Mechanical Properties of Catalyst Coated Membranes: A Powerful Indicator of Membrane Degradation in Fuel Cells

by

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M.Sc., Sharif University of Technology, 2010

Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

in the

School of Mechatronic Systems Engineering

Faculty of Applied Sciences

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Abstract

Mechanical durability of perfluorosulfonic acid (PFSA) ionomer membranes in polymer electrolyte fuel cells (PEFCs) is investigated in this thesis. This work contributes to a systematic characterization of the decay in mechanical properties of membranes and catalyst coated membranes (CCMs) that are subjected to controlled chemical and/or mechanical degradation mechanisms. During field operation of PEFCs, the membrane is subjected to a combination of chemical and mechanical degradation, resulting in the loss of mechanical integrity and ultimately leading to mechanical membrane failure.

Accelerated stress tests (ASTs) were performed in this study in order to investigate the decay rate caused by each individual degradation mechanism, and to simulate the failure modes of field operated fuel cells. Mechanical degradation was studied using humidity cycling or mechanical fatigue stress. Chemical degradation was evaluated via open circuit or elevated voltage, or Fenton’s reagents. Moreover, the combined chemical and mechanical degradations were also taken into account. In order to investigate the evolutions in mechanical properties during the degradations, different mechanical experiments were utilized including tensile, fatigue, thermal and hygral expansion, and creep tests in a wide range of hygrothermal conditions from the defined room conditions (23°C – 50% RH) to the fuel cell operating conditions (70°C – 90% RH) covering the expected range of operating conditions in PEFCs.

As a result, chemical degradation was revealed to be the dominant mechanism that controls the decay in mechanical properties of the PFSA membranes. However, pure mechanical degradation was also recognized to be capable of creating membrane physical damage but at lower rates compared to chemical degradation mechanisms. Slight decay in mechanical properties of the 8,200 hours field operated CCMs was observed, indicating their relatively milder operating conditions when compared to the accelerated stress tests, and further suggesting that the membranes were still in rather good health after this amount of field operation. According to the outputs of this work, critical degradation routes on membrane mechanical stability were diagnosed and
mitigation strategies were introduced in order to enhance the membrane mechanical durability and overall fuel cell lifetime.

**Keywords**: Fuel Cell; Membrane; Catalyst Coated Membrane; Degradation; Durability; Mechanical Properties; Relative Humidity; Temperature
To my beloved parents

For their endless love, support, and encouragement
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<th>Acronym</th>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AMDT</td>
<td>Accelerated Membrane Durability Test</td>
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<td>AMST</td>
<td>Accelerated Mechanical Stress Test</td>
<td></td>
</tr>
<tr>
<td>AST</td>
<td>Accelerated Stress Test</td>
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<tr>
<td>CCM</td>
<td>Catalyst Coated Membrane</td>
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<tr>
<td>COCV</td>
<td>Cyclic Open Circuit Voltage</td>
<td></td>
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<tr>
<td>DMA</td>
<td>Dynamic Mechanical Analyzer</td>
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<td>DOE</td>
<td>Department of Energy</td>
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<tr>
<td>GDL</td>
<td>Gas Diffusion Layer</td>
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<tr>
<td>MEA</td>
<td>Membrane Electrode Assembly</td>
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<tr>
<td>OCV</td>
<td>Open Circuit Voltage</td>
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<tr>
<td>ORR</td>
<td>Oxygen Reduction Reaction</td>
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<tr>
<td>PEFC</td>
<td>Polymer Electrolyte Fuel Cell</td>
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<tr>
<td>PEM</td>
<td>Proton Exchange Membrane</td>
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<td>PFSA</td>
<td>Perfluorosulfonic acid</td>
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<tr>
<td>PITM</td>
<td>Platinum in the Membrane</td>
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<tr>
<td>RH</td>
<td>Relative Humidity</td>
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<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
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<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
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<tr>
<td>UTS</td>
<td>Ultimate Tensile Strength</td>
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Organization of the Dissertation

This dissertation is prepared with the following organization: Chapter 1 provides an introduction to this work including the motivation and a comprehensive review on the theory and previous work. The main contributions of this work are concisely explained in Chapter 2. However, the reader can find more details on these findings in seven appendices (A-G) at the end of the thesis, where the results are organized in the format of journal publications. These papers are either published, in press, or currently under review. Chapter 3 attributes to the results of mechanical characterization of field operated fuel cells in order to demonstrate the use of mechanical properties as an indicator of membrane degradation in a real-world scenario. Finally, Chapter 4 contains a brief summary of the overall findings, conclusions, and suggested future work.
Chapter 1.

Introduction

1.1. Aims and Motivation

The objective of this work is to diagnose the major degradation mechanisms which limit the mechanical durability of perfluorosulfonic acid (PFSA) ionomer membranes during the operation of polymer electrolyte fuel cells (PEFCs). The proposed work focuses on the mechanical properties of the catalyst coated membrane, which are believed to be influenced by membrane degradation during PEFC operation and may therefore contribute new fundamental understanding of the various degradation processes that occur. Moreover, mitigation strategies are suggested based on the critical degradation mechanisms determined in this work.

Membrane durability and lifetime is one of the principal obstacles in commercialization of PEFCs. To address this issue, some researches have been directed to develop more reliable membranes through improving the chemical structure as well as physical enrichments. In addition, some studies have been focused on understanding the sources of damage during operation. However, the exact degradation mechanisms of PEFCs during operation and their interactions have not been accurately distinguished to date. Membrane mechanical deterioration is one of the basic causes of early failure in PEFCs. Therefore, the main goal of this thesis is to elevate the understandings on the degradation mechanisms and to determine the optimum operating conditions which improve the mechanical endurance of the membrane. In order to achieve these goals, the very first step is to evaluate the mechanical behaviour of the PFSA membrane as well as the catalyst coated membrane (CCM) at the beginning of life. Once baseline materials are characterized, the decay in their mechanical properties after being subjected to degradation mechanisms can be
investigated. In order to obtain partially and fully deteriorated membranes and CCMs, several accelerated stress test (AST) protocols are purposefully directed to intensify specific degradation mechanisms following available protocols or self-developed protocols.

1.2. Literature Review

A comprehensive literature review has been performed on the PEFCs, PFSA ionomer membranes, mechanical properties of membranes individually and in composite with catalyst layers, membrane degradation mechanisms, accelerated stress testing, and the decay in mechanical properties of membranes and CCMs due to degradation.

1.2.1. Introduction to polymer electrolyte fuel cells

Polymer electrolyte fuel cell (PEFC), also known as proton exchange membrane fuel cell (PEMFC) is a promising replacement for the conventional combustion engines due to its high performance, high efficiency, and zero emissions at the point of use. Hydrogen is the most prevalent type of fuel used in PEFCs which electrochemically decomposes to electrons and cations at the anode which are further combined with oxygen at the cathode to produce water as the effluent. Fuel cells are non-combustive electrochemical engines that generate power through direct conversion of chemical energy of the fuels into the electrical work in an electrochemical reaction. The direct conversion of chemical energy to electrical energy results in higher maximum theoretical efficiency of electrochemical devices when compared to the conventional combustion engines [1]. In this manner, fuel cells function similar to batteries. The main discrepancy between these two electrochemical devices is the continuous flow of fuel and oxidizer (hydrogen and air/oxygen in PEFC) in the fuel cells while the fuel and oxidizer are stored internally in the batteries.

The membrane electrode assembly (MEA) is the principal component of the PEFC where electric current is generated from electrochemical reactions at anode and cathode. A typical MEA consists of seven primary components (layers) including anode flow field channel, gas diffusion layer, anode catalyst layer, membrane, cathode catalyst
layer, gas diffusion layer, and cathode flow field channel, as presented schematically from left to right in Figure 1. Among these components, the membrane will be discussed later, and the rest will be introduced briefly in this section.

Catalyst layers are highly porous media, permeable to gases and reactants, composed of carbon nano-particles and electrocatalyst materials (generally Pt) [2,3]. The goal of using platinum is to reduce the energy of activation and consequently to enhance the rate of reactions at low temperatures [2]. At the anode catalyst, hydrogen decomposes to electrons and protons via an electrochemical reaction. Protons are transferred through the membrane toward the cathode, while electrons are collected by current collectors and traveled to the cathode through the outer circuit to create power. At the cathode catalyst, oxygen combines with the previously transported electrons and protons to produce water in an electrochemical reaction known as the oxygen reduction reaction (ORR). The main anode, cathode, and overall fuel cell reactions are summarized by Equations 1 to 3.

\[
\begin{align*}
H_2 & \rightarrow 2 \text{H}^+ + 2 \text{e}^- & \text{anode reaction} \quad \text{Eq. 1} \\
\frac{1}{2} \text{O}_2 + 2 \text{H}^+ + 2 \text{e}^- & \rightarrow \text{H}_2\text{O} & \text{cathode reaction} \quad \text{Eq. 2} \\
H_2 + \frac{1}{2} \text{O}_2 & \rightarrow \text{H}_2\text{O} & \text{overall cell reaction} \quad \text{Eq. 3}
\end{align*}
\]

The gas diffusion layer (GDL) is a core component in PEFCs generally composed of non-woven carbon fiber paper or woven carbon cloth, binder, polytetrafluoroethylene (PTFE), and micro-porous layer (MPL). GDL is responsible to improve the water management, electrons and reactants transport, and heat transfer in the MEA [4]. High hydrophobicity is ensured through treatment of GDL with Teflon-like material. Lack of water reduces the ion conduction of the membrane and elevates the contact resistance at the interface of the membrane and catalyst layer [4]. Excessive water, on the other hand, results in flooding which may interfere with the electrochemical reactions and the transport of reactants to the active sites.

Flow field plates, also known as bipolar plates, are graphite or metallic based structures that provide the fuel cell with channels to transport reactants and products and lands to collect current. Flow field plates also increase the physical strength of the fuel cell stack and may be equipped with liquid water cooling channels for thermal management purposes.
The output voltage of a single cell is limited by the fundamental electrochemical potential of the cell reaction to around 1 V [1]. The total electrical current is proportional to the active electrode area of each cell in the stack [1]. Higher levels of voltage and current as required in automotive applications can be achieved through connecting multiple cells (over 200 cells) in series and in parallel, respectively [1]. The maximum standard voltage, i.e. open circuit voltage, that can be achieved by a single fuel cell is $E^0 = 1.23$ V, where hydrogen and oxygen are utilized at 1 atm and 298.5 K [2]. In practice, the output voltage of a single cell is remarkably lower than the theoretical potential due to a number of losses including activation loss, ohmic loss, concentration loss, and OCV loss [2].

- Activation loss ($V_{act}$) [1,2,5]: The slow kinetics of reactions at the surface of the electrodes results in significant loss of the generated voltage. The activation loss represents the required energy to split hydrogen into electrons and protons, and
to combine them with oxygen at the cathode. Activation loss is the dominant loss at low current densities.

- Ohmic loss \( (V_{\text{ohm}}) \) [2,5]: The resistance of electrodes, GDLs, bipolar plates, and different interconnections in addition to the ion conduction through the electrolyte cause a reduction in voltage which linearly increases with current density.

- Concentration loss \( (V_{\text{conc}}) \) [1,2,5]: This potential loss mechanism is attributed to the mass transport limitations of the reactants in the GDLs and electrodes. As a result, the concentration gradient of the reactant is increased leading to decay in the concentration at the active sites. The concentration loss becomes more significant at high current densities.

- OCV loss \( (V_{\text{ocv}}) \) [1]: The actual OCV is about 0.2 V below the theoretical OCV predicted by the Nernst equation (1.23 V). This significant efficiency loss results by the internal currents from electron leakage through the electrolyte and the potential reaction of the reactants at the opposite electrode due to the crossover effect.

In total, the fuel cell voltage of a single cell can be calculated from Equation 4. Polarization curves are normally used to present the fuel cell potential and power density as a function of current density. A typical fuel cell polarization curve is presented in Figure 2 [2].

\[
V_{\text{cell}} = E^0 - V_{\text{ocv}} - V_{\text{act}} - V_{\text{ohm}} - V_{\text{conc}} \quad \text{Eq. 4}
\]
Figure 2. A typical polarization curve showing the cell potential and power density versus the cell current density [2].

1.2.2. Proton exchange membrane

Proton exchange membrane (PEM) is a key component in the PEFCs that acts to transfer protons from the anode to the cathode while insulating electronic current from passing through the membrane and preventing convective crossover of reactant gases [6–8]. Failure to satisfy one of these requirements will result in loss of cell performance and subsequent fuel cell failure. In order to remain functional, the proton conductivity of the PEM should be around 0.1 S.cm$^{-1}$ and the gas permeability should be $<10^{-12}$ mol H$_2$ cm$^{-1}$s$^{-1}$kPa$^{-1}$ and $<10^{-11}$ mol O$_2$ cm$^{-1}$s$^{-1}$kPa$^{-1}$ [7]. Recent structural modifications in the proton exchange membranes are directed to improve the membrane lifetime and slow down the membrane degradation [9]. As embraced by the PEFC term, membranes are polymeric-based materials consisting of cross-linked molecular chains. The membranes are also called ionomers because of the presence of hydrophilic ionic groups critical to functionalize the material and facilitate proton transport across the membrane [9]. Among various types of PEMs, perfluorosulfonic acid (PFSA) ionomer membranes are widely used in PEFCs because of the high proton conductivity at low temperatures along with the high chemical stability inherited from the Teflon-like fluorocarbon structure [6].

The molecular structure of a PFSA membrane, e.g. Nafion® developed by DuPont, is illustrated in Figure 3 [9]. Nafion® is a copolymer of tetrafluoroethylene and sulfonyl fluoride vinyl ether which exhibits semi-crystalline structure [9]. The chemical stability of PFSA ionomer membranes is attributed to the resilient and chemically inert
carbon-fluorine bonds [10]. The performance of the membrane in a fuel cell is highly dependent on the proton conductivity, which is directly related to the water content [8,11]. As Nafion® is hydrated to a critical state, swelling of ionic domains provide proton conducting channels [9]. The proton conductivity increases with the water content up to a maximum point where further humidification results in lower conductivity due to reduction in proton concentration [9,11]. Excessive humidification could possibly result in membrane and cathode flooding which slows down the cathode reactions [8,11].

![Figure 3. Monomer of a Nafion® PFSA membrane][9].

Proton conductivity in PFSA ionomer membranes is facilitated by the dissociation of –SO₃H groups at side chains in the presence of water or other polar solvents [12]. Ohmic loss is proportional to the ionic conduction of PFSA membrane [13]. At molecular level, two proton transport mechanisms were suggested in the literature for PFSA ionomer membranes known as "proton hopping" or “Grotthus mechanism” and “diffusion mechanism” or “vehicular mechanisms” [13,14]. Proton hopping mechanism is attributed to the protons jump from one hydrolyzed ionic site (SO₃⁻ H₃O⁺) to another across the membrane [13]. In this mechanism, as schematically illustrated in Figure 4.a, the produced proton from the hydrogen oxidation reaction adheres to the water molecule and forms hydronium ion, then jumps on the adjacent water molecule [13]. In the “diffusion mechanism”, as depicted in Figure 4.b, hydrated proton (H₃O⁺) diffuses through the aqueous medium due to electrochemical difference [13]. The existence of the free volumes within the polymeric chains in proton exchange membrane allows the transferring of the hydrated protons through the membrane [13].
1.2.3. Degradation mechanisms of PFSA ionomer membranes

One of the fundamental challenges facing the commercialization of automotive PEFCs is in developing durable membrane electrode assemblies (MEAs). [6]. Fuel cell industry durability targets demands development of durable MEAs that range from 5,000 h for light duty vehicles (e.g., passenger cars) to 25,000 h for heavy duty vehicles (e.g., transit buses) [15,16]. Generally, the lifetime of the PEFC is limited by the lifetime of the proton exchange membrane. The membrane durability is closely linked with the durability of the adjacent catalyst layers (CLs). Catalyst layers can also be degraded in the form of corrosion of carbon support, platinum dissolution and agglomeration, and ionomer decay which mainly exacerbate the activation and mass transport losses [17]. The automotive dynamic operating conditions including load cycles as well as startup/shutdown and freeze/thaw events make the achievement of these goals more challenging [18].

In the context of PEFCs, the known membrane degradation mechanisms can be divided into two main categories, i.e. chemical and mechanical degradation mechanisms. Chemical degradation is linked to the damage caused by radical species

Figure 4. Schematic of the proton conduction mechanisms in PFSA ionomer membrane (a) proton hopping mechanism (b) vehicular mechanism.
formed during fuel cell operation as by-products of electrochemical reactions, resulting in polymer molecular decomposition [19]. On the other hand, mechanical degradation is attributed to the fracture caused by induced mechanical and hygrothermal stresses in a constrained cell [19]. The total degradation caused by these mechanisms will result in performance losses and failure of the fuel cell through electrical shorting or excessive gas crossover.

**Chemical degradation mechanisms**

Chemical degradation has been recognized as the major cause of failure in PFSA membranes [6,7]. It is generally accepted that chemical degradation is caused by the attack of highly oxidative species such as hydroxyl (•OH) and hydroperoxyl (•OOH) radicals, initially formed during operating duty cycles, to the vulnerable polymer end groups containing H-groups resulting in initiation of the decomposition [7,20,21]. According to the reduction potentials of the oxidative radicals [6], •OH is the most reactive of the oxidizing species, highly capable to abstract hydrogen atoms from O-H and C-H bonds and form H₂O [6]. The •OOH is less reactive than the •OH and seems to be passive against C-S or C-O-C bonds and only attacks the ionomer end groups [22]. Radicals can be formed at catalyst layers as a by-product of electrochemical reactions or through decomposition of hydrogen peroxide (H₂O₂) in the presence of Fenton’s reagents in the membrane.

In addition to the radicals, hydrogen peroxide is another active species capable to decompose the membrane molecular structure; however, acting alone, it is not capable of damaging PFSA membranes [6,22,23]. Hydrogen peroxide can be generated electrochemically as another by-product of the oxygen reduction reaction (ORR), or chemically when crossover oxygen and hydrogen meet at the anode or cathode [22,23]. Many investigations have been contributed on the factors that control the rate of chemical degradation in PFSA membranes [10,22–27].

