inhomogeneities, mechanical stress and degradation. The local operation conditions around the pinholes change in comparison to normal operation. The direct chemical oxidation of hydrogen with oxygen leads to a temperature increase at the affected area. Furthermore, the formation of water is affected locally due to the direct oxidation, thus causing a higher humidification at the location of increased crossover. Additionally, the direct consumption of the reactant gases can lead to local starvation conditions further down the channels, thus affecting the electrode corrosion process and induce the formation of hydrogen peroxide in case of oxygen starvation. Hydrogen peroxide is known to be formed by incomplete oxygen reduction [11]. This affects both electrode corrosion and membrane degradation.

2.1. Membrane degradation

2.1.1. Causes for membrane degradation

Membrane degradation is triggered by hydrogen peroxide formation, which is favoured at OCV conditions. H_2O_2 can be detected within the drain water [12,13]. It decomposes to hydroxyl radicals in the presence of metal ions such as Fe^{3+} and Cu^{2+} (Equations (1)–(5)) [14].



The degradation of the perfluorosulfonic acid (PFSA) backbone of the membrane, but also of the ionomer within the electrode is quantified by measuring the fluoride content in the effluent water. Fluoride ions are emitted in form of HF and therefore, the fluoride ion emission is directly linked to the pH value of the exhaust water.

The fluoride emission rate (FER) is used to determine the decomposition of the electrolyte. However, the C–F bond is thermodynamically stable and F^- cannot be abstracted by the OH radical, formed by the homolytic cleavage of the O–O bond of hydrogen peroxide. Instead, the abstraction of a hydrogen atom by the OH radical is favoured [15].

$H \cdot$ is formed by the abstraction of a hydrogen atom from molecular H_2 by $\cdot OH$ and aggressive towards the C–F bonds in PFSA. $H \cdot$ is able to induce damage of the polymer backbone, which is

consistent with the accelerated fluoride release over time and in dependence of hydrogen crossover exhibited in chemical degradation studies of PFSA based membranes [15].

The membrane degradation is accelerated at OCV conditions, since hydrogen is not consumed and $H \cdot$ can be formed in larger quantities. The fluoride emission rate increases with low humidity, a higher partial pressure of oxygen on the cathode, high temperature and most importantly high hydrogen pressure. Due to the high boiling point of hydrogen peroxide (150 °C) compared to water, high temperatures are thought to result in a higher H_2O_2 concentration, thus accelerating the degradation. Chemical degradation is the most severe among the degradation phenomena and it results in membrane thinning and pinhole formation, leading to increased hydrogen crossover, further accelerating degradation [13].

The FER is not always clearly associable with the degree of membrane degradation. Decreasing rates have been reported, despite operation at harmful conditions. The emission of fluorine in form of C–F compounds is possible and cannot be detected by common fluoride detection methods. Therefore, FER detection is not always an accurate method for quantification of membrane degradation [16].

2.1.2. Effect of membrane degradation on the fuel cell operation

The effect of pinholes on the OCV depends on their size. A rather small pinhole with a diameter of 0.7 mm has shown close to no impact on the open circuit potential, whilst a larger pinhole with a diameter of 1.2 mm resulted in an immediate reduction of the potential [10]. At high current densities, a perforated MEA has exhibited a serious decrease in performance and strong voltage fluctuation. However, the effect was smaller at low current densities [9].

The increased hydrogen crossover results in elevated hydrogen diffusion current. The distribution of the crossed over hydrogen was visualised by spatial resolution [8]. Not only the affected area exhibits an increased hydrogen diffusion current, but also the surrounding segments.

With the C–S bond being the weakest in the polymer electrolyte, sulphur can be released as SO_2 or SO_3 , the latter via a hydrogen peroxide triggered sulfonyl radical mechanism. This also contributes to the main chain scission, increases the membrane resistance due to the loss of proton conducting species and further accelerates the degradation of the PFSA backbone [15,17].

2.2. Electrode

The process of electrode degradation is divided into carbon corrosion and catalyst degradation. Both influence each other and affect the electrochemical surface area (ECSA) by decreasing the catalytically active area.

2.2.1. Degradation of the carbon support

The rate of the corrosion of the carbon support is determined by the CO_2 content of the off-gas. Carbon nanoparticles undergo severe degradation at potentials that exceed 1 V. The CO_2 concentration is increased even more in the presence of platinum; however, a direct correlation between CO_2 evolution and platinum loading, in a sense that platinum catalyses the carbon oxidation, has not been found due to the limited area of the carbon/platinum interface [18].

The proposed mechanism of carbon corrosion follows a two-step reaction pathway (Equations (6) and (7)), that consists of a carbon oxidation step, followed by a water-gas shift reaction. The second reaction (Equation (7)) is the rate determining step. In the presence of a catalyst, it follows an alternative platinum catalysed pathway (Equations (8) and (9)) [18].

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