



## Effect of catalyst layer defects on local membrane degradation in polymer electrolyte fuel cells



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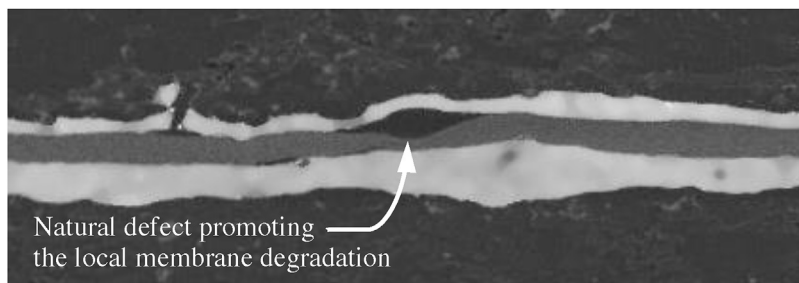
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### HIGHLIGHTS

- Customized MEAs with artificial defects are subjected to accelerated stress tests.
- Significant global membrane thinning is observed in iron oxide contaminated MEAs.
- Negligible impact is shown for catalyst layer cracks and cathode delamination.
- Locally elevated membrane degradation is revealed at anode delamination sites.
- Substantial mitigating effect is shown for Pt residuals on the membrane surface.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Aiming at durability issues of fuel cells, this research is dedicated to a novel experimental approach in the analysis of *local* membrane degradation phenomena in polymer electrolyte fuel cells, shedding light on the potential effects of manufacturing imperfections on this process. With a comprehensive review on historical failure analysis data from field operated fuel cells, *local sources of iron oxide contaminants, catalyst layer cracks, and catalyst layer delamination* are considered as potential candidates for initiating or accelerating the local membrane degradation phenomena. Customized membrane electrode assemblies with artificial defects are designed, fabricated, and subjected to membrane accelerated stress tests followed by extensive post-mortem analysis. The results reveal a significant accelerating effect of iron oxide contamination on the *global* chemical degradation of the membrane, but dismiss local traces of iron oxide as a potential stressor for *local* membrane degradation. Anode and cathode catalyst layer cracks are observed to have negligible impact on the membrane degradation phenomena. Notably however, distinct evidence is found that anode catalyst layer delamination can accelerate *local* membrane thinning, while cathode delamination has no apparent effect. Moreover, a substantial mitigating effect for platinum residuals on the site of delamination is observed.

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## 1. Introduction

High durability and reliability are of increasing importance as

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fuel cell systems are widely deployed. Based on current market requirements, a lifetime of more than 20,000 and 6000 operating hours is targeted for buses and cars, respectively, while 40,000 h of operation is demanded for stationary applications [1]. Although the lifetime targets of automotive applications are considerably lower than those of stationary applications, the fluctuating operating conditions due to vehicle dynamics, variations in loads and environmental conditions, startups and shutdowns, fuel starvation, contamination, and freeze-thaw cycles pose a significant technological durability challenge. It has been demonstrated that different degradation routes can lead to failure of various cell components, but considering the expected service times of the fuel cells, the *membrane* is considered one of the most vulnerable components which predominantly determines the lifetime of a fuel cell stack. This has led to a large number of publications on known or hypothesized mechanisms for membrane degradation, under various working conditions and from different points of view [2].

The membrane degradation mechanisms that occur in polymer electrolyte fuel cells are not yet entirely known, but the progressive deterioration of membrane properties roots in a complex series of interconnected *chemical* and *mechanical* mechanisms. Chemical degradation is generally accepted as the key factor in the membrane degradation process where membrane stability is severely affected by the existence of reactive chemical species, *i.e.*, radicals [1,3]. It has been confirmed via in-situ and ex-situ studies that the formation of free radicals during fuel cell operation plays a dominant role in the chemical degradation of the ionomer molecular structure in the membrane [4–8]; however, there are conflicting views on the formation and attack sites of these radicals. Huang et al. [9] and De Moor et al. [10] showed that degradation begins at the anode side and progresses toward the cathode, while others [11–13] have observed signs of predominant degradation on the cathode side. There are also evidences that degradation is uniform across the membrane thickness with no noticeable difference on either side [14]. Radicals can be produced through two distinct pathways [15], with  $\text{H}_2\text{O}_2$  as the intermediate species or via direct reaction of  $\text{H}_2$  and  $\text{O}_2$  on the surface of Pt [16–21].  $\text{H}_2\text{O}_2$  would be formed on the anode or cathode catalyst layers. As proposed by Damjanovic et al. in the 1960s [22], oxygen is reduced via a direct four-electron oxygen reduction reaction (ORR), forming water. However, ORR may also proceed through two-electron reduction to  $\text{H}_2\text{O}_2$  ( $E^0 = 0.695$  V vs. SHE) followed by the reduction of  $\text{H}_2\text{O}_2$  to water ( $E^0 = 1.77$  V vs. SHE). In this case,  $\text{H}_2\text{O}_2$  may detach from the catalyst surface, enter the bulk of the membrane, and decompose to radicals in the presence of transition metal cations or heat [4,11,23]. Although the four-electron pathway is dominant on noble metals such as Pt, two-electron reduction occurs simultaneously in varying ratios [24]. It has also been suggested that the presence of carbon supported Pt catalyst [25] or Pt band in the membrane [26] originating from catalyst layer degradation may facilitate the kinetics for the formation of hydrogen peroxide under specific operating conditions. Finally, considering the reaction potentials, the anode side is a more favorable site for the two-electron reduction where the potential is lower than the reaction potential (0.695 V vs. SHE) and oxygen may be present due to gas crossover [27,28].