The cathode and anode sides of the membrane are subjected to harsh chemically oxidizing and reducing environments, respectively [9]. Two major mechanisms of radical generation from H₂ and O₂ have been reported by Rodgers et al. [22]. In the first mechanism (Equations 5 to 7), hydroxyl radicals are generated by the
decomposition of previously formed hydrogen peroxide in the presence of cation contaminants (Equation 7) [22].

\[ \text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O}_2 \]  
Eq. 5

\[ 2\text{H}^+ + \text{O}_2 + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2 \]  
Eq. 6

\[ \text{H}_2\text{O}_2 + \text{M}^{2+} \rightarrow \cdot\text{OH} + \text{OH}^- + \text{M}^{3+} \]  
Eq. 7

The second mechanism (Equations 8 to 12) is attributed to the crossover of oxygen molecules and their incomplete ORR at the anode [22]. The active radicals (\(\cdot\text{OH}\) and \(\cdot\text{OOH}\)) formed during the incomplete ORR are harmless provided that they remain attached to the catalyst surface [22].

\[ \text{H}_2 \rightarrow 2\cdot\text{H} \]  
via Pt catalyst  
Eq. 8

\[ \cdot\text{H} + \text{O}_2 \rightarrow \cdot\text{OOH} \]  
diffused to anode  
Eq. 9

\[ \cdot\text{OOH} + \cdot\text{H} \rightarrow \text{H}_2\text{O}_2 \]  
can diffuse into membrane  
Eq. 10

\[ \text{H}_2\text{O}_2 + \text{M}^{2+} \rightarrow \cdot\text{OH} + \text{OH}^- + \text{M}^{3+} \]  
decomposition of \(\text{H}_2\text{O}_2\)  
Eq. 11

\[ \cdot\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \cdot\text{OOH} \]  
\(\cdot\text{OOH}\) attacks membrane  
Eq. 12

In addition to the indirect membrane chemical degradation mechanisms, Mittal et al. [24,28] expressed that the formation of active species from \(\text{H}_2\text{O}_2\) decomposition or the direct formation of active oxygen species in the oxygen reduction reaction are not the dominant membrane degradation mechanisms in PEFCs. Instead, membrane degradation occurs because molecular \(\text{H}_2\) and \(\text{O}_2\) react on the surface of the Pt catalyst to form the membrane-degrading species [7,22,24,28]. Pt deposition in the membrane due to electrode degradation facilitates the formation of radicals via direct reactions [7]. The reaction between hydrogen and oxygen is highly exothermal, sufficient to deteriorate the membrane at the reaction site [18]. Wu et al. [29] studied the chemical degradation of PFSA membranes under \textit{in-situ} “close to open circuit voltage (OCV)” conditions and observed a jump in the rate of degradation after 800 hours. As they expressed, this rapid increase was attributed to the direct exothermic reactions between the reactants due to elevation of the gas crossover rate [29].

Beside the hydrogen atoms at the polymer backbone, two other major sources of abstractable hydrogen atoms are hydrogen gas and hydrogen peroxide, as presented by
Equations 13 and 14 [6]. Hydrogen radical can produce further •OOH as shown in Equation 15 due to high oxidizing power [6].

\[
\text{•OH} + H_2 \rightarrow \text{•H} + H_2O \quad \text{Eq. 13}
\]
\[
\text{•OH} + H_2O_2 \rightarrow \text{•OOH} + H_2O \quad \text{Eq. 14}
\]
\[
\text{•H} + O_2 \rightarrow \text{•OOH} \quad \text{Eq. 15}
\]

Formation of radicals by the decomposition of H$_2$O$_2$ can be facilitated significantly when foreign cation contaminants such as Fe$^{2+}$ exist at the membrane or catalysts through Fenton’s reactions [9,18]. Possible sources of these contaminants can be from corrosion of stack components, impurities in the gas streams, and humidifier reservoirs [9,18]. Formation of •OH and •OOH in the presence of minor impurities of Fe$^{2+}$ and Cu$^{2+}$ cations was reported by Inaba et al. [25]. The mechanism of membrane degradation in the presence of Fe cations is presented in the following equations (Equations 16 to 20) resulting in membrane thinning and decay in performance [9,18].

\[
\text{H}_2\text{O}_2 + \text{M}^{2+} \rightarrow \text{•OH} + \text{OH}^- + \text{M}^{3+} \quad \text{Eq. 16}
\]
\[
\text{M}^{2+} + \text{•OH} \rightarrow \text{M}^{3+} + \text{OH}^- \quad \text{Eq. 17}
\]
\[
\text{H}_2\text{O}_2 + \text{•OH} \rightarrow \text{•OOH} + \text{H}_2\text{O} \quad \text{Eq. 18}
\]
\[
\text{M}^{2+} + \text{•OOH} \rightarrow \text{M}^{3+} + \text{OOH}^- \quad \text{Eq. 19}
\]
\[
\text{M}^{3+} + \text{•OOH} \rightarrow \text{M}^{2+} + \text{H}^+ + \text{O}_2 \quad \text{Eq. 20}
\]

In addition to the generation of oxidative species, metal cations can abstract hydrogen directly from the sulfonic acid groups in the PFSA membrane due to the higher affinity of sulfonic acid groups to almost all cations (except Li$^+$) than H$^+$ [9]. The exchange of metal cations for H$^+$ may reduce the membrane water uptake capacity. Lower water uptake capacity increases the concentration of H$_2$O$_2$ and consequently results in a greater concentration of destructive hydroperoxyl radicals [9]. The distribution of Fenton cations in the membrane is another important factor that affects the rate of chemical degradation. At constant volume fraction of impurities, concentration near anode is less detrimental than near cathode, however, a uniform distribution across the thickness is the least destructive [9].

Inherited from the degradation caused by cations (Equations 16 to 20), Fenton’s reagent test have been used as a simple accelerated stress test approach for PFSA
membranes [9,30,31]. Using nuclear magnetic resonance (NMR) spectroscopy and mass spectrometry (MS), Healy et al. [23] detected common degradation products in in-situ (fuel cell operation) and ex-situ (Fenton’s reagent test) testing of Nafion® membranes.

Once oxidative species are generated, the PFSA membrane degradation proceeds by different mechanisms; three of them are summarized here [22]:

1. The first mechanism is attributed to the three-step abstraction of hydrogen from carboxylic acid end groups of membrane via unzipping reactions as proposed by Curtin et al. [32]. Carboxylic acid end groups contain H-bonds that are vulnerable to radical attack [22]. The mechanism begins with the production of perfluorocarbon radical by the abstraction of hydrogen via radicals (Equation 21) [22]. In the second step, perfluorocarbon radical reacts with a hydroxyl radical to produce hydrogen fluoride and an acid fluoride (Equation 22) [9,22]. The final products of this mechanism include another carboxylate acid end group along with fluoride acid generated during the hydrolyzing of acid fluoride (Equation 23) [22]. Since the carboxylate end group is regenerated (Equation 23), continuation of the proposed mechanism (unzipping) along the membrane main chain could potentially result in lower molecular weight membrane. According to this mechanism, the rate of chemical degradation can be measured by monitoring the fluoride content of product water [9].

\[
\begin{align*}
R_f – CF_2COOH + \cdot OH & \rightarrow R_f – CF_2\cdot + CO_2 + H_2O \quad \text{Eq. 21} \\
R_f – CF_2\cdot + \cdot OH & \rightarrow R_f – CF_2OH \rightarrow R_f – COF + HF \quad \text{Eq. 22} \\
R_f – COF + H_2O & \rightarrow R_f – COOH + HF \quad \text{Eq. 23}
\end{align*}
\]

2. Chemically modified Nafion® membranes were obtained by pre-treatment of the Nafion® polymer with elemental fluorine during extrusion resulting in minimized reactive end groups [7,32]. These chemically stabilized membranes exhibited much lower fluoride release rate and better durability due to the reduced number of reactive end groups [7]. In addition to the end group radical attack, under dry conditions, hydroxyl radicals can attack the C–S bonds in the side chain of Nafion®, where the acidic proton is located on the –SO₃ group as –SO₃H [22,33].
Hydroxyl radicals abstract the hydrogen to form $-\cdot\text{SO}_3$ containing relatively weak C–S bonds which easily fragment to generate the perfluororadicals (Equation 24) [10,22]. Fluororadicals can produce oxyradicals at the main chain of Nafion$^\circledR$ (Equation 25) which can create further fluorocarbon radicals [10,22]. The initiation of this mechanism requires very dry conditions, though the propagation of degradation can continue in a relatively hydrated membrane [22]. Other side chain degradation mechanisms have been proposed by different research groups as summarized by Rodgers et al. [22].

$$R_f - \text{CF}_2\text{SO}_3\cdot \rightarrow R_f - \text{CF}_2\cdot + \text{SO}_3 \quad \text{Eq. 24}$$

$$R_f - \text{CF}_2\cdot \rightarrow R_f - \text{CO}\cdot + 9 \text{HF} + 5 \text{CO}_2 \quad \text{Eq. 25}$$

3. The third mechanism is associated with the action of hydrogen molecules [10]. Under exposure to $\text{H}_2$, the polymer backbone of PFSA membrane preferentially reacts with hydrogen due to strong HF bonds (571 kJ/mol) as presented in Equation 26. [6,10,18,22]. The defluorination of membrane and production of CH$_2$ groups make the membrane vulnerable to the attack by radicals due to the introduction of more hydrogen containing groups which accelerate the degradation process mainly at the anode side [9,22].

$$-\text{CF}_2- + 2\text{H}_2 \rightarrow -\text{CH}_2- + 2\text{HF} \quad \text{Eq. 26}$$

The chemical decomposition of the PFSA membrane is a function of the reactant gas crossover, Pt dissolution, and transition metal ion contaminants [6,22]. The degradation rate of PFSA membranes via radical species will be accelerated at higher temperature, low humidification, high gas pressure, and high cell voltage (open circuit voltage at the extreme) [6,7,18,22,29,34–37]. Chemical degradation can be monitored by quantifying the fluoride emission rate or via electrochemical monitoring of hydrogen gas crossover [6,22]. Moreover, uniform thinning of the membrane is another sign indicating the polymer is being chemically degraded [22]. The membrane thinning gradually results in elevated rates of gas crossover and mechanical instability that ultimately accelerate the cell failure. The effect of membrane thickness on the fuel cell performance was studied by Yuan et al. [36] under OCV degradation test for 1,000
hours. They reported more severe OCV degradation in the thinner membranes which was attributed to higher gas crossover [36].

Several qualitative and quantitative characterization methods have been utilized in order to evaluate the rate of chemical degradation in PEFCs:

- Hydrogen crossover rate: The crossover rate of hydrogen can be measured in-situ electrochemically to evaluate both in-situ chemical and mechanical degradations [7,22]. During hydrogen crossover, hydrogen is applied to the anode while the cathode is exposed to nitrogen and an external voltage is applied to the cell [22]. The cathode potential is set to be around 0.4 V higher than the anode potential [7]. Under the applied voltage, the crossover hydrogen oxidizes and generates current which is directly proportional to the hydrogen crossover rate [7,22]. The hydrogen partial pressure at the anode, temperature, and membrane thickness and permeability are factors that affect the hydrogen crossover rate [22]. The membrane permeability for oxygen, which is almost half of that of hydrogen, can be quantified analogously [7].

- Fluoride release rate (FRR): The rate of chemical degradation of fluorinated membranes can be quantified by analyzing the rate of release of fluoride ions in the product water [7]. FRR can be continuously monitored by fluoride ion selective electrodes [7].

- Open circuit voltage (OCV): The reactant crossover can also be measured by OCV but the results are not as quantitative as the ones obtained by the hydrogen crossover method [7,22]. The results obtained by OCV can be correlated to the FRR measurements [22]. A sound membrane exhibits a relatively stable OCV and very little FRR, while the OCV reduces from 1 V to about 0.7 V in a close to failure membrane [7].

- High frequency resistance (HFR): HFR characterizes the deviations in the membrane resistance due to the degradation using in-situ impedance spectroscopy [7,22]. The membrane thinning caused by chemical degradation results in lower resistance, however, the decline in proton conductivity would
compensate this effect [7,22]. Hence, the reliability of HFR outputs in order to diagnose the membrane failure seems to be limited [7,22].

- Microstructural analysis: *Ex-situ* microscopic analysis using scanning electron microscopy (SEM) is an established approach to detect the microscopic damage such as cracks, pinholes, and delamination as well as the membrane thinning occurred during operation [7]. Recent SEMs are equipped with energy-dispersive x-ray spectroscopy (EDS) capable to provide the chemical analysis of the membrane indicating the presence of contaminants [7].

There are possible methods to reduce the chemical degradation in PFSA membranes including avoiding metal contamination [9,22]; decreasing the permeability of gases through the membrane [9,22]; optimizing the water content [9]; and improving membrane stability chemically, physically, or through the incorporation of radical scavengers/inhibitors [22]. Radical inhibitors or sacrificial materials could be used to postpone or minimize the direct attack on the membrane [9]. Membrane durability was reported to be enhanced through introducing cerium oxide (CeO$_2$) nano-particles in the membrane as reported by Trogadas et al. [38] and Pearman et al. [39]. By incorporating Ce$^{3+}$ and Mn$^{2+}$ ions in the membrane, Coms et al. [10] reported dramatic reduction in the chemical degradation rates of PFSA-based MEAs under harsh OCV conditions [10]. The fluoride release rates are dramatically reduced by factors of approximately 1,000 and 100 with Ce$^{3+}$ and Mn$^{2+}$, respectively [10]. In addition, due to vulnerability of reactive end groups, it is desired to reduce the number of them by chemically modifying the membrane via alternative synthesis processes [7].

Fluctuations in the voltage during operating conditions result in the dissolution of the platinum located at cathode catalyst and re-deposition in the membrane [40]. The effect of platinum in the membrane on the degradation rate of the membrane is debated. In some literatures, platinum deposition inside the membrane was reported to be an acceleration factor for radical generation and chemical degradation via Fenton’s reagent mechanism [41,42]. On the other hand, some studies reported the mitigation of chemical degradation, thereby improving durability and performance through decomposition of hydrogen peroxide to water and oxygen [22,40,43]. The mitigation of membrane
degradation by the introduction of platinum band in the membrane has been studied by Macauley et al. [40]. The results indicated significant reduction in chemical degradation and enhancement of membrane longevity with the formation of platinum band [40].

**Mechanical degradation mechanisms**

Mechanical degradation, on the other hand, can be induced in the membrane during the expansion and contraction due to the swings in the temperature and relative humidity. Inside a fuel cell, membrane is constrained by the electrodes, gas diffusion layers (GDLs), and bipolar plates which confine the membrane to freely swell or shrink. Hence, the generated mechanical stresses in the membrane in the form of hygrothermal fatigue and creep can lead to the lack of mechanical integrity, initiation and propagation of mechanical cracks, and ultimate failure. Moreover, it is desired to reduce the membrane thickness in order to improve the performance of fuel cells via decreasing the ohmic losses, to reduce the cost, and to facilitate the membrane hydration [8]. The average thickness of PFSA membranes has been reduced from few hundreds of microns to less than 25 µm (e.g. Nafion®-211). As a result, the thinner membrane will be exposed to higher mechanical stresses which require higher mechanical stability to maintain the cell integrity.

The dynamic operating conditions of automotive PEFCs causes the membrane to experience cycles of hydration and dehydration, exposing the membrane to hygrothermal fatigue loading [6]. Fatigue stresses lead to mechanical degradation through the initiation and propagation of microscopic cracks that elevate the rate of reactant gas crossover [6,9]. Reactant gas crossover through the microcracks is one of the major reasons for membrane failure at early stages of operation [44]. The reaction of crossover gases at catalyst surface results in significant drop in the cell voltage and dramatic reduction in the cell performance [6,9]. Furthermore, the heat of the gas crossover reactions may locally melt the membrane exacerbating the rate of degradation [9]. As a result of these stressors, several types of mechanical damage can be observed, including cracks, through the thickness tears, pinholes, and delamination between the membrane and the electrodes [9,45].
Mechanical properties of proton exchange membranes strongly depend on the temperature and relative humidity. In automotive fuel cell applications, the membrane is subjected to wide range of operating conditions from freezing to thaw and from dry to fully wet [6]. Phase transformations and changes in the volume of water are detrimental to the lifetime of the fuel cell [22]. Inadequate humidification is detrimental to the membrane, as it reduces the membrane toughness and induces contractive tensile stresses to the membrane [9]. Furthermore, low water content decomposes the crystal structure, reducing ion channels and electrochemical activity [9]. Several mechanisms are involved to reach the dehydration such as rapid variations in current density during duty cycles [9,46], lack of water management and low-humidified reactant gas streams [46], and evaporation and removal of water vapor through the channels at high operating temperature [46].

The rate of mechanical degradation is intensified significantly once the membrane is subjected to high temperature, high pressure, and low humidity conditions, separately or simultaneously [9]. In addition to the operating conditions, manufacturing imperfections can also exacerbate the rate of mechanical degradation. Non-uniform membrane thickness and penetration of catalyst particles into the membrane has been observed to create locally high stresses [9]. Additionally, the non-uniform mechanical stresses on the membrane at the interface of the lands and channels of the bipolar plates make these areas susceptible to cracks and tears formation [18]. Introduction of pinholes and foreign elements during manufacturing could create crack nucleation sites in the membrane [7].

Although mechanical degradation of PFSA membranes is one of the dominant lifetime limiting factors in PEFCs, it can be minimized with several mitigation approaches. Manufacturing procedures must be directed to minimize the fraction of defects and non-uniformity in the membrane. Also, great care should be taken during assembling and disassembling of fuel cells. Improvement of the membrane dimensional stability during hygrothermal cycles could reduce the mechanical stresses and enhance the membrane durability. Through investigating the membrane durability when subjected to humidity cycling, it is reported that major fractions of the micro-cracks and pinholes initiated under the channel regions, indicating the mitigating role of bipolar plate
compression on the MEA durability [22]. Moreover, mechanical properties and dimensional stability can be boosted by reinforcing the ionomer through adding additives or developing composite membranes [7,22]. Chemical and physical approaches have been proposed to enhance the membrane mechanical durability as summarized by Subianto et al. [47].

