# In-situ diagnostics and degradation mapping of a mixed-mode accelerated stress test for proton exchange membranes

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## HIGHLIGHTS

- A mixed-mode accelerated stress test for PEM fuel cells is proposed.
- High spatial resolution to diagnose PEM degradation is achieved via a segmented fuel cell.
- The experimental results have been validated using traditional diagnostic methods.

## ARTICLE INFO

## ABSTRACT

With increasing availability of more durable membrane materials for proton exchange membrane fuel cells, there is a need for a more stressful test that combines chemical and mechanical stressors to enable accelerated screening of promising membrane candidates. Equally important is the need for in-situ diagnostic methods with sufficient spatial resolution that can provide insights into how membranes degrade to facilitate the development of durable fuel cell systems. In this article, we report an accelerated membrane stress test and a degradation diagnostic method that satisfy both needs. By applying high-amplitude cycles of electrical load to a fuel cell fed with low-RH reactant gases, a wide range of mechanical and chemical stressful conditions can be created within the cell which leads to rapid degradation of a mechanically robust Ion Power™ N111-IP membrane. Using an in-situ shorting/crossover diagnostic method on a segmented fuel cell fixture that provides 100 local current measurements, we are able to monitor the progression and map the degradation modes of shorting, thinning, and crossover leak over the entire membrane. Results from this test method have been validated by conventional metrics of fluoride release rates, physical crossover leak rates, pinhole mapping, and cross-sectional measurements.

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## 1. Introduction

One of the key challenges facing the commercialization of automotive fuel cells is the development of membrane electrode assemblies (MEAs) that can meet durability targets. In proton exchange membrane (PEM) fuel cells, the PEM serves to conduct protons from the anode electrode to the cathode electrode of the fuel cell while simultaneously insulating electronic current from passing across the membrane and preventing crossover of the reactant gases, $H_2$ and $O_2$. State-of-the-art PEM fuel cells for high power density operation utilize perfluorosulfonic acid (PFSA) membranes that are typically no more than 25 μm thick. To be viable for automotive applications, these membranes must survive

10 years in a vehicle and 5500 h of operation including transient operation with start-stop and freeze-thaw cycles. Fuel cells cannot operate effectively if even small amounts of gas are able to permeate the membrane through microscopic pinholes. Ultimately, fuel cells can fail because such pinholes develop and propagate within the polymer membranes. Fuel cells can also fail if electronic current passes through the membranes and causes the system to short. It is critical that these membranes are sufficiently robust to cracking and shorting over the range of conditions experienced during fuel cell operation. In automotive fuel cell systems, there are three primary root causes of membrane failure: (1) Chemical degradation: polymer decomposition caused by the direct attack on the polymer from radical species generated as byproducts or side reactions of the fuel cell electrochemical reactions; (2) Mechanical degradation: membrane fracture caused by cyclic fatigue stresses imposed on the membrane via humidity and thermal fluctuations in a constrained cell; and (3) Shorting: electronic current passing

though the membrane caused by local over compression and creep due to cell over compression or topographical irregularities of the neighboring components such as electrodes and gas diffusion layers (GDL).

Chemical degradation of PFSA membranes can be characterized by membrane thinning and the emission of HF, $CO_2$ and $H_2SO_4$ in the fuel cell exhaust streams. The thinning leads to increased rates of gas crossover and mechanical weakening that ultimately result in cell failure. The rate of chemical degradation can be conveniently monitored *in situ* by quantifying the fluoride emission using a variety of analytical techniques. Although the degree of chemical degradation can be expressed in terms of total membrane fluoride inventory loss, whether this value can provide a meaningful indication of membrane health highly depends on the uniformity of degradation. Liu et al. reported that the MEA can fail at an inventory loss from a low of about 1% when degradation is very localized to as high as 50% under uniform degradation [1]. In general, the rate of chemical degradation of PFSA membranes can be accelerated by high temperature, low relative humidity, low electrochemical load, and high reactant gas pressures [1–4]. To assess PEM's chemical durability, the U.S. Department of Energy (DOE) has recommended the use of open circuit voltage (OCV) hold test [5] at a relatively hot and dry test condition of 90 °C and 30%RH. In this test, the health of membranes can be monitored through $F^-$ release, $H_2$ crossover, high frequency resistance (HFR), and shorting resistance. A chemically durable membrane should be able to endure more than 500 h in this test without significant degradation according to the durability metrics and targets.

