



# Effects of isolated chemical and mechanical degradation stressors on the ionomer morphology in fuel cell membranes



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## ABSTRACT

The present work aims to understand the specific effects of isolated chemical and mechanical degradation stressors on the morphology and physico-chemical properties of fuel cell membranes. Chemical and mechanical degradation stressors are isolated in two specific, carefully designed accelerated stress tests of fuel cells. Degraded membranes are then extracted and systematically analyzed through contrast enhanced transmission electron microscopy, thermogravimetric analysis, and water sorption measurements. Statistical analysis of the ionomer morphology shows that chemical degradation dilates hydrophilic pores and disintegrate ionomer bundles, while the water uptake per unit area decreases. However, significant ionomer mass loss is found to reverse the water sorption trend, leading to an increased water uptake per ionomer mass unit, in agreement with the dilation effect. In contrast, mechanical degradation merely causes a slight ordering of the morphology and a marginal increase in water uptake due to bulk water residing in membrane cracks formed by fatigue-fracture. Compounded chemical and mechanical degradation effects are therefore considered particularly harmful, given the ability to bridge mesoscale morphological alterations induced by chemical degradation to macroscale damage propagation under mechanical stress cycles, leading to ultimate membrane failure.

## 1. Introduction

Polymer electrolyte fuel cells (PEFCs) using hydrogen fuel are the most commonly used technology for electrochemical energy conversion in zero-emission fuel cell electric vehicles and many other mobile and stationary power applications where they generally serve to minimize environmental impact. PEFCs are subjected to strong oxidizing and reducing conditions, humidity variations, liquid water, fluctuating temperatures, high electrochemical potentials, reactive radical species, high currents, and large voltage gradients during operation. These factors lead to mechanical, electrochemical, and chemical degradation of components in an operating fuel cell [1]. Failure of the membrane used to separate the two electrodes in a fuel cell causes sudden performance loss as well as significant hydrogen leaks [1] and is hence a key factor in building durable and reliable fuel cells. The most widely used polymer electrolyte for fuel cell applications is the per-fluorosulfonic acid (PFSA) ionomer membrane. The molecular structure of the PFSA membrane plays a vital role in the performance and durability of PEFCs due to its unique hydrophobic fluorocarbon main chains and side chains with hydrophilic end groups. The important functional properties of the membrane such as proton conduction, water retention, and mechanical stability are associated with its unique

morphology, which forms water nanochannels when hydrated and a robust network of backbone fiber bundles [2,3]. At present, thin PFSA ionomer membranes are a state-of-the-art material for PEFC applications which delivers high power density with relatively low degradation rates. However, membrane degradation over time is still a concern, especially for applications with stringent reliability and durability standards [4,5] such as transit buses, trams, and trains.

In an operating PEFC, chemical stressors that arise during high voltage operation may induce locally elevated membrane degradation [6] while mechanical stressors arising from hygrothermal fluctuations support propagation of damage [7] in a combined chemical and mechanical stress situation [8–12]. Accurate knowledge about the role of individual stressors and their respective effects on the ionomer is critical in order to elucidate the complex overall membrane degradation mechanisms that occur during fuel cell operation. Chemical stress in the form of reactive radicals has been shown to degrade the end groups, ether-linked side chains, and main chains in the PFSA ionomer [13–15]. Such structural degradation led to a decrease in ‘d’ spacing (distance between adjacent hydrophilic domains) which affected the crystallinity of the material [16,17]. Luo *et al.* [18] found an increase in the hydrophilic domain radius due to the evolved heat and gases through the Fenton's reaction, which is an *ex situ* technique to aggressively

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accelerate chemical degradation by immersion of a membrane specimen in a chemical solution. Such morphological changes due to severe chemical degradation led to reduced water uptake, ion-exchange capacity, and proton conductivity while the water permeation and proton mobility increased [14,18]. Furthermore, chemically degraded regions may form pinholes due to local chemical erosion [19]. Mechanical stress arising from confined membrane expansion and contraction during hygrothermal variations, on the other hand, theoretically leads to permanent plastic deformation due to anisotropic swelling [20,21] and fatigue-fracture upon repeated cycling [22]. Uniaxial tensile stress cycling was shown to cause preferential alignment of ion-rich domains prior to fracture [23], while *in situ* humidity cycling in fuel cells may cause a reduction in the average molecular weight of the ionomer [7,24,25]. Severe mechanical damage from extended humidity cycling may also facilitate reduced ultimate tensile strength, final strain, and fracture toughness due to ductile to brittle transition, followed by ultimate membrane failure by fracture [26]. In both degradation scenarios discussed in the literature, it is suggested that the membrane microstructure is affected, but the severity and mode of microstructural changes induced by the individual stressors were not explored in detail. Also, most previously reported structure-property relationship studies were carried out *ex situ* in order to simplify the experimental procedures and hence used bare membranes. In an operating fuel cell, however, membranes are sandwiched between anode and cathode catalyst layers, and the *ex situ* approach is not a true representation of the stress scenarios encountered in fuel cell operation. A significant body of work [27–30] promulgated that the properties of catalyst coated membranes used in actual fuel cells differ from those of bare membranes; hence, *in situ* studies are necessary to better understand the realistic degradation processes.