### 1.2.4. Mechanical properties of PFSA membranes and CCMs

In order to minimize the ohmic losses, improve the performance of the fuel cell, and simultaneously reduce the total cost required for the membrane material, it is desired to reduce the thickness of the membrane [6,48,49]. However, reduction in the membrane thickness hinges on the development of mechanically robust membranes capable to maintain their structural integrity under higher levels of mechanical stresses at wide range of temperatures (-40°C to 120°C) and relative humidities (ambient to 100%) during the fuel cell operation [50]. As a result, many researches have been contributed to the characterization of mechanical properties of pristine PFSA membranes and CCMs [33,45,51–67]. Several mechanical testing approaches can be utilized in order to obtain the static and time-dependent mechanical properties of PFSA membranes including tensile, fatigue, creep, compression, and expansion tests.

Tensile test is the most common mechanical characterization experiment providing valuable information on the material toughness, strength, ductility, and stiffness that is frequently utilized in the study of membrane and CCM mechanical properties [51,52,54,55,58,63–66,68]. Tensile test includes the stretching of the membrane specimen under constant strain rate until the fracture point at ambient or controlled environments. Tensile properties of PFSA membrane and CCM are known to be highly dependent on the hygrothermal conditions as reported in many researches [51,52,55,58,64–66,68]. A comprehensive finding of these studies is that the elevation in temperature and relative humidity reduces the membrane stiffness and tensile strength while increasing the membrane ductility and fracture strain [51,52,54,55,64,68]. Statistical analysis confirmed that temperature has greater impact than relative humidity on the tensile and fatigue properties of PFSA membranes [52,64]. Beside the hygrothermal conditions, the tensile strain rate was also shown to remarkably alter the
elastic modulus and yield stress as reported by Lu et al. [68]. Yoon et al. [66] developed a nonlinear viscoelastic-viscoplastic model capable to predict the tensile properties of Nafion®-111 at different environmental conditions and strain-rates. Through an experimental study, the sensitivity of membrane tensile properties to the hydration/dehydration was found to be moderated by applying ion exchange solutions to the membrane as studied by Kundu et al. [58]. They correlated their observations to the crosslink sites provided by salt ions for the linkage between sulfonic acid groups [58]. The tensile properties of an expanded polytetrafluoroethylene (ePTFE) reinforced membrane at different hygrothermal conditions were investigated and compared with the Nafion® 112 by Tang et al. [65] via experimental and modeling approaches. The ePTFE reinforced membrane exhibited higher mechanical strength and dimensional stability which resulted in less plastic deformation during simulated fuel cell operation [65]. Finally, slight strengthening in PFSA membrane tensile properties was observed in the manufacturing machine direction when compared to the transverse machine direction [64].

The membrane in PEFCs is subjected to cyclic loading resulting from wet-dry cycles. Therefore, in addition to the tensile tests, fatigue experiments were also performed on the membrane and CCM as recently reported in [45,54,56,57,59,69]. Under fatigue testing, the membrane is subjected to successive cyclic loadings defined by the minimum and maximum stresses and the frequency of the cycle. The mechanical response of Nafion® 211 membrane under ex-situ tension-tension fatigue loadings was investigated by Khorasany et al. [57]. According to the results of this study, the fatigue endurance is considerably reduced at high temperature and relative humidity [57]. An increase in temperature is shown to exponentially reduce the membrane fatigue lifetime [57]. An elastic-plastic constitutive model was developed by Khorasany et al. [56] based on the experimental results reported in [57] and was applied to assess the membrane fatigue lifetime under hygrothermal loading conditions. It was declared that simultaneous oscillations of temperature and humidity exacerbate the mechanical damage and results in shorter lifetime when compared to the individual humidity or thermal fatigue [56]. By modeling the membrane response to hygrothermal loading, Kusoglu et al. [45] reported the development of residual tensile stresses in the membrane during cooling/drying steps of hygrothermal loading. The magnitude of the induced tensile stress was
determined to be comparable to the membrane yield strength capable to generate mechanical cracks inside the membrane [45].

Inherited from the viscoelastic-viscoplastic nature of PFSA membranes, the membrane response to external forces is time-dependent. Therefore, in addition to the tensile and fatigue experiments, creep and expansion tests are utilized to capture the time-dependent mechanical properties of PFSA membranes [61,62,67,70]. Creep test measures the membrane tendency to continuous deformation while constant stress is applied to the membrane. In a similar manner, expansion tests assess the time-dependent response to hygrothermal variations. Analogous to the static mechanical properties, the time-dependent behaviour of PFSA membranes is substantially influenced by the hygrothermal conditions [61,62,67]. In this context, Solasi et al. [62] evaluated the creep failure of Nafion®-111 at a range of temperature and relative humidities. The slope of the stress-rupture plots with respect to the time to failure was found to be independent of the hygrothermal conditions [62]. Majsztrik et al. [67] investigated the influence of temperature and hydration on the tensile creep response of the membrane and recognized that creep strain is significantly influenced by environmental factors. Moreover, an increase in the temperature always results in higher creep strains while the relative humidity impact varies depending on the test temperature [67]. In the medium temperature range (40 °C < T < 90 °C) the creep deformation was lowest at intermediate humidity due to the mutual interaction of the aforementioned mechanisms [67]. Through comparing the creep behaviour of Nafion®-115 and titania-Nafion®-115, Satterfield et al. [61] reported that the creep deformation of Nafion®-115 was slowed down in the composite structure. The resistance to gas leakage of three commercially available membranes under fatigue and creep was investigated by Li et al. [33] through conducting cyclic and static biaxial blister tests. Due to the relatively identical creep and fatigue response at high temperature and relatively dry conditions, it was concluded that the lifetime was dominated by the total loading time rather than the number of cycles [33].

Liquid water is recognized to act as a membrane plasticizer at low temperatures, weakening the membrane mechanical stability, while at the elevated temperatures, water increases the membrane stiffness and mechanical strength due to stabilization of
the hydrophilic clusters [51,67]. Kusoglu et al. [60] investigated the changes in membrane water uptake under compressive stresses through modeling and experimental works. The results indicated that the membrane water content and conductivity are affected by external compression, particularly at low temperatures and high humidities [60]. Linear and second order curves were observed by Hinatsu et al. [71] in water uptake of two types of PFSA membranes with respect to variations in temperature. In another study, by assuming anisotropy in the membrane swelling, Kusoglu et al. [59] concluded that lower in-plane dimensional changes during wet-dry cycles could potentially result in better fuel cell performance. Moreover, the membrane dimensional changes due to water sorption were recognized to be influenced by catalyst layers and GDLs, as recently reported by Goulet et al. [53]. The confinement imposed by the adjacent layers in the MEA structure constrained the membrane in-plane swelling and contraction and consequently resulted in lower peak stress when compared to the membrane with no support [53].

As a summary of these studies, hygrothermal conditions are recognized to have profound influence on the mechanical integrity of PFSA membranes and CCMs. Membrane mechanical strength was declined when temperature and relative humidity increased which should be taken into account considering the relatively high temperature operating conditions of the PEFCs. However, under fuel cell operating conditions, high relative humidities result in compressive in-plane stresses which are less detrimental when compared to the induced tensile stresses at dry conditions. Another key understanding obtained from comparison between mechanical behaviour of PFSA membranes and CCMs is the significant impact of catalyst layers on the membrane mechanical properties, hence it is crucial to characterize the mechanical properties of PFSA membranes in the composite structure with catalyst layers [52,58].

1.2.5. Accelerated Stress Testing

The goal of the accelerated stress tests (ASTs) is to determine the status of the durability and performance of current fuel cell components without applying time-consuming and costly tests at use level conditions [37,72–75]. In these tests, certain mechanisms known to be responsible for degradation are elevated beyond regular
operating condition levels [37]. Accelerated stressors are applied on the factors that significantly affect the performance of the fuel cell in order to evaluate the performance decay and component damage level [37]. These stressors may include operating temperature and humidity, cell voltage, and current density [76]. The prevalent membrane oriented AST procedures include applying temperature and relative humidity (RH) cycling, open circuit voltage (OCV), load cycling, Fenton reagent test, start up and shut down cycling, and tensile fatigue [50,76]. The US Department of Energy’s (DOE) Hydrogen Program established accelerated stress test protocols for PEFC components including electrocatalysts and membranes [72,77]. AST has been utilized extensively in the study of durability and degradation mechanisms of MEA components as reported in several studies [23,35,44,48,76,78–95].

Oscillations in relative humidity during operation as well as inadequate or excessive hydration are important mechanical degradation stressors. Hence, RH cycling test is designed to measure mechanical degradation through inducing compressive and tensile stresses inside the membrane during swelling (high RH half cycle) and shrinkage (low RH half cycle), respectively [22,50]. Mechanical stresses result in the initiation and propagation of cracks which lead to subsequent failure due to gas crossover [50]. In an inert nitrogen atmosphere, the durability of the ionomer under isolated mechanical AST conditions can be evaluated [50]. When nitrogen is replaced by hydrogen and air, a combination of chemical and mechanical degradation can be obtained [50]. Monitoring the gas crossover is a well-accepted approach to measure the membrane failure under mechanical AST [50]. Despite the advantages on the electrochemical kinetics and water management, increasing the temperature negatively affects the membrane durability by intensifying the chemical and mechanical degradations [37]. Therefore, relative humidity and temperature are two important factors in the conducted mechanical ASTs [37].

RH cycling mechanical AST has been recently utilized by several groups to evaluate the mechanical durability of the PFSA membranes (in the MEA structure) under severe mechanical degradation [44,84–86,90,93,94]. Lai et al. [44] studied the failure of PFSA membranes subjected to 2min/2min wet/dry cycles at 80°C for 20,000 cycles with humidity swings from supersaturated conditions (150% RH) to 0%, 50%, and 80% RH at dry cycles. Through conducting different magnitudes of humidity swings, Lai et al. [44]
indicated that the initiation of crossover cracks was postponed as the range of oscillations was reduced (i.e., more humidified gas used in the dry cycles). No electrical current and H$_2$ were used in this study in order to ensure failure by purely mechanical stresses. In contrast, Kang and Kim [85] utilized H$_2$ and air as fuel and oxidant during RH cycling test. They observed through-plane cracks in the SEM cross section microstructure of 1,200 cycles (5min/20min wet/dry cycles at 65ºC) degraded MEAs which are mainly initiated from the catalyst layers [85]. Vengatesan et al. [94] reported a gradual loss in the fuel cell performance in the early stages of RH cycling test followed by rapid performance decay after certain level of degradation. The degradation of PFSA membrane under two different RH cycling protocols, i.e. DOE (2min/2min cycles) and Gore (10s/50s wet/dry cycles) were characterized and modeled by Khattra et al. [86]. Furthermore, they also applied RH cycling only at anode and kept the cathode RH constant and observed lesser stresses inside the membrane compared to the RH swings at both sides [86]. Uchiyama et al. [93] evaluated the formation of cracks in catalyst layers during the membrane deformation under humidity cycling tests. Through modeling, they expressed that by reducing the in-plane swelling ratio via constraining the plastic strain in catalyst layers, the crack formation in catalyst layers can be controlled [93]. RH cycling was employed by Panha et al. [90] to study the decay in performance of PEM fuel cells under isolated accelerated mechanical stresses. Through comparison the RH cycling with a fully wet (100% RH) test, they reported more rapid drop in PEM fuel cell performance when subjected to RH swings [90]. Moreover, microstructural analysis indicated that RH swings resulted in the formation of more pinholes and defects in the membrane, accelerating the failure [90].

In addition to the aforementioned mechanical AST studies based on RH cycling, Collette et al. [48] and Shi et al. [96] performed mechanical aging under constant RH at high temperature and examined the mechanical evolutions resulting from aging. Higher elastic modulus, tensile strength, hardness, and lower creep deformation were observed due to the molecular rearrangement and formation of crosslinks and bonds between the sulfonic acid groups [48,96]. An ex-situ fatigue based mechanical durability testing approach was introduced by Aindow and O’Neill [78] in order to predict the membrane mechanical durability and the remaining lifetime during humidity cycling. A biaxial fatigue stress test was conducted by Pestrak et al. [97] to evaluate the MEA resistance against
the formation of cracks. By applying experimental leak tests, they observed shorter fatigue lifetime in the MEA when compared to the pure membrane [97].

Open circuit voltage (OCV) test is designed to measure the chemical degradation through exacerbating the membrane degradation [37]. At the OCV state, the reactant gases are at their maximum partial pressures, which elevates the rate of crossover and the deterioration of the membrane [98,99]. Since no fuel and oxidant are being consumed electrochemically during the OCV, there is potentially more crossover and subsequently more peroxide formation and radical attack [50]. Hydrogen peroxide can be generated either through incomplete reduction of oxygen at the cathode under normal operating conditions, or the reduction of hydrogen and oxygen when significant gas crossover occurs at the anode catalyst/membrane interface [37]. Massive ionomer loss, high fluoride release, and significant uniform reduction in the membrane thickness are typical evolutions during OCV degradation [37]. In case of the PFSA membranes, the release of fluoride ion is a signature of membrane degradations indicating the decay in membrane lifetime [50].

Currently, OCV is a well-accepted chemical AST procedure in order to evaluate the chemical degradation of PFSA membranes in short time [76,82,83,89,91,92,95,100,101]. An in-situ chemical aging test of MEAs was introduced by Liu and Case [89] through applying cyclic current loading conditions and the results were compared with the ones obtained at constant current. The polarization curves indicated reduction in the OCV as a function of degradation due to elevation in hydrogen crossover, while the slope of the curves remained unchanged to the close of the experiment [89]. On the other hand, constant current chemical AST exhibited constant OCV and decreasing slope of the mass transport region of polarization curves with respect to the experiment time [89]. Decay in mechanical properties of PFSA membranes after being subjected to OCV test was characterized by Patil et al. [91]. In the context of mechanical membrane properties, they observed a significant reduction in the modulus and failure strain of Nafion® membranes after being subjected to chemical degradation under the OCV AST [91]. In another study, Patil et al. [92] reported mitigation in mechanical properties of Titania-reinforced Nafion® membranes compared to Nafion® 112 before and after the OCV test. The Titania-reinforced membrane
resembled enhancement in toughness and modulus, less creep strain, and better dimensional stability [92]. Yoon and Huang [95] conducted OCV tests at 30% RH and 80°C using two different sets of gas compositions at the anode and cathode (H₂/air vs 4%H₂/O₂) in order to understand the differences in the degradation pattern as well as the decay in mechanical strength and toughness. The H₂/air composition resulted in more degradation at the cathode-side while opposite results (more severe degradation at the anode-side) were obtained by 4% H₂/O₂ composition [95]. An in-situ model of chemical membrane degradation was developed by Wong and Kjeang [27] indicating the initiation of chemical degradation from side chains and further propagation toward main chain scission. The proposed model is capable to predict the ionomer degradation, membrane thinning, OCV, fluoride release rate, and ionic resistance [27]. A transient in-situ membrane degradation model was subsequently introduced [102] to improve the current understandings on the effect of iron ions on the chemical degradation of PEFCs. According to the model, the membrane degradation resulted by the Fe²⁺ concentration can be decreased by reducing the cell voltage [102]. A redox reaction-transport cycle of iron ions was discovered that depends on the cell voltage and thereby controls the rate of chemical membrane degradation.

While the OCV test provides a useful in-situ approach to investigate chemical degradation, ex-situ study of chemical degradation stressors is facilitated by Fenton’s reagent test [37]. Hydroxyl and hydroperoxyl radicals can be formed in the presence of Fe²⁺ through decomposition of hydrogen peroxide due to oxidation of Fe²⁺ to Fe³⁺ [9,37]. Trace concentrations of transition metal ion contaminants, iron cations in particular, in the MEA are adequate to activate the Fenton reactions [103].

The ability of Fenton’s reagent tests to simulate the fuel cell chemical degradation was demonstrated by Healy et al. [23]. According to the nuclear magnetic resonance (NMR) and mass spectrometry analytical results, Healy et al. [23] exhibited similar reaction products in both in-situ and ex-situ degradation analysis. It is further revealed by Kinumoto et al. [104] that in the presence of H₂O₂, the decomposition rates of main and side chains by Fe²⁺ and Cu²⁺ ions are equal. The Fourier transform infrared spectroscopy (FTIR) and NMR analysis reported by Tang et al. [35] indicated the initiation of ionomer decomposition from the end of the main chain when Nafion® was
subjected to the solution of H$_2$O$_2$ and metallic cations (Fe, Ni, and Cr). Furthermore, SEM micrographs of the Fenton’s treated membranes showed the initiation of small bubbles on the surface of the membrane which could create pin-holes in the later stages of degradation [35]. Kundu et al. [87] investigated and compared two distinct Fenton’s reagent tests on Nafion® 112 membrane, one with pre-existed iron ion and peroxide inside the solution, and the other one with the doped Fe$^{2+}$ ions inside the membrane prior to being submerged in the solution of H$_2$O$_2$. Despite relatively similar chemical and mechanical characteristics obtained by these experiments, the pre-existed iron ion approach resembled large bubbles inside the membrane while the doped Fe$^{2+}$ ions approach resulted in small pores close to the surface of the membrane [87]. Recently, Gubler et al. [81] reported fundamental differences in the reaction pathways and radical concentrations between in-situ fuel cell test and ex-situ Fenton’s reagent test. The detected concentration for •OH and •OOH radicals in Fenton test were extremely higher than in-situ fuel cell test, while no traces of •H was found in Fenton test in contrary to the in-situ results [81].

In addition to the isolated chemical or mechanical AST procedures, combined procedures including RH cycling at fixed load followed by load cycling at fixed RH are also developed to simulate the fuel cell operating conditions where both mechanisms are available simultaneously [79,80,82,88]. Through conducting isolated mechanical as well as combined chemical and mechanical ASTs, Crum and Liu [79] evaluated and compared the membrane lifetime and level of degradations obtained by two degradation procedures [79]. Huang et al. [82] compared the failure modes produced by chemical and mechanical AST protocols. Failure analysis of the fracture surfaces revealed remarkable difference between the crack initiation positions resulted by chemical and mechanical AST [82]. Cracks initiated by mechanical AST were usually formed close to the anode while a brittle and clean fracture surface obtained by chemical AST [82]. A combined chemical and mechanical degradation mechanisms and failure modes were recently studied via introduction of Ballard Power Systems’ cyclic open circuit voltage (COCV) AST protocol [88]. It was recognized that the accumulation of both degradation mechanisms intensify the membrane degradation when compared to each independent mechanism [88]. The failure modes were in agreement with the ones in field operation, including membrane thinning, pinholes, and microcracks. Tensile testing at ambient
conditions exhibited a significant decay in mechanical strength, which is expected to induce local membrane damage [88].
Chapter 2.