Mechanical degradation of membranes is driven by the fatigue stresses caused by the hygrothermal expansion and contraction of the constrained membrane. As the membrane is weakened by the fatigue stresses, microscopic cracks initiate and propagate through the thickness of the membrane, resulting in the crossover of reactant gases. Although numerous ex-situ tests and material models have been developed to characterize the membrane's mechanical properties to facilitate material screening and development [6–14], the most relevant mechanical durability test remains the humidity cycling test that was proposed by Gittleman et al. [15,16] and later adapted by the U.S. DOE [5]. Cycling between 0% and supersaturated conditions at 80 °C in a non-operating fuel cell, the test can introduce mechanical degradation mimicking that in an operating fuel cell. In this test, the health of the membrane can be monitored through the gas crossover and shorting resistance. A mechanically durable membrane should endure 20,000 humidity cycles without exceeding the crossover criterion established by the U.S. DOE.

Shorting occurs when electrons flow directly from the anode to the cathode instead of through the device being powered. Shorting not only can reduce the performance of fuel cells, but also can lead to local heat generation in the vicinity of the short, causing membrane damage that can ultimately result in gas crossover failure in fuel cells. The diagnostic for shorting can be as straightforward as monitoring the ohmic resistance of the fuel cell. However, early detection of shorts can be difficult because shorting is often localized and the sensitivity of shorting measurement on the cell level can be greatly diminished even for a severe but localized short. Although the U.S. DOE has not published a recommended membrane shorting test, two shorting tests have recently been proposed in the literature. A shorting resistance test using a non-operating single fuel cell fixture was used by Mittelsteadt and Liu [17] to measure the specific resistance of the specimen at a voltage of 0.5 V applied across the cell at 95 °C and 100%RH or under the U.S. DOE humidity cycling test condition with inert nitrogen gas flowing on both sides of the membrane. As the test proceeds, the compression load of the cell is increased stepwise through a pre-determined compression schedule. As opposed to the constant voltage

applied to the cell to measure the shorting resistance, an alternate shorting test proposed by Gittleman et al. [18] calls for the application of 0–5 V of potential sweeps to expose the critical soft short in a fuel cell by escalating the soft short into a hard short after the membrane is conditioned at 95 °C and 0%RH in nitrogen gas for 1 h. The critical soft short can be reached by the stepwise increase of the fuel cell compression after each 1-h conditioning and potential cycling step.

The above mentioned tests represent some of the so called accelerated stress tests (AST) that are designed to accelerate the degradation rate for certain failure mode by controlling the severity of the specific stressor. Through such ASTs, one can improve the ability to predict the fuel cell lifetime or the understanding of the degradation mechanisms. Rodgers et al. [19] has reviewed more ASTs and the underlying membrane degradation mechanisms that these ASTs were designed for. In this article, they correlated the AST results with fuel cell lifetimes and found that many of these ASTs can indeed significantly accelerate the degradation rates. Four common methods or the combination of these are generally used in these ASTs, which include (1) high temperatures, (2) reduced humidity, (3) OCV, and (4) cycling (humidity, temperatures, voltage, freeze/thaw, and start/stop). In practice, the ASTs of single degradation modes are often sufficient as initial screening steps to select material candidates in developing fuel cell systems as they can provide a direct feedback for material developers to improve against a specific stressor. With the increasing availability of more durable membrane materials, however, there is an increasing need for even more stressful tests that can further separate these materials. There is also a need to evaluate these membranes in a realistic fuel cell condition that requires the utilization of a combination of more severe temperatures, humidities, electrochemical loads, or cycling of those stressors to achieve a greater acceleration in the durability test. In the complex mixed-mode testing, a more sophisticated diagnostic method is then required to understand the role of different stressors and how they interact with each other before leading to the ultimate membrane failure. Consider the example of an ohmic short that can generate heat and increase local temperature which accelerates chemical degradation locally and thus leads to weakening of membranes that allows cracks to form mechanically. The increased crossover through the cracks can then increase the rate of chemical degradation that exacerbates the membrane thinning and reduces the mechanical resistance to carbon fiber penetration which further worsens the ohmic shorting. As such, a vicious cycle of shorting, thinning, and cracking can take place regardless of the initiator. Because of this synergistic effect, it can be easy to misjudge the critical weakness of the membrane if solely relying on postmortem analyses. The ability to detect initiation of degradation, to distinguish modes of degradation, and to continuously monitor the progress of degradation without interrupting the durability test would be highly desirable if a mixed-mode durability test is to be used and a deeper understanding of the material is required. Furthermore, as fuel cells often fail by highly localized degradation, there is an additional need for a diagnostic technique that provides sufficient spatial resolution to detect the localized degradation. In this article, we will report a mixed-mode AST and a diagnostic method that can satisfy these needs.

## 2. Experimental

The fuel cell consisted of an MEA with carbon supported Pt catalyst (0.4 $mg_{Pt}$ $cm^{-2}$) applied to an Ion Power™ N111-IP membrane (25 μm) using a decal transfer method [20] and two 180 μm Toray™ TGP-H-060 gas diffusion media (GDM) coated with 25 μm micro porous layers (MPL). The gas diffusion layer (GDL, i.e. GDM