Corrosion of stack components and external impurities originating from reactant air or humidifier reservoirs could bring small quantities of metal contaminants into the cells. Traces of metal impurities may also be detected in as-received membranes and other component materials. With emphasis on transportation applications in urban areas, fuel cell systems are also exposed to various air pollutants present in the environment. After extended operation, the membrane electrode assembly (MEA) of the fuel cell is expected to contain measurable amounts of  $\text{Ca}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Mg}^{2+}$  [1]. The presence of impurities such as  $\text{Fe}^{3+}$  ions

can contribute to the chemical membrane degradation process by catalyzing the radical formation reactions [29]. In a recent work by Wong et al. [30], a transient membrane degradation model was developed to capture the redox cycle of iron ions within the membrane electrode assembly, which sustains the presence of harmful  $\text{Fe}^{2+}$  ions in the membrane even at low contamination levels and results in the most severe chemical degradation at open circuit voltage. As originally proposed by LaConti et al. [31], hydroxyl ( $\text{HO}\cdot$ ) and hydroperoxyl ( $\text{HOO}\cdot$ ) radicals are formed from hydrogen peroxide in the presence of these ions.

Commonly used perfluorosulfonic acid (PFSA) ionomer membranes are composed of a PTFE backbone featuring periodic fluorine-ether side chains with sulfonic acid end groups, providing mechanical stability and proton conductivity, respectively [32,33]. It was first determined that chemical degradation is predominantly initiated through OH radical attack on the main chain carboxylic acid terminal groups [16,34–36] or on the C–S or O–C bonds of the side chain [15,16,35–42]. However, as new generations of membranes have been chemically stabilized, the concentration of terminal carboxylic acid groups has been decreased to negligible levels [34,35] and degradation therefore occurs mainly on the side chain of the ionomer [43].

While chemical degradation mechanisms are responsible for the gradual deterioration of membrane properties, mechanical degradation is considered as a major cause for sudden membrane failures. Originating from hygrothermal cycles during fuel cell operation, varying temperature and relative humidity result in repetitive expansion and contraction of the membrane, inducing fatigue, creep, and tension which ultimately leads to cracks and holes associated with membrane failure [44–52]. Manufacturing imperfections can introduce local stress points where cracks and holes may evolve [53–55], while certain operating conditions such as low humidity [20,55,56] can render the membrane brittle and fragile, making it more vulnerable to further mechanical stress.

Although the majority of available literature focuses on membrane degradation as a *global* phenomenon, it is generally accepted that catastrophic membrane failures are due to *local* failure points [57] leading to destructive reactant gas transfer between the opposing electrodes. It is therefore hypothesized that local defects and variations in the MEA structure may influence the local rates of membrane degradation and form preferential sites for eventual failure. Kundu et al. [53] categorized the possible morphological defects imparted on catalyst coated membranes in their beginning-of-life state. It is assumed that these defects are mainly introduced during the manufacturing and processing. They classified these anomalies into six major categories of catalyst layer cracks, delamination, orientation, electrolyte clusters, platinum clusters, and thickness variations, among which the first two are expected to be of primary relevance for membrane degradation. *Cracks* are prone to form in fresh and aged MEAs and are commonly present in both anode and cathode catalyst layers. A fuel cell can generally operate in the presence of such defects; however, performance and durability may be negatively affected. For a fresh MEA, these features could be formed during manufacturing or be a consequence of poor handling, bending, or stretching of the MEA. Membrane expansion and contraction during fuel cell operation may also result in catalyst layer cracks [45,51,53]. *Delamination*, which is observed when the catalyst layer is separated from the membrane, may also occur during the manufacturing processes or during operation [45,51]. As discussed by Kundu et al. [53], the high temperature applied in the catalyst layer drying stage can cause vapor to form at the catalyst layer/membrane interface, and create areas of poor adhesion. Differences in thermal and expansion properties of membranes and catalyst layers may also be responsible for delamination during both manufacturing and operation. It

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