Summary of Contributions

The main contributions of the current dissertation are included in the form of seven journal articles and manuscripts provided in Appendix A-G. A summary of these contributions, their objectives and novelties, and their connections to the main objectives of this work are briefly explained in this chapter. Some of the components of these studies and the resulting contributions were carried out in collaboration with other graduate and undergraduate students at the SFU Fuel Cell Research Laboratory (FCReL), as well as engineers and researchers at Ballard Power Systems Inc. under the umbrella of the “Development of Next Generation Heavy Duty (Bus) Fuel Cells with Enhanced Durability” project. As the senior supervisor, Dr. Erik Kjeang directly supervised and contributed in all of the following publications. It is also specified in this chapter if any part of the presented contributions were beyond the scope of this dissertation.

2.1. Creep Properties of Catalyst Coated Membranes for Polymer Electrolyte Fuel Cells

Prior to the study of degradation mechanisms and interpreting their impact on the membrane mechanical properties, it is crucial to understand and characterize the mechanical properties of the pristine PFSA membrane, individually or in the composite CCM. In this context, static and dynamic mechanical properties of the membrane and CCM materials were previously investigated by our group, using tensile and fatigue stress experiments [52,55–57]. However, inherited from the viscous characteristics, mechanical properties of PFSA membranes are strongly time-dependent, and no previous studies had addressed the creep behaviour of PFSA membranes when constrained within the CCM. The catalyst coated PFSA membranes were expected to
exhibit significantly different time-dependent creep behaviour from the individual PFSA membrane. Therefore, due to the lack of knowledge on the creep properties of the CCM, the objective of the present study was to measure and compare the time-dependent mechanical behaviour of PFSA membranes and CCMs.

The present journal paper evaluated and compared the creep responses of membranes and CCMs using tensile creep – recovery experiments. A dynamic mechanical analyzer (DMA) was used to measure the creep properties of the samples. Experimental assistance in conducting creep experiments on PFSA membrane and CCM samples were provided by Mr. Aronne Habisch. The creep – recovery tests included two hours of loading at constant tensile stress (creep) followed by two hours of unloading (recovery). The corresponding creep – recovery strains were calculated accordingly. The creep strain represented the total elongation at the end of the loading step. The recovery strain was separated into three stages, i.e., instantaneous recovery (immediate strain restoration during stress restoration), time-dependent recovery (strain restoration during recovery time), and permanent deformation (total unrecovered strain). The effect of hygrothermal conditions and tensile creep stress were also investigated through conducting the tests under a wide range of temperature, relative humidity, and creep stress. Moreover, as PEFCs are subjected to the combinations of cyclic and constant stress conditions, which induce fatigue and creep stresses to the CCM, the accumulation of creep damage during operation was simulated by conducting successive cycles of creep and recovery. It was assumed that during each creep – recovery cycle, portions of creep strain might be retained inside the membrane as permanent deformation and accumulated gradually until the failure.

Overall, this study demonstrated the vulnerability of PFSA ionomer membrane and CCM to the applied creep stress. Through comparing the creep responses of membrane and CCM, it was revealed that coating the membrane with catalyst layers strengthens the membrane resistance against creep deformation. Furthermore, the creep deformation of the CCM was remarkably promoted with the increase in the hygrothermal conditions where statistical analysis indicated larger impact of temperature when compared with the RH. The effect of creep stress on the creep response of CCM became more significant once the stress elevated to higher stresses beyond the yield
point of the CCM. Microstructural characterization exhibited formation of cracks at the cathode catalyst layers when the stress increased to the yield point. Further increase in creep stress resulted in the delamination and detachment of cathode from the membrane which deteriorated the supporting effect of cathode catalyst layer and exacerbated the creep deformation. Finally, the simulated fuel cell operating conditions revealed significant accumulation of permanent deformation even at below the yield point, which may pose a concern for fuel cell operation.

For further information, more detailed results are provided in Appendix A or [105].

2.2. Decay in Mechanical Properties of Catalyst Coated Membranes Subjected to Combined Chemical and Mechanical Membrane Degradation

The goal of this work was to systematically characterize the mechanical properties of catalyst coated membranes subjected to in-situ combined chemical and mechanical degradation, indicative of operating conditions where both stressors occur simultaneously. The CCMs that were used in this study were previously degraded under a cyclic open circuit voltage accelerated stress test (COCV AST) developed at Ballard Power Systems under supervision of Dr. Chan Lim and Mr. Michael Lauritzen. Open circuit voltage (OCV) was implied at a relatively high temperature and low RH conditions to impose chemical degradation, followed by periods of wet-dry cycles to create mechanical degradation stressors. Due to the relatively long period of each wet-dry cycle, the applied mechanical stresses were mainly creep type stresses. The COCV AST procedure was conducted on a standard test station at Ballard Power Systems and the partially degraded as well as the end of life MEAs were extracted for the subsequent mechanical analysis.

Tensile and expansion tests were utilized to determine the ex-situ static state as well as the time-dependent mechanical properties, respectively, using DMA. Installation and troubleshooting of DMA as well as the development of analysis approaches to extract desired properties from the mechanical tests were supervised by Mr. Marc-Antoni Goulet. Furthermore, Mr. Jeetinder Ghaustaurah provided assistance in conducting
mechanical testing and in extracting mechanical properties from the obtained results. Tensile experiments at two different hygrothermal conditions (23°C – 50% RH and 70°C – 90% RH) revealed dramatic reduction in membrane toughness and fracture strain as a function of AST cycles where after only five cycles the CCM behaved like a brittle material and fractured near the yield point. Furthermore, the ultimate tensile strength (UTS) was reduced linearly indicating that once the CCM was subjected to degradation, the crack initiation and failure could occur at much lower stresses. On the other hand, thermal and hygral expansion experiments were applied in order to characterize the evolutions in time-dependent response of CCM to the variations in temperature and humidity. Hygrothermal expansion procedures were suggested by Dr. Ramin Khorasany. At each stage of degradation, thermal and hygral expansions increased with a linear trend as temperature and humidity increased, respectively. However, the slope of increase in the hygrothermal expansions was slowed down when subjected to AST degradation.

Overall, significant decay in mechanical properties of CCMs was observed after being subjected to the combined chemical and mechanical degradation mechanisms. Results of tensile tests exhibited slight increase in elastic modulus accompanied with quick reduction in final strain and UTS with respect to the AST cycles. The rapid decay in the fracture toughness in early stages of degradation was likely due to locally elevated chemical degradation. The overall decay in hygrothermal expansion properties correlated well with the reduction in membrane thickness, fluoride content, and UTS. The loss in hygrothermal expansion and the reduced fracture toughness made the CCM more susceptible to crack formation. From the results of this study, it was summarized that the interaction between chemical and mechanical degradation led to decay in mechanical properties and early failure during fuel cell operation. Additionally, this study provided a benchmark for further membrane durability analysis using ASTs where each degradation mechanism was isolated to understand the attributed impact on the decay in mechanical integrity of the membrane.

For further information, the reader is directed to Appendix B or [106].
2.3. Microstructural and Mechanical Characterization of Catalyst Coated Membranes Subjected to In-Situ Hygrothermal Fatigue

The objective of this contribution was to investigate the mechanical and microstructural properties of in-situ purely mechanically (in the form of hygrothermal fatigue) degraded catalyst coated membranes. A custom-developed, aggressive fatigue based mechanical AST procedure was utilized to apply rapid cycling between fully humidified and fully dehydrated states. Furthermore, the role of accelerated mechanical stress testing (AMST) factors such as the length of wet-dry cycles and stack temperature were investigated through conducting a secondary AMST. The AMSTs were co-supervised by Mr. Michael Lauritzen and conducted by Mr. Zachary Nunn at Ballard Power Systems. In the proposed in-situ AMST, the chemical degradation was completely eliminated by using inert gas and avoiding any electrochemical diagnosis tests.

The two independent AMSTs were continued until 20,000 cycles while the leak rate was measured after every 4,000 cycles. Initiation of membrane failure was observed after 20,000 hygrothermal cycles. At the end of the AMSTs, no major membrane thinning was detected and the thickness of the membranes was preserved indicating that chemical degradation was successfully excluded. Cross sectional and top surface microstructural analyses using SEM indicated the formation of through plane cracks in the membrane and catalyst layers as well as delamination of membrane and adjacent catalyst layers. The failure analysis and microstructural evaluations were co-supervised by Ms. Erin Rogers. Tensile and time-dependent mechanical properties were measured and compared with the previously reported COCV AST results [106] in order to reveal the role of the purely mechanical degradation mechanism on the durability of PFSA membranes in PEFCs. Mechanical tests were assisted by Mr. Aronne Habisch using DMA. Stress – strain curves showed ongoing reduction in the CCM fracture toughness as a function of AMST, however, contrary to the end of life CCMs in the COCV AST study [106], the degraded CCMs in AMST exhibited fair toughness even at the end of the test. On the other hand, hygrothermal expansion tests exhibited no significant changes in the time-dependent response of the membrane from the BOL-conditioned
state to the end of test. The preservation of hygrothermal expansion properties during the in-situ wet – dry cycles indicated that the observed hygrothermal expansion decays in the COCV AST [106] were mainly caused by chemical degradation mechanisms. It was therefore postulated that the mild decay in fracture toughness observed during the AMST was caused by the micro-crack development in the membrane rather than from changes in molecular structure otherwise observed with chemical degradation. The interpretation of the obtained results was supported by Dr. Ramin Khorasany.

In summary, the decay in mechanical properties of CCMs subjected to the pure mechanical degradation were quantified and correlated with the microstructural evolutions. In this manner, results of tensile testing showed significant reduction in UTS, final strain, and fracture toughness indicating the transformation of material behaviour from ductile to relatively brittle due to the initiation and propagation of micro-cracks. In contrast, hygral and thermal expansion properties and elastic modulus remained constant during the fatigue process suggesting that the time-dependent response of the CCM was not affected by fatigue stress. According to the results obtained by this study, it is essential to develop mitigation strategies to limit the in-situ mechanical stresses in order to achieve the fuel cell durability and lifetime goals.

For further information, please refer to Appendix C or [107].

2.4. Ex-situ Tensile Fatigue-Creep Testing: A Powerful Tool to Simulate In-situ Mechanical Degradation in Fuel Cells

The objective of this contribution was to demonstrate the capability of the ex-situ tensile fatigue and creep experiment as an economic approach in simulating mechanical degradation mechanisms and generating decay in mechanical properties of PFSA ionomer membranes similarly to the previously reported in-situ hygrothermal AST [107]. The relative humidity oscillations at relatively high temperature during the operation of PEFCs were known to be the main mechanical degradation mechanism inducing fatigue and creep stresses inside the membrane. Therefore, this work suggested the ex-situ tensile fatigue and creep accelerated stress test (TFC-AST) to be an alternative for the
*in-situ* AST. CCMs used in this study were cut in dog bone shape and were subjected to tension – tension fatigue experiments at 80°C – 50% RH with 10 Hz frequency and 0.2 minimum to maximum stress ratio. The TFC-AST protocol was made use of an experimental method previously developed by our group [57]. TFC-ASTs were continued until 20%, 40%, 60%, and 80% of the total fatigue lifetime.

The mechanical properties of partially degraded CCMs were evaluated using tensile and expansion experiments. Experimental assistance was provided by Mr. Will Kim. Post-test tensile testing at 70°C – 90% RH indicated rapid decay in fracture strain and elastic modulus in early stages of degradation accompanied with increase in UTS only after being subjected to fatigue and creep stresses for about 20% of lifetime. In terms of expansion properties, the TFC-AST degraded CCMs surprisingly exhibited negative expansion, i.e. contraction, to the stepwise increase in RH and temperature. These findings were in contrast to the previous studies on the CCMs degraded by combined chemical and mechanical AST [106] and *in-situ* hygrothermal AMST [107]. Further analysis on the membrane microstructure using transmission electron microscopy (TEM) revealed the rearrangement of the membrane hydrophilic clusters (i.e. sulfonic acid groups) along the fatigue and creep stress direction in the sample due to elongation of the material. Mr. Senthil Venkathesan contributed in capturing and processing of TEM microstructural images. Therefore, the measured contraction in the CCM length against stepwise rise in hygrothermal conditions was attributed to a recovery of the membrane microstructure from the elongated state back toward the original state. This recovery in elongation further demonstrates that the permanent deformation and fracture of the material was caused by fatigue action rather than creep. As a summary of this study, tensile fatigue and creep based accelerated stress test was shown to be a practical *ex-situ* mechanical AST approach capable of generating mechanical degradation in the CCM in a fraction of the time and cost of the corresponding *in-situ* approaches.

For further information, please refer to Appendix D or [108].
2.5. Accelerated Membrane Durability Testing of Heavy Duty Fuel Cells

The objective of this work was to evaluate an accelerated membrane durability test (AMDT) protocol, established by Ballard Power Systems for heavy duty fuel cells following the characteristic duty cycle of transit buses. In contrast to the COCV AST protocol reported in [88,106], the proposed AMDT applied milder conditions, resulting in more realistic degradation characteristics. Additionally, under AMDT conditions the influence of RH cycling (as the main source of mechanical degradation) and platinum in the membrane (as an approach to control the chemical degradation) were investigated. In the scope of the current dissertation, membrane thinning and mechanical properties of the degraded CCMs were evaluated and interpreted under different AMDT conditions, including baseline mid-life, baseline end of life, constant 90% RH, constant 100% RH, and two platinum in the membrane (PITM) experiments. The detailed specifications of these tests are provided in Appendix E or [109]. Baseline AMDTs involved intensive electrochemical loading (chemical degradation) and also RH cycling (mechanical degradation).

Using CCMs extracted from the AMDTs, membrane thinning which is an indicator for chemical degradation was measured and indicated significant reduction in baseline and constant RH AMDTs while membrane thickness was preserved in PITM AMDTs expressing the mitigation in chemical degradation via introduction of Pt to the membrane. Regarding tensile properties, dramatic reduction in the CCM ductility was observed for the baseline and constant RH AMDTs as CCM fractured quickly after passing the yield point. In contrast, PITM samples resembled ductile behaviour comparable to BOL CCMs. Since mechanical properties of constant RH AMDTs were decayed significantly while mechanical degradation mechanisms were excluded during these tests, it was summarized that deterioration in mechanical properties was mainly due to the chemical degradation. The relatively tough and ductile behaviour of PITM AMDTs where chemical degradation was slowed down via H₂O₂ or crossover gas decomposition by Pt particles proved the important role of underlying chemical degradation on CCM mechanical durability.
In conclusion, the result of tensile tests on the AMDT degraded CCMs demonstrated the significant impact of chemical degradation on the deterioration of mechanical properties. Constant RH AMDTs resembled lower rate of decay in electrochemical properties (OCV, leak rate, FRR) and lasted significantly longer when compared to baseline AMDTs, confirming that RH cycling accelerated the membrane degradation. However, in terms of the membrane mechanical properties, both baseline and constant RH AMDTs exhibited identical decay in tensile properties which indicated that chemical degradation was the main controlling factor for the mechanical properties.

For further information, the reader is referred to Appendix E or [109].

2.6. **Ex-situ Chemical Degradation of PFSA Membranes Subjected to Fenton’s Reagent test**

The main objective of this contribution was to evaluate the durability of PFSA membranes against *ex-situ* chemical degradation stressors using Fenton’s reagent test. In addition, the effects of time, pH of the solution, and the presence of platinum ions inside the solution on the rate of chemical degradation were evaluated. In the framework of this thesis, the microstructural evolutions and the decay in mechanical properties of the *ex-situ* chemically degraded PFSA membranes were investigated considering the role of the aforementioned factors.

Fenton’s Reagent test is a well-established *ex-situ* approach capable to extensively elevate the formation rate of radical species in the presence of Fenton’s reagents (Fe$^{2+}$, Cu$^{2+}$, etc.). The Fenton’s solution used in this study was composed of 20% H$_2$O$_2$ and 10 ppm Fe$^{2+}$ with neutral pH (~7) at 80°C. Membrane samples were subjected to four different Fenton’s reagent solutions (baseline (pH = 7 and Pt = 0 ppm), Pt in the solution (5 ppm), high acidic solution (pH < 0), and combination of Pt and high acidic solution). The Fenton’s solution was renewed every 12 hours to ensure desired concentration of Fe$^{2+}$ and H$_2$O$_2$. The Fenton’s reagent test and the preparation of partially degraded membranes were performed by Dr. Lida Ghassemzadeh. In order to characterize the evolutions in mechanical properties and microstructural characteristics, partially degraded membranes were extracted and acid washed at three different
exposure times, i.e. 12, 36, and 48 hours. Top surface and cross sectional microstructural SEM characterization of the degraded baseline membranes at 36 and 48 hours exhibited the formation of characteristic Fenton’s test blister defects originated from the middle of the membrane and expanded towards the surface. Fractions of the expanded blisters finally fractured and formed micro-cracks at the top surface of the membrane which created stress concentration sites. The rest of the membranes showed no significant changes in microstructure. In terms of mechanical properties, significant decay in tensile properties was observed in the baseline membranes where UTS, final strain, and elastic modulus were decreased and the ductile membrane was transformed to a relatively brittle material. Decay in membrane modulus of elasticity was in agreement with the solution method results reported by Kundu et al. [87]. However, the decay in the elastic modulus and UTS was in contrast with the in-situ chemically degraded CCMs as studied by constant-RH AMDT [109]. Constant-RH AMDTs exhibited high elastic modulus comparable to the BOL state, accompanied by insignificant reduction in UTS [109]. The higher elastic modulus of constant-RH AMDT samples could be due to the catalyst layer support which elevated the membrane resistance against the deformation at the early stages of stress application. The reduction in the UTS of Fenton’s degraded membrane can be attributed to the high fractions of microcracks formed all over the membrane surface. In contrast, introducing Pt to the solution and/or reducing the pH of the solution mitigated the decay in mechanical properties where no remarkable deterioration in mechanical properties was detected even after 48 hours.