It was recently discovered by our group that the mesoscale morphology of PFSA ionomer membranes is considerably altered during combined chemical and mechanical degradation in a fuel cell [10]. Important mesoscopic aspects regarding membrane fracture development were identified; however, the scope of the work lacked critical information about the roles of the individual chemical and mechanical stressors and their specific influence on the overall process. The objective of the present work is therefore to decouple the effects of *in situ* chemical and mechanical stressors during fuel cell operation and determine their individual influence on the mesoscale degradation phenomena in the membrane. This will address the current limitations in the knowledge base of the mesoscale degradation phenomena during combined chemical and mechanical membrane degradation that are responsible for the development of macroscopic membrane failure [9–11,31].

## 2. Experimental

Research grade membrane electrode assemblies (MEAs) were made by hot pressing anode and cathode gas diffusion electrodes (GDEs) with a non-reinforced PFSA ionomer membrane. GDEs were prepared by coating a carbon black and polytetrafluoroethylene (PTFE) based microporous layer on a non-woven carbon paper gas diffusion layer (GDL) substrate followed by coating a catalyst layer consisting of carbon-supported platinum catalyst and PFSA ionomer.

### 2.1. Chemical membrane degradation

*In situ* chemical membrane degradation was induced by applying a high voltage hold at fixed temperature and relative humidity (RH) to a research scale ten cell stack with graphitic bipolar plates with co-flow configuration. This test condition is based on our previous work on accelerated membrane durability testing (AMDT) of heavy duty fuel cells for transit bus applications reported by Macauley *et al.* [19]. The baseline AMDT utilized combined chemical/mechanical stress resembling fuel cell bus operating conditions to accurately evaluate *in situ*

membrane durability. The authors also developed complementary AMDT protocols to evaluate the specific effects of RH cycling and platinum in the membrane (PITM) on the membrane durability. Here, the 100% constant RH AMDT option was applied in order to eliminate potential influences from cyclic hygrothermal stress and associated mechanical degradation. Isolated *in situ* chemical degradation was thus facilitated by supplying hydrogen and oxygen to anode and cathode at the flow rates of 5 and 10 slpm, respectively, while strictly kept at 100% constant RH throughout the entire duration of the experiment. To ensure rapid membrane failure despite the absence of mechanical stressors, a high stack voltage of 9.0 V (0.90 V per cell) was used, while the temperature and oxygen partial pressure were raised to 85 °C and 45%, respectively, in order to accelerate chemical degradation. This stack reached membrane failure after 643 h, as detected by a critical hydrogen leak rate exceeding 10 sccm per cell. This lifetime was considerably longer than for the baseline AMDT where combined chemical/mechanical degradation led to earlier failure due to the action of mechanical stress cycles induced by RH cycling. The membrane failure mode obtained under isolated chemical degradation consisted of major global membrane thinning (~35% on average) and smooth pinholes (average diameter of 40 μm; 1.2 holes per cm<sup>2</sup>) accompanied by a gradual leak rate growth, mild open circuit voltage (OCV) decay, and a relatively constant fluoride release rate. All damage appeared to be chemical in nature. *Post mortem* tensile tests revealed a transition from ductile to brittle mechanical properties as a result of chemical degradation. More information about the adopted chemical degradation AMDT experiment can be found elsewhere [19].

### 2.2. Mechanical membrane degradation

*In situ* mechanical membrane degradation was induced by applying an accelerated mechanical stress test (AMST) procedure based in part on the US Department of Energy accelerated stress test for mechanical membrane degradation [32] to a research scale five cell stack. The AMST procedure was originally developed by our group [26] to investigate the effects of *in situ* hygrothermal fatigue on the microstructure and mechanical properties of the membrane. The AMST was carried out by applying rapid, deep wet/dry cycles at relatively high temperature and ambient pressure. Inert nitrogen gas was used at both anode and cathode in order to eliminate any occurrence of chemical degradation. Diagnostic tests involving hydrogen and/or oxygen were also avoided for the same reason. Successive RH cycles of 2 min wet (90% RH) and 2 min dry (0% RH) states at 80 °C and 9.0 slpm flow rates were applied until membrane failure was reached, which occurred after 20,000 cycles, as indicated by a significant increase in gas transfer leak (> 10 sccm per cell) at the inlet region. *Post mortem* analysis revealed membrane and catalyst layer cracks as well as delamination as a result of the applied cyclic hygrothermal stress. No significant thinning or other signs of chemical degradation were identified. Tensile tests indicated a membrane material transformation from the originally ductile state to a relatively brittle state with reduced stress tolerance due to the initiation and propagation of micro-cracks. In contrast, the elastic modulus and hygral and thermal expansion properties did not change considerably, which suggests that the membrane response to hygrothermal fluctuations was not altered by mechanical degradation. Further information about the adopted mechanical degradation experiment can be found elsewhere [26].

### 2.3. Morphological studies

A pristine PFSA ionomer membrane was used as baseline rather than extracting the membrane from a beginning-of-life (BOL) MEA in order to explicitly compare the pristine morphology with the degraded morphology. The pristine membrane sample was stained in saturated lead acetate solution for about 48 h in order to enhance the electron image contrast of ionic clusters by selectively exchanging protonic sites

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