Overall, formation of micro-cracks at the top of the blister shaped defects in addition with the membrane molecular degradation reduced the mechanical integrity of the degraded membrane. Failure analysis at the tensile fracture surface resembled the propagation and connection of these micro-cracks perpendicular to the tensile direction which resulted in the final failure. The role of Pt in controlling the membrane degradation was scavenging the radical species and subsequently reducing the rate of chemical degradation. On the other hand, reducing the solution pH slowed down the rate of radical formation, consequently resulting in the lower rate of chemical degradation.

For further information, the reader is referred to Appendix F.
2.7. Fuel Cell Durability Enhancement with Cerium Oxide under Combined Chemical and Mechanical Membrane Degradation

The objective of this contribution was to propose a mitigation strategy to enhance the PEFC membrane durability. The effectiveness of stabilizing the membrane with cerium oxide (CeO$_2$) was evaluated under combined chemical and mechanical membrane degradation using the COCV AST protocol [88,106]. In the context of this dissertation, the decay in mechanical properties of CeO$_2$ reinforced CCMs was characterized after being subjected to COCV AST until failure point at 1,244 hours (electrochemical failure was detected by hydrogen leak test) and compared to the baseline CCMs at the COCV AST failure threshold (186 hours). In addition to the prolonged lifetime, CeO$_2$ stabilized CCMs exhibited much lower fluoride release rate and more uniform cell voltage profile when compared to the baseline CCMs.

Tensile tests were conducted on the CeO$_2$ stabilized and baseline CCMs at the BOL and EOL conditions, at 70°C and 90% RH. Both BOL CCMs exhibited similar curves with ductile behaviour indicating that the stabilizing with CeO$_2$ induced negligible changes on the membrane tensile properties. At EOL, the baseline CCMs fractured quickly after the initiation of tensile test (2.3% elongation) indicating an extremely brittle behaviour due to massive degradation. In contrast, CeO$_2$ stabilized CCMs revealed ductile behaviour with stress – strain curves relatively identical to the ones obtained for BOL CCMs despite being subjected to harsh COCV AST degradation conditions around six times longer than the baseline CCMs.

The excellent mechanical properties of the EOL CeO$_2$ CCMs accompanied by the electrochemical characterization results obtained in this study demonstrated that chemical degradation was mitigated to a great extent. It is believed that the CeO$_2$ particles slowed down the rate of chemical degradation through the hydroxyl radical scavenging mechanism by oxidation of Ce$^{3+}$ into the Ce$^{4+}$ and then regeneration of Ce$^{3+}$ via reaction of Ce$^{4+}$ with the hydrogen peroxide and peroxy radicals. It was summarized that stabilizing the membrane by CeO$_2$ greatly enhanced the membrane mechanical integrity and delayed the mechanical failure. However, as the chemical degradation was mitigated by introducing CeO$_2$ particles, the relevance of mechanical/hygrothermal
fatigue degradation on the failure of the stabilized cells may become more significant when compared to the baseline cells.

For further information, the reader is directed to Appendix G or [110].
Chapter 3.

Decay in Mechanical Properties of Catalyst Coated Membranes during Field Operation

As a complementary study to the contributions described in the previous chapter, mechanical characterization of field operated catalyst coated membranes (CCMs) was performed in order to demonstrate the use of mechanical properties as an indicator of membrane degradation in a real-world scenario. Transit buses powered by Ballard HD6 fuel cell modules were operated in Whistler, BC, Canada for five years. The fuel cells were subjected to high voltage periods during idling at stops and traffic lights as well as frequent humidity cycling due to dynamic acceleration and deceleration. The driving conditions at Whistler also imposed relatively harsh temperature conditions ranging from -12°C to 27°C and frequent up-hill and down-hill driving. In order to evaluate the degree of membrane degradation during the field operation, partially degraded MEAs were extracted after different time of field operation, i.e. 2,800, 4,400, and 8,200 hours, from the Whistler, BC fuel cell bus fleet.

In order to prepare CCMs for tensile testing, all MEAs were selected consistently from the inlet region and were cut along the transverse machine direction into 25 mm x 2 mm rectangular shapes using a plotter cutter machine. GDLs were detached from the sides of the MEA and the remaining CCMs were kept between glass slides for a few days to ensure consistency. To avoid edge stress concentrations a 5:1 gauge length to width aspect ratio was considered. A schematic of the tensile sample used in this study is presented in Figure 5. Tensile tests were conducted using a dynamic mechanical analyzer (DMA; TA Instruments Q800) equipped with an environmental chamber (TA Instruments DMA-RH Accessory). The gauge length was 10 mm and the remaining length of the sample was used in the clamp area. After sample installment in the DMA, the temperature and relative humidity were equilibrated to the desired conditions (23°C –
50% RH and 70°C – 90% RH) while a small preload force (0.003 N) was applied to keep the sample under tension. As equilibrated, the CCM was stretched until the fracture point or the DMA travel length limit (~26 mm) under a constant relatively low strain rate (0.01 min\(^{-1}\)). At least three identical samples were tested at each test condition to ensure statistical relevance.

**Figure 5. Schematic of a CCM specimen prepared for tensile testing.**

The results of the tensile tests are illustrated in Figure 6. as a function of the field operation time. The error bars on each column exhibit two standard deviations which cover 95% of the distribution. The average elastic modulus which was calculated from the maximum slope of the stress – strain curves in the elastic region slightly decreased from BOL to 8,200 hours, as presented in Figure 6.a. In the same manner, according to Figure 6.b, the average UTS, i.e., the maximum stress tolerated by the CCM during the tensile testing, was marginally reduced as a function of degradation time. Moreover, the CCM final strain, which is an indicator of the total elastic and plastic deformation captured during the tensile test, was preserved within the DMA travel limit (~160%), as presented in Figure 6.c. Among all experiments conducted on the partially degraded CCMs, only three tests (one at 2,800, one at 4,400, and one at 8,200 hours) were fractured during the tensile testing prior to reaching the DMA limit. The insignificant reduction in elastic modulus and UTS indicated that the degraded CCMs exhibited good resistance against deformation and crack initiation, even after 8,200 hours. Furthermore, the interestingly retained ductility and toughness of the degraded CCMs revealed that the currently utilized PFSA ionomer membranes are capable to largely resist the induced *in-situ* stresses caused by the periodically high cell voltage and hygrothermal swelling and contraction during the dynamic duty cycle of the fuel cell buses in the presently analyzed condition and duration.
The preserved mechanical properties of the field operated MEAs demonstrated that the in-situ degradation mechanisms were controlled to a great extent. The presence of platinum band inside the membrane, which was detected in the cross sectional microstructure of the field operated membranes, may have contributed to this result [109]. Within the scope of this thesis, it was confirmed that the formation of a platinum band inside the membrane (PITM) could slow down the rate of chemical degradation to a great extent, and hence mitigated the decay in mechanical properties (Appendix E or [109]). Furthermore, it should be mentioned that the PEFC operating conditions are highly acidic due to the nature of the PFSA ionomer membranes. Therefore, as experimentally proved by the ex-situ Fenton’s reagent experiments (Appendix F), formation of radical species through decomposition of hydrogen peroxide via Fenton’s reagents was alleviated at acidic environments (low pH). It can be summarized that rate of chemical degradation was remarkably slowed down inside the field operated membranes due to the simultaneous influence of PITM and acidic environment mitigation mechanisms. Additionally, the fluctuations in RH, known as the main source of mechanical stress, were predominantly milder during the field operating conditions when compared to the RH fluctuations applied in the AMDT [109], COCV AST [106], and AMST [107]. Overall, the field operated MEAs revealed superior mechanical (tensile) characteristics, comparable to the freshly fabricated CCMs, due to the preservation of chemical degradation stressors as well as lower level of mechanical stressors.

Although the results of the tensile tests on the field operated MEAs showed promising membrane durability, dynamic mechanical properties could further be measured via creep or expansion tests with the aim of monitoring the significance of chemical degradation during the operation. It should be noted that according to the previous expansion tests, dynamic properties were not altered significantly during mechanical degradation as indicated by the in-situ AMST [107]. Furthermore, improved understanding of the rate of mechanical degradation could be obtained through investigating field operated MEAs at higher level of degradation (i.e., longer operating time). A qualitative comparison between the tensile properties of 8,200 hours field operated and COCV AST degraded samples suggested that the field operated CCMs were merely at an early stage of membrane degradation at 8,200 hours.
Figure 6. Tensile properties of BOL CCM and partially degraded field operated CCMs, i.e. a) elastic modulus, b) ultimate tensile strength, and c) final strain, at 23°C – 50% RH and 70°C – 90% RH.
Chapter 4.

Conclusions and Future Work

4.1. Conclusions

The present dissertation was devoted to characterizing the effect of different degradation mechanisms on the mechanical stability of PFSA ionomer membranes and also to propose mitigation strategies in order to minimize the rate of decay in mechanical integrity. To accomplish these goals, the baseline membrane and CCM mechanical behaviour were documented first. Then, multiple accelerated stress tests, each oriented to intensify specific stressors, were conducted on MEA samples (in-situ) or pristine membrane or CCM samples (ex-situ). The obtained partially or fully degraded membranes and CCMs were prepared to evaluate the evolutions in mechanical properties and, in some cases, microstructural characteristics. The main contributions and findings of this work are summarized as follows:

- The time-dependent mechanical properties of PFSA membranes and CCMs were benchmarked using creep – recovery experiments in order to provide comprehensive understanding of their dynamic mechanical behaviour. As a primary finding of this study, it was shown that coating the membrane with catalyst layers promotes membrane resistance to creep. The effects of hygrothermal conditions (temperature and relative humidity) and the induced mechanical stress were characterized and demonstrated that under fuel cell operating conditions, irreversible damage can be generated and accumulated inside the membrane and catalyst layers capable to reach the failure. Due to the significant impact of hygrothermal conditions on the creep deformation in the CCM, reducing the operating temperature is recommended to slow down the mechanical damage caused by creep stress. Overall, it was validated that
mechanical degradation can occur not only by fatigue stress (wet – dry cycles), but also via creep stress during idling or steady state operation of fuel cells.

- Decay in mechanical properties of PFSA membranes and CCMs was investigated through conducting a number of *in-situ* and *ex-situ* AST experiments under pure chemical (Fenton’s reagent and constant RH AMDT), pure mechanical (AMST, mechanical fatigue, and to some extent PITM AMDT), and combined chemical and mechanical (COCV AST and baseline AMDT) degradation mechanisms. The failure modes and degradation level were characterized for each mechanism and compared to the field operated CCMs.

- Dramatic decay in mechanical properties of CCM was detected when MEAs were subjected to the combined chemical and mechanical degradation mechanisms during COCV AST [106] and baseline AMDT [109]. The overall decay in mechanical properties showed the interaction between chemical and mechanical membrane degradation during the fuel cell operation.

- Baseline AMDT was capable to simulate the failure modes observed in the field operated CCMs and created a benchmark to study membrane degradation. Complementary AMDT studies via constant RH and PITM AMDTs provided firm understandings on the correlation between each degradation mechanism and the mechanical integrity of the membrane. The lack of mechanical integrity observed in the constant RH AMDTs confirmed the strong impact of chemical degradation. However, the extension in membrane lifetime during constant RH AMDTs when compared to the baseline AMDTs proved the accelerating effect of RH cycling. On the other hand, the preservation of chemical degradation via introducing PITM revealed significant mitigation of the deterioration in mechanical properties where the CCM exhibited remarkable toughness and elongation at the end of life AMDT. In total, the results of the AMDT studies demonstrated that the chemical degradation is the dominant mechanism responsible for the decay in membrane mechanical properties; however, the rate of degradation is intensified in the presence of mechanical degradation.
• A comprehensive study on the in-situ hygrothermal AMST showed that isolated mechanical stressors in the form of fatigue could result in the mechanical failure of the membrane after 20,000 cycles of 4 min wet/dry cycles through formation of microscopic cracks inside the membrane, which further resulted in mild decay in fracture toughness. Notably however, the hygral and thermal expansion properties of the CCM were retained during this process.

• An ex-situ tensile fatigue and creep approach was established to simulate the mechanical degradation obtained by the in-situ AMST at lower cost and time. The capability of the proposed experiment was verified through evaluating the tensile and hygrothermal expansion properties as well as the morphological evolution of the degraded CCMs. Rapid decay in the fracture strain and elastic modulus was observed in the early stages of degradation while UTS increased. Hygrothermal expansion tests exhibited contraction in the CCM length with stepwise rise in the hygrothermal conditions, which was attributed to material recovery from previously induced elongation due to tensile creep. Nevertheless, fracture failure of the specimen was primarily attributed to fatigue stress rather than creep, provided the permanent fatigue damage created by the experiment.

• Ex-situ chemical degradation via Fenton’s reagents indicated the significant reduction in the decay rates of the mechanical membrane properties when either platinum was added to the Fenton’s solution or highly acidic solution was utilized as a consequence of more benign conditions for radical attack. The findings of this study can justify the superior mechanical properties of the field operated CCMs where chemical degradation was likely conserved by the low pH operating conditions and formation of platinum band in the membrane.

• The temperature was shown to have detrimental effects on the membrane integrity due to acceleration of both chemical and mechanical degradation processes. Furthermore, fluctuations in the temperature may induce thermal fatigue in the membrane. Therefore, in order to extend the membrane mechanical durability it is recommended to apply uniform temperature and potentially reduce the operating temperature.
Oscillations in relative humidity were also shown to be a key mechanical degradation factor. The wider range of oscillation can result in more severe degradation and shorter time to failure. In this manner, the dry phase applied tensile stresses which were more critical than the compressive stresses in the wet phase. The field operated MEAs experienced oscillations in membrane hydration during the typical field operating conditions. However, larger oscillation magnitude can be expected at accelerated stress test conditions. In addition, membrane dehydration can indirectly lead to rapid degradation due to an increase in the internal temperature. Therefore, improvement of fuel cell water management and prevention of sudden dehydration and RH oscillation can slow down the rate of mechanical degradation which enhances the membrane mechanical durability.

It was also revealed that the rate of chemical degradation can be minimized when a platinum band is formed inside the membrane. Thus, PITM can be used as another strategy to enhance the membrane mechanical stability.

Membrane mechanical durability enhancement via reinforcing the membrane with CeO\textsubscript{2} particles was validated through conducting COCV AST experiments on both CeO\textsubscript{2}-reinforced and baseline membranes. The CeO\textsubscript{2}-reinforced CCMs revealed superior tensile properties at EOL, after being subjected to COCV AST for 1,244 hours, comparable to the BOL CCMs. This suggests that the failure mode in this case was primarily due to mechanical membrane degradation.

The use of mechanical property measurements as an indicator of membrane health was demonstrated on field operated CCMs, showing mild degree of degradation compared to the EOL states observed from the various accelerated stress tests.

The outputs of this work can provide the community with valuable experimental results in order to develop empirical models to predict the fuel cell lifetime and durability as well as to evaluate new materials.
4.2. Future Work

- Mechanical properties of pristine membranes and CCMs were investigated in a wide range of hygrothermal conditions in this thesis as well as in previous studies in our group. However, during fuel cell operation, the membrane may also be in contact with liquid water which may lead to a different state of hydration. Therefore, conducting mechanical testing (tensile and fatigue) in the presence of liquid water would be useful in order to obtain better understanding of the membrane behaviour in wet conditions.

- In this work, fresh membranes and CCMs were assumed to be free of manufacturing defects and the failure was assumed to result from pure degradation effects. However, in practice, minor defects are expected to be generated inside the membrane or at the interface of membrane with the catalyst layers during the manufacturing process. A complementary study on the effect of manufacturing defects on mechanical durability could be useful to validate these assumptions and identify potential issues related to manufacturing. In this manner, ex-situ mechanical degradation (via fatigue) or chemical degradation (via Fenton's reagents) can be applied on pre-damaged membranes.

- The ex-situ mechanical fatigue AMST was performed by tension – tension fatigue experiments; however, the fuel cell operating conditions induce tension – compression fatigue. Thus, a complementary ex-situ fatigue study using tension – compression cycles would be valuable to provide supplementary information on the in-situ response of the membrane to the cyclic loading.

- Mechanical characterization of field operated CCMs were conducted up to 8,200 hours in this work. However, it is desired to continue this study on CCMs exposed to longer operating times. Moreover, the evolution of microstructural damage (micro-cracks, delamination, and divots) during operation can be examined using SEM to support the lifetime prediction models.

- Although presence of platinum particles in the Fenton's reagent solution resulted in durability improvement of the PFSA membrane, it can be beneficial to study
the Fenton’s reagent tests on a membrane with a previously developed platinum band analogous to the ones observed in the field operated membranes.
References


Appendix A.

Creep Properties of Catalyst Coated Membranes for Polymer Electrolyte Fuel Cells

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Creep properties of catalyst coated membranes for polymer electrolyte fuel cells

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HIGHLIGHTS

- Creep properties of catalyst coated membranes were compared to pure membranes.
- CCM creep was strongly influenced by the applied stress and hygrothermal conditions.
- Catalyst layer microcracks were formed at the yield point of the CCM.
- Accumulation of creep damage was observed during successive creep-recovery steps.

Abstract

Creep as a time-dependent mechanical damage acting either independently or in conjunction with other degradation mechanisms is known to reduce the membrane durability of polymer electrolyte fuel cells (PEFCs). Due to the important ionomer coupling of membrane and catalyst layers in PEFCs, the present work evaluates membrane creep when constrained within a catalyst coated membrane (CCM). Three key factors dominating creep life in commonly used perfluorosulfonic acid (PFSA) ionomer membranes, including creep stress, temperature, and relative humidity, were investigated by applying ex-situ creep loading and unloading experiments under controlled temperature and humidity conditions. The creep strain and recovery of the CCM were found to be highly dependent on the environmental conditions and applied stress levels, where the temperature effect on creep strain was the most significant. Repetitive creep – recovery cycles revealed that significant creep damage can accumulate in the material over time. This accumulated creep damage was found to be independent of the loading frequency while both peak strain and permanent deformation increased with the stress duration. Based on the present findings, it is recommended to reduce the operating temperature and ensure adequate membrane hydration in order to mitigate harmful creep effects in PEFCs.

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1. Introduction

Polymer Electrolyte Fuel Cells (PEFCs) are a promising alternative to combustion engines in automotive applications. One of the main challenges facing the commercialization of PEFCs is in the development of membrane electrode assemblies (MEAs) that meet automotive industry durability targets [1] that range from 5000 h for light duty vehicles (e.g., passenger cars) to 18,000 h for heavy duty vehicles (e.g., transit buses) [2,3]. Currently, perfluorosulfonic acid (PFSA) ionomer membranes (e.g. Nafion® from DuPont) are the most commonly used membrane type in PEFCs due to the high...
Young’s modulus and yield stress of Naion relative humidity. The effect of environmental conditions on the polymer as permanent deformation. Maksimov et al. [19] observed an increase in the initial creep rate although the final strain was similar [20]. They expressed that at 50% RH, in the early stages humidity acts as a plasticizer and facilitates chain slip in the amorphous phase. However, the increase in crystallinity due to the structural rearrangement caused by creep strain slows down the creep rate [20].

Launay et al. [21] modeled non-linear mechanical response of cyclic creep and recovery in a polymer matrix composite of polyamide. They proposed an equivalence principle between the temperature and humidity validated by obtaining similar behavior at 70 °C–72% RH and 90 °C–50% RH [21]. In addition to conventional creep and creep rupture tests, Tweedie and Van Vliet [22] studied the creep behavior of different visco–elastic polymers using nanoindentation as a function of maximum creep force, force rate, and stylus geometry. A similar approach was utilized by Lu et al. [23] to study the linear visco-elastic properties of polymethyl methacrylate (PMMA) and polycarbonate (PC). Based on the time-temperature superposition principle, Achiereini et al. [24] investigated the long-term creep behavior of polypropylene via accelerated testing by elevating the temperature in brief steps. By rescaling the results of short-term tests, master curves for long-term creep capable to predict polypropylene creep response at different times were summarized [24].

PFSA ionomer membranes as visco-elastic – visco-elastic materials encompass viscous characteristics [17,25]. Under constant stress, the typical response of a viscous polymer includes an instantaneous increase in strain due to the elastic–plastic response followed by continuous straining at a non-constant rate due to the mixed elastic–plastic and viscous effects [17,26,27]. This continuous straining under constant stress is defined as creep. The polymer will continue to deform slowly with time until rupture. As the stress is released, an immediate strain recovery occurs followed by a gradual strain recovery. In most cases some strain is not completely recovered and remains permanently inside the membrane after stress removal [17]. Creep damage in PFSA membranes may either cause crack initiation or reduction in the membrane thickness until the membrane fails to separate the reactant gases [28]. Majažnik et al. [29] investigated the influence of temperature and hydration on tensile creep in Naion® N1110 and realized that the creep strain is greatly affected by both factors. At constant humidity, an increase in temperature always leads to higher creep strains while the impact of relative humidity varies depending on the test temperature [29]. At temperatures below 40 °C, high humidity resulted in low creep resistance due to the plasticizing effect of water, while at high temperatures above 90 °C, high humidity resulted in high creep resistance due to the adverse stiffening effect [29]. In the medium temperature range (40 °C < T < 90 °C) the creep resistance was highest at intermediate humidity due to the mutual effect of the aforementioned mechanisms [29]. From the same group, Satterfield et al. [30] compared the creep behavior of Naion® 115 and Titania/Naion® composite and expressed that lower creep strain was observed in the composite membrane. Creep failure of Naion® NR111 was examined under various hydration and temperature levels by Solasi et al. [28]. The slope of the stress–rupture curves with respect to the time to failure was found to be independent of temperature and humidity in the applicable range. Through conducting cyclic and static biaxial blister tests, Li et al. [31] investigated the resistance to gas leakage in three different commercially available membranes under fatigue and creep loading. Due to the relatively identical creep and fatigue behavior at 90 °C and 2% RH, the lifetime was dominated by the
total loading time rather than the number of cycles [31].

Despite the important ionomer phase coupling of membrane and catalyst layers in PEFCs, no previously published studies have considered membrane creep when constrained within a CCM. As reported previously by our group [14], membrane mechanical properties are significantly altered when coated by catalyst layers. Therefore, the objective of the present work is to thoroughly characterize the ex-situ creep response of catalyst coated PFSA membranes compared to pure membranes subjected to a variety of hygrothermal and mechanical stress conditions. Furthermore, accumulation of creep strains during conditions representative of dynamic PEFC operation will be evaluated through a series of successive creep stress and recovery cycles. In conjunction with our previous report on the static properties of CCMs [14], the outcomes of this work will provide complementary fundamental understanding of the dynamic behavior of CCMs in PEFCs.

2. Experimental procedure

2.1. Sample preparation

PFSA membranes and MEAs used for this study were provided by Ballard Power Systems. MEAs were prepared by coating a carbon supported platinum catalyst layer with PFSA ionomer on microporous layer (MPL) covered gas diffusion layer (GDL) to fabricate gas diffusion electrodes (GDE). Then, anode and cathode GDEs were hot pressed with a PFSA membrane to form the MEA. In order to prepare creep samples, PFSA membranes and MEAs were all cut into rectangular shapes (25 × 2 mm) along the transverse (cross-machine) direction. Then, GDLs were detached from both sides of the MEA and the remaining CCM and PFSA membrane samples were stored between glass slides in ambient conditions prior to creep testing.

2.2. Creep testing

Tensile creep tests were applied at various levels of controlled temperature, relative humidity, and stress on PFSA membrane and CCM samples using a dynamic mechanical analyzer (DMA; TA Instruments Q800) equipped with an environmental chamber (TA Instruments DMA-RH Accessory). Samples of 25 mm length were loaded at 6 mm initial gauge length and the remaining 19 mm length was used to clamp the sample. The exact gauge length and sample width were measured for all samples by the DMA and optical microscope, respectively, while the average thickness was quantified by digital micrometer prior to the test at ambient conditions. Approximate sample dimensions are illustrated in Fig. 1, schematically.

As explained before, creep testing requires long periods of loading to reach sample failure due to the slow propagation of creep damage. Therefore, in this study, creep experiments were...
designed to measure the creep and recovery response in a reduced time period of a few hours, which is deemed sufficient for fuel cell applications [29]. Prior to creep test initiation, the samples were loaded at ambient conditions and equilibrated to the desired temperature and relative humidity conditions while a small pre-load tensile stress (0.1 MPa) was applied to keep the sample under tension. In order to avoid shocking the samples with a jump in stress, the creep stress was elevated to the predetermined stress at a relatively high rate (5 MPa min\(^{-1}\)). With the aim of assessing the effects of hygrothermal conditions, stress, and time on the creep response of the materials, three types of creep experiments were conducted:
1. Constant stress tests: With the purpose of understanding the effect of hygrothermal conditions on the creep behavior, regular creep tests were applied on the PFSA membranes and CCMs at different temperatures (23 and 70 °C) and relative humidities (50% and 90%). The creep properties of the CCM were compared to the membrane under equivalent stress (2.5 MPa) and equivalent force. Additional creep tests were performed on CCMs at intermediate temperature (50 °C) and relative humidity (70%) to provide more details on the impact of the environmental conditions on the creep response of the CCM. As depicted in Fig. 2, samples were stretched under constant creep stress for 120 min followed by 120 min of unloading to evaluate the creep strain, instantaneous and time-dependent factors of recovery, and permanent deformation. Creep strain represents the strain at the end of the loading step, while instantaneous recovery and time-dependent recovery indicate the strain restoration during stress reduction and during the recovery, respectively. Finally, permanent deformation shows the total unrecovered strain stored inside the membrane. As explained, applying a small tensile stress value (0.1 MPa) during the unloading was mandatory in order to keep the samples straight during the test. Each of the aforementioned tests was repeated at least two times according to the ASTM D2990 creep standard [32] and the average creep strains were reported.

2. Variable stress tests: A similar procedure was applied to measure the creep deformation of CCMs as a function of creep stress at four combinations of temperature and relative humidity (23 °C-50%, 23 °C-90%, 70 °C-50%, and 70 °C-90%). The stress values were selected to be 40%, 60%, 80%, 100%, 120%, and 140% of the yield strength of the CCM at the desired test conditions as...
previously reported by Goulet et al. [14]. In the same manner, the average of at least two tests was reported for each testing conditions [32].

3. Fuel cell simulated (FCS) tests: Under automotive operating conditions, the membrane is subjected to cycles of hygrothermal loading and unloading in addition to the static mechanical compression of the MEA. Understanding the accumulation of creep damage was accomplished through applying successive steps of creep and recovery at room and fuel cell conditions (23 °C-50%RH and 70 °C-90% RH, respectively), as presented in Fig. 3. Fuel cell simulated tests were repeated three times at each test parameter as per the ASTM D2990 requirements [32].

2.3. Microstructural analysis

Top surface microstructural analysis of the CCM samples after being subjected to the variable stress creep experiments was performed using scanning electron microscopy (SEM; FEI Dualbeam 235 FIB-SEM) at Simon Fraser University’s nano-imaging facilities at 4D LABS. SEM images were captured from the gauge section of the creep samples using 5 kV electron beam accelerating voltage.

3. Results and discussion

The creep properties of catalyst coated PFSA membranes (CCMs) were systematically evaluated and compared to pure membranes using ex-situ tensile creep tests. First, the creep behavior of CCMs was analyzed under various levels of temperature and relative humidity. Then, the effect of creep stress on the creep strain and recovery was evaluated. Finally, the accumulation of creep deformation during simulated fuel cell operating conditions was investigated under cyclic periods of loading and unloading.

3.1. Constant stress tests

The physical and mechanical properties of PFSA membranes in PEFCs are highly sensitive to the environmental conditions, primarily due to the hygroscopic nature of the ionomer material. In automotive PEFCs, an MEA is subjected to significant variations in temperature and relative humidity, for instance from ambient conditions (e.g., 23 °C and 50% RH) to fuel cell operating conditions (e.g., 70 °C and 90% RH) during startup, which may lead to membrane creep and subsequent damage. As explained in the experimental procedure, two types of constant stress creep tests were conducted in order to evaluate and compare the CCM creep behavior to that of a pure PFSA membrane. In addition, the anticipated reinforcing effect of the catalyst layers on the CCM creep resistance was examined. The two types of creep tests performed on the reference membrane samples were CCM identical force (membrane - A) and CCM identical stress (membrane - B). Strain – time curves for the CCM and membranes subjected to creep at 23 °C-50% RH are shown in Fig. 4. In addition, the total creep and recovery data extracted from the strain – time curves at various environmental conditions are illustrated in the bar charts of Fig. 5. As expected, the creep strain and recovery was higher.

![Fig. 8](image-url)

*(a) Total creep strain, (b) instantaneous creep recovery, (c) time-dependent creep recovery, and (d) permanent creep deformation in the CCM as a function of temperature and relative humidity under 2.5 MPa creep stress.*
in membrane-A than for membrane-B due to the higher applied force (and stress). Approximately three times higher stress was applied on membrane-A, resulting in approximately ten times higher creep strain. At identical force (CCM and membrane-A), the creep strain of the CCM was remarkably lower than that of the membrane, indicating the reinforcement provided by the catalyst layers. It can be summarized that the catalyst layers improved the membrane resistance to creep deformation independent of the environmental conditions.

Table 2
Summary of the CCM yield strength measured by Goulet et al. [14], using the same CCM material as in the present study.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Relative humidity (%)</th>
<th>Yield strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>50</td>
<td>3.7</td>
</tr>
<tr>
<td>70</td>
<td>50</td>
<td>2.0</td>
</tr>
<tr>
<td>23</td>
<td>90</td>
<td>2.3</td>
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<tr>
<td>70</td>
<td>90</td>
<td>1.1</td>
</tr>
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Fig. 9. CCM creep strain curves at different levels of stress at four combinations of temperature and relative humidity. The stress is indicated relative to the yield stress (Y.S.) under each environmental condition. Due to the large variations in strain under different stress levels, the low stress curves were magnified and reproduced in a separate window below each corresponding plot.
conditions, as the creep strain was reduced by 88% and 56% at 23 °C–50% RH and 23 °C–90% RH, respectively. In a similar manner, the total strain recovery (instantaneous and time-dependent) was reduced by 85% and 52% respectively. It should be mentioned that at 70 °C–50% RH and 70 °C–90% RH, the membrane-A tests were terminated due to the relatively large creep strains approaching the DMA travel length limit (~26 mm); hence, no recovery data were measured in these cases. On the other hand, at identical stress (CCM and membrane-B), the CCM exhibited higher creep strain than the membrane at all environmental conditions, which revealed a lower creep resistance in the catalyst layers compared to the membrane. The porous structure accompanied with the fragile bonding among particles limit the mechanical strength of the catalyst layers [14]. For this reason, the membrane is the main load bearing part of the CCM.

The ratio of creep recovery and permanent deformation to the total creep strain in the CCM and membrane-B (identical stress) are presented in Fig. 6. At low temperature, the portions of recovery and permanent deformation were relatively identical for the two materials, although the permanent deformation ratio increased with humidity. However, the aforementioned ratios were substantially altered as the temperature increased, where the permanent deformation of the CCM was considerably higher than for the membrane due to a lack of time-dependent recovery. According to our previous study [14], the applied 2.5 MPa creep stress was beyond the CCM yield point at high temperature (70 °C) while it was well below the membrane yield point. Therefore, due to the viscoplastic deformation of the CCM compared to the mainly viscoelastic deformation of membrane-B under 2.5 MPa creep stress, smaller portions of the creep strains were reclaimed during the time-dependent recovery of the CCM compared to the membrane.

A supplementary study on the effect of hygrothermal conditions on the creep behavior of the CCM was conducted by measuring the creep and recovery at an intermediate temperature (50 °C) and relative humidity (70%) following the constant stress creep test. Fig. 7 shows the CCM creep strain curves as a function of temperature and relative humidity. It is evident from Fig. 7 that an increase in temperature or relative humidity always results in higher creep strain and deformation. Creep occurs when sufficient driving force is provided by the applied stress to overcome the molecular interactions of the polymer. The requisite driving force decreases exponentially as temperature increases due to the thermally activated nature of creep in polymers [28]. Therefore, Arrhenius type equations are suggested to express the exponential contribution of temperature and humidity on the creep strain rate [28]. F-test analysis of variance (ANOVA) was applied to quantitatively study the effects of the environmental conditions using the lowest and highest temperature and relative humidity values. According to the ANOVA outcomes summarized in Table 1, it appears that the influence of temperature on the creep strain and permanent deformation is more significant than the impact of relative humidity while the interaction has the lowest effect when compared to each individual parameter. Based on the p values in Table 1, at a significance level of 0.01, the effects of temperature and relative humidity are both statistically significant while the interaction effect is not. As the temperature increases, the internal energy of the membrane...
enhances the motion of molecules and the relative slip of adjacent chains, resulting in higher elongation under creep stress. In contrast, relative humidity facilitates creep deformation through swelling and distancing the molecular chains.

The impact of the coupled hygrothermal conditions on the individual steps of creep and recovery in the CCM is exhibited in Fig. 8. The effect of relative humidity on the creep strain and recovery was more significant at low temperatures (e.g. 23°C) than at high temperatures (e.g. 70°C). As an example, the total creep strain at 23°C (Fig. 8a) increased by nearly eleven times when the RH was raised from 50% to 90%, while at 70°C (Fig. 8a), the total creep strain increased by merely 40%. Nafton® membrane creep responses at lower humidities than the ones addressed in our study on CCMs were reported by Majsztrik et al. [29]. Their results on the humidified membranes (8% and 65% RH) at temperatures below 70°C are qualitatively in agreement with our findings for the CCM [29]. However, a completely different behavior was observed in fully dried (0% RH) membranes where the creep strain above 50°C was higher than for the humidified membranes (8% and 65% RH). At low temperatures, the water absorbed in the ionomer acts as a plasticizer and enhances the slip of polymer molecules; hence, increasing the humidity generally facilitates the flow of molecules. As the temperature is increased, due to the adequate thermal energy obtained by the molecular chains, molecular flow under the creep stress is facilitated. Thus, the plasticizing effect of relative humidity becomes less significant on the creep deformation.

Similar behavior was observed in the recovery stage (Fig. 8b–d) after the creep stress was released. It is noteworthy that the creep stress (2.5 MPa) applied in these experiments was in some cases higher than the yield stress of the CCM, as previously measured by our group [14] and exhibited in Table 2 at four temperature and relative humidity combinations. It can be seen from Fig. 8 that at high temperatures and relative humidities, where the yield point was passed, most of the creep strain was stored in the sample after the recovery and only minor portions were released during the recovery stage. In contrast, at conditions below the yield point, most of the creep strain was reclaimed during the recovery. For example, by comparing Fig. 8a with Fig. 8d, at 70°C–90% RH, 71% of the creep strain remained inside the sample after recovery as permanent creep deformation. While at 23°C–50% RH, only 27% of the creep strain remained as permanent creep deformation.

### 3.2. Variable stress tests

In this section, the effect of the creep stress on the CCM creep strain and recovery was investigated under fixed hygrothermal conditions by means of tensile creep measurements under different stress levels from 40% to 140% of the CCM yield stress [14]. Among the environmental conditions studied in the previous section, four combinations of temperature (23 and 70°C) and relative humidity (50% and 90% RH) were considered here, with results shown in Fig. 9. Due to the large variations in strain at different stress levels, the strain curves related to low stress levels (40%, 60%, and 80% of the yield stress) were magnified and reproduced in an additional plot window. As expected, the higher stress magnitude resulted in
higher creep strain, independent of the environmental conditions. The most dramatic variation was observed at 23 °C−50% RH where the creep strain increased from 2.2% to 288% at 40% and 140% of the yield stress, respectively. At higher temperature and humidity, the rate of increase in creep strain due to stress elevation decreased (e.g., from 3.1% to 94% at 70 °C–90% RH) but still remained significant.

The total creep strain and various recovery portions were extracted from the creep strain curves and illustrated in Fig. 10 as a function of normalized stress. The normalized stress was calculated as the ratio of the applied creep stress to the yield stress at the corresponding temperature and relative humidity. As expected, the creep strain increased nonlinearly with an increasing slope as the stress was elevated. The instantaneous portion of recovery remained relatively constant in the 10−25% range under most conditions, except under room conditions (23 °C−50% RH) where a much higher degree of instantaneous recovery (up to 45%) was obtained for stress values below the yield point (Fig. 10b), indicative of a more elastic behavior. Creep deformation generally occurs due to the breakage of cross links between polymer molecules under creep loading. During recovery, the intermolecular bonds tend to re-entangle and reproduce the cross links. At high temperature and/or humidity, however, the molecular vibrational energy is high enough to decelerate the re-arrangement of lateral links shortly after stress removal. Therefore, the portion of instantaneous recovery of creep strain is small and varies negligibly with the creep load. In contrast, the low molecular vibrational energy at room conditions facilitates the re-arrangement of intermolecular forces quickly after release of stress, resulting in larger portions of instantaneous recovery.

On the other hand, the time-dependent strain recovery inherited from the partially viscous nature of the PFSA ionomer was found to reach a maximum level around the yield point for each hygrothermal condition (Fig. 10c), which is a consequence of the viscoelastic behavior below the yield stress compared to the viscoplastic behavior above the yield stress. The irreversible viscoplastic creep accompanied with strain hardening restricted the time-dependent recovery and enlarged the permanent deformation. Reorientation of the sulfonic acid groups in the hydrophilic clusters combined with the deformation of the PTFE matrix contribute to the time-dependent recovery [29]. Below the yield point, the stress facilitated the reorientation of sulfonic acid groups resulting in an increasing regime in time-dependent recovery strain. However, beyond the yield point, due to the flow of polymer molecules, the relative contribution of time-dependent recovery is reduced and overshadowed by the permanent deformation.

Finally, significant permanent deformation of at least 30% of the total creep strain was observed under all conditions (Fig. 10d), even for applied stresses below the yield point. Interestingly, the relative permanent deformation at high humidity (90% RH) was almost constant at 50−60%, independent of the applied stress level, while at low humidity (50% RH) the relative permanent deformation was observed to increase past the yield point, as would normally be expected due to plastic deformation. At high RH, the plasticizer role of water is likely to reduce the sensitivity to stress, resulting in a constant fraction of permanent deformation. It should be noted that the two-hour creep recovery time used in the experiments was deemed sufficient in order to reach a relatively stable condition at which the permanent deformation could be reliably measured.

The microstructural evolution of the cathode catalyst layer portion of the CCMs subjected to different levels of creep stress at 70 °C−90%RH was investigated using scanning electron microscopy (SEM), with typical images shown in Fig. 11. The cathode catalyst layer was distributed uniformly on the membrane in the pristine CCM (Fig. 11a), with random indentations created by adjacent GDL fibers evident on the surface. Once the creep stress was applied, the membrane and catalyst layers were stretched accordingly. However, as deformation continued, the catalyst layers were not capable of elongating in the same manner as the membrane, due to the brittleness of the porous catalyst layer structure. Below the yield stress, the structural integrity of the pristine CCM was preserved during creep testing without resembling noticeable changes in the microstructure. At the yield stress, permanent microcracks were formed through the whole thickness of the cathode catalyst layer perpendicular to the stress direction (Fig. 11b). As the creep stress passed the yield point, islands of catalyst layer were formed on the surface of the membrane surrounded by interconnected macrocracks, as shown in Fig. 11c. Further microstructural analysis at 60° tilt revealed the detachment between catalyst layer and membrane, as illustrated in Fig. 11d. Membrane elongation is restricted in the presence of catalyst layers [14]. However, due to the large creep deformation beyond the yield point of the CCM and the relatively low ductility of the catalyst layers, the catalyst layers failed to
elongate in this regime. This resulted in the initiation and propagation of cracks in the cathode where the crack size increased with increasing level of stress past the yield point. The cathode failure and detachment is a further evidence of the rapid growth of creep strain beyond the yield point as presented in Fig. 10a. Here, membrane flow was readily facilitated because of the loss of reinforcement otherwise provided by the catalyst layers. Similar microstructures depicted in Fig. 11 were also observed at the other temperature and humidity conditions.

3.3. Creep under simulated fuel cell conditions

When situated inside an operating fuel cell, the CCM experiences significant dynamics due to startup/shutdown cycles and changes from low to high power that generate stress inside the material. The cyclic and static forces during operation impose fatigue and creep deformation in the membrane. As a result, portions of creep strain may remain inside the membrane, i.e., permanent deformation, and accumulate gradually until membrane failure. The sequence of working at high and low stresses can be simulated via successive steps of creep and recovery. Multi-step creep experiments were therefore conducted at room and fuel cell operating conditions (23 °C–50% RH and 70 °C–90% RH), and the resulting creep responses of the CCM are presented in Fig. 12. The creep stress was selected to be 80% of the CCM yield stress at the desired temperature and relative humidity. During recovery, a 0.1 MPa tensile stress was applied to keep the samples under tension. It can be seen that creep strain and permanent creep were accumulated gradually as the steps continued, with more significant deformation at fuel cell conditions than at room conditions. Ultimately, at room conditions, less than 50% of the creep strain was stored in the sample in the form of permanent deformation; while at fuel cell conditions, the permanent deformation was more than 65% of the creep strain, as presented in Table 3. As previously discussed, the high vibrational energy of the ionomer molecules at fuel cell conditions prevents the intermolecular cross links to be reconfigured during the recovery steps, resulting in larger permanent deformation when compared to room conditions. As presented in Fig. 6, the recovery of the membrane was limited in the presence of catalyst layers at high temperatures while the recovery portions of membrane-B were not affected by the temperature. It can be summarized that membrane-B would experience lower creep deformation at high temperatures when compared to CCM. In the same manner, higher fractions of strain were reclaimed during instantaneous recovery steps at room conditions when compared to fuel cell conditions (Table 3). This was due to the reconstruction of intermolecular bonds quickly after the stress relaxation at low temperature.

The accumulation of creep strains during the loading and unloading steps is further illustrated in Fig. 13 for the present combinations of step time and environmental conditions. From Fig. 13a, it is apparent that the creep strain increased almost linearly after the first step, with a higher rate at room conditions compared to fuel cell conditions. Furthermore, the creep curves corresponding to identical environmental conditions resembled higher creep strain in the CCMs subjected to creep loading and unloading for a longer time step (60 min as compared to 30 min).

At room conditions, the instantaneous and time-dependent
recovery strains increased as the test progressed. On the other hand, at fuel cell conditions, the magnitude of instantaneous and time-dependent recovery strains remained essentially constant after the first step. The constant recovery at fuel cell conditions shows that only certain amounts of creep strain can be restored elastically in each step and the rest of the creep strain accumulated during loading periods will be stored plastically. A comparison between the amount of strain released during recovery and the creep strain shows that larger portions of creep strain were released at room conditions compared to the fuel cell conditions. This, as explained before, is related to the facile reconstruction of cross links among molecules at room conditions due to the lower internal energy of polymer. Permanent deformation, according to Fig. 13d, increased similarly to the creep strain at both fuel cell and room conditions. It can be concluded that the creep damage accumulated gradually during each step and the magnitude of strain are related to the duration of the applied stress.

In order to reveal the role of the creep step frequency (time of each step), the curves in Fig. 13 are reproduced in Fig. 14 with respect to the test duration. In this figure, only the first three steps of each 60 min test are compared to all six steps of each 30 min test, where the CCMs experienced similar loading and unloading time in total. The curves corresponding to similar environmental conditions are observed to match very well except for the time-dependent recovery where slightly higher recovery was observed in the 60 min tests. In summary, at constant time and creep stress, the total creep strain is independent of the number of creep cycles, i.e., the frequency of the creep steps. In contrast, the dominating factor that controls the creep deformation is the total time that the sample endured the creep stress.

4. Conclusions

The creep behavior of catalyst coated membranes was evaluated through conducting tensile creep – recovery experiments as a function of temperature, relative humidity, and stress. It was observed that coating the membrane with catalyst layers strengthens the membrane resistance against creep deformation. Furthermore, the creep strain of the CCM was significantly promoted when the aforementioned variables were increased. Statistical analysis showed that temperature plays a greater role than humidity in the context of creep strain. The effect of stress on the creep response of CCM became more significant beyond the yield stress. Below the yield point, cross links can be re-entangled as the stress releases due to the lower internal energy of the membrane. Beyond the yield point, however, a longer time is required to retrieve the intermolecular bonds, not only because of the high internal energy of the membrane, but also due to the failure of the catalyst layers to reinforce the membrane. The mechanical support provided by the catalyst layers was only effective up to the yield point, at which permanent catalyst layer cracks were generated perpendicularly to the principal direction of the stress. Accumulation of creep damage during the multi-step creep tests intended to simulate fuel cell conditions in the sub-yield regime was shown to be independent of the cycle frequency. In contrast, the total strain was primarily controlled by the duration of the creep stress, revealing significant accumulation of permanent deformation even below the yield point, which may pose a concern for fuel cell operation. Overall, the present analysis revealed the critical role of the catalyst layers in determining the creep deformation of the membrane under relevant fuel cell conditions and further provided
a benchmark to improve the fundamental understanding of the creep response of fuel cell materials, which is important in the context of durability.

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References

Appendix B.

Decay in Mechanical Properties of Catalyst Coated Membranes Subjected to Combined Chemical and Mechanical Membrane Degradation

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Decay in Mechanical Properties of Catalyst Coated Membranes Subjected to Combined Chemical and Mechanical Membrane Degradation

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Abstract

The mechanical stability of catalyst coated membranes (CCMs) is an important factor for the overall durability and lifetime of polymer electrolyte fuel cells. In this article, the evolution of the mechanical properties of degraded CCMs is comprehensively assessed. A combined chemical and mechanical accelerated stress test (AST) was applied to simulate field operation and rapidly generate partially degraded CCM samples for tensile and expansion experiments under both room and fuel cell conditions. The tensile results indicated significant reductions in ultimate tensile strength, toughness, and fracture strain as a function of AST cycles, accompanied by a mild increase in elastic modulus. The increased brittleness and reduced fracture toughness of the CCM, caused primarily by chemical membrane degradation, is expected to play an important role in the ultimate failure of the fuel cell. The expansion tests revealed a linear decay in hygrothermal expansion, similar in magnitude to the loss of mechanical strength. The decline in CCM sensitivity to environmental changes leads to non-uniform swelling and contraction that may exacerbate local degradation. Interestingly, the hygrothermal expansion in the late stages of degradation coincided with the fracture strain, which correlates to in situ development of fractures in chemically weakened membranes.

Keywords: Accelerated Stress Test, Degradation, Durability, Fuel Cell, Mechanical Properties, Membrane

1 Introduction

One of the key challenges facing the commercialization of polymer electrolyte fuel cell (PEFC) technology is the development of membrane electrode assemblies (MEAs) that can meet industry durability targets [1]. PEFCs are currently the principal fuel cell type for automotive applications because of their high performance at low temperature [1]. Perfluorosulfonic acid (PFSA) ionomer membranes (e.g., Nafion® from DuPont) are commonly used in PEFCs due to high proton conductivity and chemical stability inherited from the polytetrafluoroethylene (PTFE) base structure [1, 2]. However, in order to address industrial requirements and commercially compete with hybrid engines, the durability and lifetime of PFSA membranes must be enhanced.

Chemical and mechanical degradation are the primary reasons for membrane failure in fuel cells. Each of these degradation mechanisms can be intensified by the presence of the other [1]. Chemical degradation is caused by the attack of radi-
membranes with different thicknesses under idling condition for 1000 hours at constant current of 0.5 A. Results of various electrochemical tests on degraded samples showed that thin membranes lead to more rapid OCV loss due to higher gas crossover [9]. Trogadas et al. [11] demonstrated mitigation of chemical membrane degradation under OCV conditions using cerium oxide nanoparticles embedded in the membrane. Pearson et al. [12] further investigated this concept and showed dramatically reduced OCV decay and fluoride emission rate [12]. In our group, mitigation of membrane degradation by a platinum band in the membrane was investigated by Macaulley et al. [14]. According to electrochemical leak test and fluoride emission rate results, the platinum band reduced the chemical degradation significantly and enhanced the membrane durability [14].

Mechanical membrane degradation, on the other hand, originates from hygrothermal cycles during fuel cell operation. Variations in hygrothermal and relative humidity result in significant dimensional changes due to water sorption in PFSA membranes [15–17]. Inside a fuel cell, membrane expansion and contraction due to water sorption is constrained by other fuel cell components, which may exacerbate mechanical degradation. Hydration and dehydration accompanied by changes in temperature during start up and shut down and cyclic operating conditions induce mechanical stresses such as hygrothermal fatigue, creep, and tension in the membrane.

Recent efforts have been directed to reduce the membrane thickness in order to minimize ohmic losses and improve fuel cell performance. Therefore, membrane mechanical durability and integrity has become a critical challenge. Mechanical properties of PFSA membranes [18–22] and CCMs [23–25] were comprehensively investigated in the literature. Under different temperature and relative humidity conditions, Tang et al. [18] studied the tensile properties of Nafion® 112 PFSA membrane and expressed that yield stress and Young's modulus decreased as temperature and humidity increased. Tang et al. [19] investigated the degradation in mechanical properties of Nafion® 111 samples and determined the safety limit for fatigue strength to be 10% of the tensile strength. Using a dynamic mechanical analyzer (DMA), Bauer et al. [20] studied the effect of temperature and relative humidity on Nafion® 117 elastic modulus. They discovered that the maximum elastic modulus with respect to humidity is temperature dependent and therefore concluded that water mainly acts as a membrane plasticizer and stiffener at low and high temperatures, respectively [20].

Further research revealed that the mechanical properties of the membrane are altered by the presence of catalyst layers coated on the membrane. Through experiments and modeling, Huang et al. [23] studied the tensile properties of an MEA as a function of relative humidity and reported that reduction in ductility combined with constrained drying strain led to mechanical failure [23]. Mechanical durability of MEA samples were studied by Aindow et al. [24] via fatigue lifetime experiments to evaluate the remaining lifetime of as-received and degraded MEAs. The mechanical properties of CCMs and PFSA membranes were systematically compared in a previous study by our research group [25]. The membranes showed higher yield stress, yield strain, and elastic modulus when compared with the equivalent CCMs at all environmental conditions in the tested range. For both materials, the yield stress and elastic modulus decreased when temperature and/or relative humidity increased. Moreover, the swelling and contraction of the membrane with respect to relative humidity were nearly two times greater than for the CCM. It was thus concluded that the catalyst layers reinforce the membrane [25] and that the mechanical properties of the composite CCM should generally be measured and applied for in situ modeling, as recently demonstrated by Khorasany et al. [26].

Accelerated stress testing (AST) is a powerful method to benchmark the durability of fuel cells and determine mitigation approaches at a reasonable time and cost [3, 21, 27–29]. In these tests, certain stressors known to cause degradation are elevated beyond regular duty cycle levels [3]. These stressors may include operating temperature and humidity, cell voltage, and current density [30]. The US Department of Energy's hydrogen program established AST protocols for membrane degradation in PEFCs [27]. An open circuit voltage (OCV) AST protocol was developed to intensify the chemical degradation mechanisms, while an RH cycling AST protocol was designed to accelerate the mechanical degradation mechanisms [5]. In the context of mechanical membrane properties, Patil et al. [31] observed a significant reduction in the modulus and failure strain of Nafion® membranes subjected to chemical degradation under the OCV AST. Similar results were obtained by Huang et al. [23], who compared the failure modes of the chemical and mechanical AST protocols. Microstructural examination of the membrane fracture surface revealed that crack initiation sites formed close to the anode after mechanical AST while chemical AST led to a clean and brittle fracture surface [23]. In another study, Patil et al. [32] reported improvements in toughness and modulus accompanied with less creep deformation of Titania-reinforced Nafion® membranes compared to Nafion® 112 prior and after subjecting to OCV test. Furthermore, the reinforced membrane showed enhanced resistance against dimensional changes caused by contractile stresses due to variation in humidity [32]. In our group, combined chemical and mechanical degradation mechanisms and failure modes were recently investigated via introduction of Ballard Power Systems' cyclic open circuit voltage (COCV) AST protocol [33]. The joint action of chemical and mechanical stressors was found to intensify the membrane degradation and lead to more rapid failures than the independent mechanisms. Furthermore, results of fluoride emission, cross-sectional microscopy, and solid state 31P NMR analysis revealed a combination of side chain and main chain degradation in the polymer. The failure modes were consistent with those observed in field operation, and comprised of membrane thinning, pinholes, and microcracks. Room-temperature tensile traction tests indicated a significant loss in mechanical strength, which is expected to induce local membrane damage [33].
The objective of the present work is to systematically characterize the mechanical properties of catalyst coated membranes subjected to combined chemical and mechanical degradation, indicative of field operation where both stressors occur simultaneously. This article is a continuation of our previously published study by Lim et al. [33], in which the overall degradation mechanism and failure modes were determined. In contrast, the present work focuses exclusively on determining the evolution patterns of mechanical CCM properties during degradation. Tensile mechanical properties are measured under a wide range of precisely controlled temperature and humidity conditions as a function of membrane health state. The emphasis is on the properties obtained at fuel cell conditions (elevated temperature and humidity), which is a novel contribution of this article and expected to be more representative of \textit{in situ} operation and degradation. Additionally, the degradation induced changes in CCM thermal and humidity expansion properties are determined, which contributes a previously missing essential link between \textit{in situ} swelling and contraction due to hygrothermal variations and the \textit{ex situ} measured tensile properties under an externally applied force. Unique correlations are provided between the degradation induced evolution of expansion and tensile properties that can be used to inform future advances in MEA durability. The role of the obtained property changes in the joint chemical and mechanical membrane degradation mechanism is discussed. The present scope is limited to CCMs based on PFSA ionomer membranes and the results are expected to be generally valid for this category of materials.

2 Experimental

MEAs used for this study were fabricated by coating carbon paper based gas diffusion layer (GDL) substrates with micro-porous layers, followed by coating carbon supported platinum catalyst layers containing perfluorosulfonic acid ionomer to form gas diffusion electrodes (GDEs). Then, MEAs were prepared by hot pressing the anode and cathode GDEs with PFSA membranes. The obtained MEAs were subjected to combined chemical and mechanical degradation under Ballard Power Systems’ cyclic open circuit voltage (COCV) accelerated stress test (AST) protocol [33]. Research-scale stacks were assembled in a standard test hardware including five 45 cm² cells separated by graphite bipolar plates with quasi-uniform conditions over the active area. Co-flow parallel straight channels and high gas flow conditions were utilized, ensuring to minimize pressure drop between channels and avoid changes in reactant composition from stack inlet to outlet. Uniform compression between MEAs and bipolar plates was achieved using a pressurized bladder. A Ballard fuel cell test station equipped with computer controlled mass flow controllers (MFCs), back pressure control system, pre-heated water circulating coolant loop, electronic load, and two water-injected evaporator type humidifiers was used to apply accelerated stress tests on research-scale stacks. Prior to AST operation, the MEAs were conditioned by operating the cells at constant current for a few hours. Each AST cycle, as shown in Figure 1, included a high temperature/low RH steady state OCV phase to accelerate chemical degradation followed by a set of wet/dry humidity cycles in N₂ to provide mechanical degradation. In the wet period, the inlet gases were oversaturated by injecting water into the evaporator type humidifier in an amount larger than that obtaining the saturated vapor pressure. In the dry period, the inlet gases were kept in a relatively dry state by closing the water supply pumps of the humidifiers. Membrane failure was determined by measuring a threshold convective hydrogen leak rate via an electrochemical leak detection test. Further information regarding the COCV AST is provided elsewhere [33].

In order to investigate mechanical properties, partially degraded MEAs were removed from the AST stack after conditioning, two, five, eight, and ten AST cycles and were prepared for mechanical testing. Degraded MEAs were cut to rectangular shapes (25 × 2 mm) along the transverse direction to ensure consistency. The GDLs were removed from both sides of the MEAs and the remaining CCM specimens were stored between two microscope glass slides at room conditions until testing. A dynamic mechanical analyzer (TA Instruments Q800 DMA) equipped with an environmental chamber (TA Instruments DMA-RH Accessory) was used for both tensile and expansion experiments. Tensile test specimens were loaded with a 5:1 length to width aspect ratio to avoid edge stress concentration [25]. The remaining portion of the specimen (15 mm in length) was positioned under the tensile grips. A specimen mounted for tensile and expansion characterization in the DMA chamber is illustrated schematically in Figure 2.
The exact gauge length and width of each specimen were measured prior to test initiation by the DMA and optical microscope, respectively, while the average membrane thickness was measured by micrometer through subtracting the catalyst layer thicknesses from the CCM thickness.

Tensile tests were conducted at standardized room conditions (23°C and 50% RH) and fuel cell conditions (70°C and 90% RH) on beginning of life (BOL), BOL conditioned, and AST degraded CCMs. To ensure consistency and statistical relevance, four identical specimens were tested at each condition. The measurement variability presented in the form of error bars represents two standard deviations, which statistically covers about 95% of the data. Specimens were loaded and equilibrated to desired environmental conditions while a small preload tensile force (0.003 N) was applied to ensure tension. After equilibration, a fixed strain rate (0.01 min⁻¹) was applied to slowly stretch the specimens until the fracture point or until reaching the maximum DMA clamp travel length of 26 mm (160% elongation for 10 mm initial length). Elastic modulus, ultimate tensile strength (UTS), and final strain were calculated from the obtained stress-strain curves using the membrane thickness for normalization, assuming that the membrane was the main load bearing part of the CCM [33]. The elastic modulus was determined from the maximum slope of a 5th order polynomial fit to the initial section between 0 and 0.5% strain [25]. The UTS and final strain were calculated as the maximum stress and total strain (elastic and plastic), respectively.

Expansion tests similar to those reported by Goulet et al. [25] were performed on CCM specimens extracted after BOL conditioning, five (half-life), and ten (end of life) AST cycles. Specimens were equilibrated at the desired initial condition under a constant tensile force (0.003 N). Humidity expansion tests were conducted by measuring the length of the specimen after equilibration at fixed temperature (23°C and 70°C) while the humidity was raised from 25% to 50%, 50% to 70%, and 70% to 90% RH. Temperature expansion tests were performed in the same manner at fixed humidity settings (50% and 90% RH) while the temperature was increased from 20°C to 40°C, 40°C to 55°C, and 55°C to 70°C in discrete steps.

3 Results and Discussion

3.1 AST Results

Firstly, the overall results of the combined chemical and mechanical COCV AST experiments are described. The OCV decay behaviour and the results of the electrochemical leak detection test (ELDT) ΔV are plotted in Figure 3 as functions of the number of COCV AST cycles. The OCV decay rate increased gradually with respect to AST cycles and was observed to correlate well with the ELDT results which indicated a gradually rising rate of hydrogen leaks across the membrane due to the combined chemical and mechanical membrane degradation process. Major hydrogen leaks were detected after ten AST cycles (EOL) in accordance with the MEA failure criterion of the COCV AST [30]. The leaks were facilitated by the initiation of small membrane pinholes and cracks during the intermediate AST phase (third to eighth cycle) and accelerated significantly due to rapid growth of localized fractures in the final phase of the test (eighth cycle to EOL). Increased gas crossover through the degraded membrane was responsible for the concurrent OCV decay as a result of mixed electrode potentials and subsequently lead to local heat generation via the exothermal water formation reaction. Figure 4 shows the
variation in the average membrane thickness as a function of
the number of AST cycles, which indicates significant mem-
brane thinning due to chemical degradation caused by radical
attack on the polymer structure [33]. While the original mem-
brane thickness was retained during conditioning and the first
two AST cycles, uniform thinning proceeded from the third
cycle and onwards until the final failure of the MEA after the
tenth cycle, with 66% of the original thickness remaining. The
cumulative amount of anode, cathode, and total fluoride loss
gathered from effluent water as a function of AST cycles is pre-
sented in Figure 5. Fluoride loss, as a strong evidence of global
chemical membrane degradation during the OCV phase,
shows a relatively steady increase during the intermediate
phase of the experiment, in agreement with the rate of mem-
brane thinning observed in Figure 4. The fluoride loss detected
through the cathode side was somewhat higher than at the
anode for the entire duration of the experiment.

3.3 Tensile Properties

The elastic modulus of the membrane (in the CCM) was
calculated from the slope of the stress-strain curves in the
initial, elastic region and presented in Figure 7 as a function of
COCV AST cycles. In principle, the elastic modulus defines
the resistance of the material against elastic deformation. Due to
the non-linear viscoelastic behaviour of the membrane, the
maximum slope of the viscoelastic region in the stress-strain
curve was selected as the elastic modulus. The average elastic
modulus was found to increase slightly from BOL to EOL at
both room and fuel cell conditions. These results were
obtained based on the actual thickness of the membrane after
each corresponding AST cycle and therefore takes membrane
thinning into account in order to extract the true properties of
the remaining material. On the contrary, should the BOL
membrane thickness be used and assumed to be constant, the
elastic modulus would decrease from BOL to EOL. Previous
work has reported a reduction in elastic modulus due to
chemical membrane degradation [31], although the calculation
method was not disclosed. The increasing behaviour of the
elastic modulus determined here indicates that the membrane
became progressively stiffer during exposure to combined
chemical and mechanical membrane degradation.

The total elongation of the CCM at the termination of the
tensile test is displayed in Figure 8 as a function of AST cycles.
As mentioned previously, the maximum measurable strain is
160% due to the DMA travel length limitation. Therefore, the
final strain obtained for both pristine materials (BOL and
BOL-conditioned CCMs) reached 160% due to the absence of
fracture. However, the final strain of the degraded CCMs
decreased dramatically from ductile behaviour with high elon-
gation values to brittle behaviour with almost no elongation at
final fracture. At fuel cell conditions, the partially degraded
CCM extracted after two AST cycles exhibited relatively high variability, as some specimens fractured at 91–130% elongation while others reached the DMA displacement limit without fracture. This pattern suggests that the first few AST cycles resulted primarily in localized degradation with potential fracture sites located far apart and still requiring substantial fracture energy to fail. However, the half-life CCM extracted after five cycles appeared to have lost almost all elongation capacity before failure, exhibiting less than 10% final strain. In addition, the half-life CCM had much more consistent failures than the previously extracted CCMs, as demonstrated by the reduced variability, suggesting that the degradation process had proceeded to become more global in nature with more closely spaced fracture sites. The continued degradation process in the second half of the AST experiment led to further reductions in final strain, down to very small elongation values of less than 2% at EOL. The high hydrogen leak rates and severe damage of these CCMs suggest that pre-existing membrane holes and cracks contributed to rapid mechanical failures in the tensile test.

Fig. 6 Stress-strain curves measured at (a) room conditions and (b) fuel cell conditions for partially degraded CCM specimens extracted after different numbers of COCV AST cycles (as indicated). For graphical clarity, the origin was shifted horizontally by 5% for each curve, although all measurements were started at zero strain.
The ultimate tensile strength (UTS) of the CCMs is depicted in Figure 9 as a function of AST cycles. The UTS was found to decrease in a linear pattern from BOL to EOL, where the CCM had lost 49% and 69% of its initial stress tolerance under room and fuel cell conditions, respectively. Interestingly, the decreasing UTS trend follows qualitatively the trends observed previously for membrane thinning and fluoride release. This suggests that the decay in UTS was caused by global chemical degradation. Reductions in polymer molecular weight and main chain length due to chemical degradation are expected to be the main source of UTS decay, in agreement with previous literature [31]. However, the overall impact of the molecular changes is likely exacerbated by the application of mechanical stress, acting to disentangle the ionomer bundles and disintegrate the ionic clusters, either in the form of ex situ stress applied by the tensile experiment or in the form of in situ stress applied by the intermittent wet/dry cycles in the COCV AST. Indeed, the small UTS resulting in tensile failure of heavily degraded CCMs would likely be equivalent to the stress generated in situ during wet/dry cycling, where actual failures were evident. In addition, the variability observed in the UTS data was found to increase gradually with degradation, in particular under fuel cell conditions, suggesting that pre-existing, randomly located membrane holes and cracks may lead to lower local stress tolerance and earlier tensile fractures. This effect would also contribute to the in situ growth of holes and cracks during wet/dry cycling and more rapid failures during combined chemical and mechanical degradation.
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3.4 Expansion Properties

While tensile properties are convenient to measure ex situ and useful in the context of membrane degradation, the externally applied mechanical stress is fundamentally different to the stresses generated in situ due to variations in hygrothermal conditions. Understanding the CCM in situ mechanical behavior is crucial due to the time-dependent response under variations in hygrothermal conditions, inherited from the elastic-viscoplastic characteristics of PFSA ionomer membranes. Furthermore, the effect of catalyst layers coated on the membrane on the swelling and contraction of membrane was evaluated by Goulet et al. [25] and confirmed the significant reinforcing role of catalyst layers limiting the membrane dimensional changes. It was previously observed that the time-dependent response of a PFSA membrane may be altered by chemical degradation, as shown by Patil et al. [31, 32] via tensile creep experiments. In order to capture the correct trends for the in situ fuel cell environment, complementary hygrothermal expansion tests were conducted to assess the evolution of the mechanical behavior of the degraded CCMs in response to changes in temperature and humidity. The expansion tests were performed under a constant preload force by applying a step change in either temperature or relative humidity (RH) and measuring the resulting strain upon specimen equilibration. The obtained thermal expansion results at constant RH of 50% and 90% are provided in Figures 10 and 11, respectively. The data points represent thermal expansion in specimen length from 20°C to the desired temperature (as indicated). A linear trend was found for thermal expansion in all cases. Thermal elongation at fixed RH is likely due to a combination of thermal expansion and increased water uptake, as the moisture content of the air increases with temperature despite the constant RH. Depending on membrane preparation conditions, Hinatsu et al. [15] observed linear and second order curves for water uptake with respect to variation in temperature in Nafion® 117 and 125 samples, in reasonable qualitative agreement with the present results. The highest thermal expansion was obtained with the pristine CCM (at BOL), both in terms of total expansion and expansion rate, as shown in Table 1. The thermal expansion of the CCM was significantly reduced at the half-life degradation state and further reduced at the final EOL state. The overall decay in thermal expansion from BOL to EOL was approximately 80% at both humidity conditions (from 7.9% to 1.5% at 50% RH and from 6.4% to 1.4% at 90% RH). Similarly, Figures 12 and 13 represent the corresponding hygral expansion results at constant temperatures of 23°C and 70°C, respectively. In this case, the response of the CCM to changes in humidity was less significant than for temperature changes and was only marginally reduced by the AST degradation (25–30% overall decay).

<table>
<thead>
<tr>
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<th>50% RH</th>
<th>90% RH</th>
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<tr>
<td>BOL</td>
<td>0.00157</td>
<td>0.00117</td>
</tr>
<tr>
<td>Half-life</td>
<td>0.00108</td>
<td>0.00042</td>
</tr>
<tr>
<td>EOL</td>
<td>0.00030</td>
<td>0.00031</td>
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Fig. 10 CCM thermal expansion at 50% RH for BOL, half-life (five AST cycles), and EOL (ten AST cycles) degradation states. Expansion is shown for heating from 20°C to 40°C, 55°C, and 70°C.

Fig. 11 CCM thermal expansion at 90% RH for BOL, half-life (five AST cycles), and EOL (ten AST cycles) degradation states. Expansion is shown for heating from 20°C to 40°C, 55°C, and 70°C.

Fig. 12 CCM hygral expansion at 23°C for BOL, half-life (five AST cycles), and EOL (ten AST cycles) degradation states. Expansion is shown for humidification from 25% RH to 50%, 70%, and 90% RH.
Correlations between the trends in CCM expansion properties and tensile properties may provide valuable linkages between the ex situ measured mechanical behaviour and the combined chemical and mechanical membrane degradation process occurring in situ. The overall decay in hygrothermal expansion properties appears to correlate reasonably well with the decay in membrane thickness, remaining fluoride content, and ultimate tensile strength. Additionally, the loss of hygrothermal expansion is analogous to the loss of ductility observed in the stress-strain curves after only a few AST cycles. Although loss in hygrothermal expansion capabilities can be favourable in order to decrease the mechanical stresses occurring in situ, localized degradation may lead to non-uniform dimensional changes that can accelerate crack initiation and propagation in these areas. The main implication of this loss, as mentioned previously, is the reduced fracture toughness, which makes the CCM more susceptible to crack formation. More importantly, while the net hygrothermal expansion at BOL could easily be accommodated within the elastic regime without major implications, the ~2% hygrothermal expansion observed at EOL is within the same range of strain as the final tensile strain, which indicates that the membrane is sufficiently weakened for ruptures to form as a direct result of the hygrothermal variations during wet/dry cycling. This finding is expected to play a key role in the development of membrane damage and ultimate failure due to combined chemical and mechanical membrane degradation.

4 Conclusions

The decay in mechanical properties of catalyst coated PFSA membranes was investigated in the context of combined chemical and mechanical membrane degradation representative of regular duty cycle fuel cell operation. Ballard’s COCV AST protocol, which deploys elevated chemical and mechanical stressors, was utilized to generate partially degraded CCM materials for analysis. Tensile test results demonstrated a mild increase in elastic modulus accompanied by dramatic reductions in final strain and ultimate tensile strength during the degradation process, which indicates a gradual membrane transformation from a soft and ductile material to a stiff and brittle object with local variations in properties. The rapid decay in fracture toughness observed during the early stages of degradation was likely caused by locally elevated chemical degradation leading to potential sites for fracture initiation. Moreover, the brittleness caused by chemical degradation reduced the membrane resistance against crack propagation due to mechanical degradation via wet/dry cycles. Expansion test results revealed linear reductions in CCM hygrothermal expansion characteristics during the membrane degradation process. A critical linkage between hygrothermal expansion and fracture strain was identified in the late stages of degradation. In this regime, given the underlying chemical degradation and weakened ionomer structure, the regular hygrothermal cycles occurring in situ are deemed to be sufficient to generate fractures and to proliferate the overall membrane damage towards ultimate failure. Overall, the decay in mechanical properties determined in this work forms the core for the interaction between chemical and mechanical membrane degradation during fuel cell operation. Prevention of such decay is essential for development of suitable membrane/CCM stabilization strategies toward enhanced fuel cell durability and lifetime.

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References

Appendix C.

Microstructural and Mechanical Characterization of Catalyst Coated Membranes Subjected to In-Situ Hygrothermal Fatigue
Catalyst coated membranes (CCMs) in polymer electrolyte fuel cells are subjected to mechanical stresses in the form of fatigue and creep that deteriorate the durability and lifetime of the cells. The present article aims to determine the effect of in-situ hygrothermal fatigue on the microstructure and mechanical properties of the CCM. The fatigue process is systematically explored by the application of two custom-developed accelerated mechanical stress test (AMST) experiments with periodic extraction of partially degraded CCMs. Cross sectional and top surface scanning electron microscope (SEM) images of the end-of-test CCMs reveal the formation of mechanically induced cracks and delamination due to cyclic tensile and compressive fatigue stress. Tensile and expansion tests are conducted at different stages of degradation to evaluate the evolution in the mechanical and hygrothermal properties of the CCM. The tensile test results indicate gradual reductions in final strain, ultimate tensile strength, and fracture toughness with increasing number of fatigue cycles. The decay in tensile properties is attributed to the microstructural damage and micro-cracks formed during the AMST. Moreover, it is shown that the hygrothermal expansion of the CCM is more sensitive to conditioning than mechanical degradation.

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Polymer electrolyte fuel cells (PEFCs) are a prime candidate to replace gasoline and diesel internal combustion engines for transportation applications due to their environmental benefits combined with rapid start-up, high efficiency, and high power density at relatively low operating temperature. The commercialization of PEFCs is dependent on the development of membrane electrode assemblies (MEA) capable of meeting the automotive industry durability targets. However, the current PEFC technology is facing insufficient longevity, mainly because of the deterioration of the proton exchange membrane (PEM) component. Hence, an essential step to accomplish the commercialization requirements for PEFCs is to enhance the membrane durability and lifetime. Among various types of membranes utilized in PEFCs, perfluorosulfonic acid (PFSA) ionomer membranes (e.g., Nafion from DuPont) are the most widely used materials due to the superior chemical stability attributed to the chemically inert C-F bonds of the polytetrafluoroethylene (PTFE) base structure.

Chemical and mechanical degradation mechanisms are recognized as the principal root causes for lifetime limiting failures of PFSA ionomer membranes in fuel cells. Understanding of the degradation mechanisms, their interactions, and the corresponding failure modes could provide valuable insight toward decelerating the rate of the membrane degradation and thereby extend the lifetime. Chemical degradation is caused by the attack of radical species in the form of hydroxyl (OH) and hydroperoxyl (OOH) radicals generated through decomposition of hydrogen peroxide (H₂O₂) by metal contaminants. Hydroxy radicals also form as a by-product of the electrochemical reaction between H₂ and O₂ on the surface of Pt due to gas crossover. Mechanical degradation, on the other hand, is originated by the hygrothermal stresses induced by fluctuations in the relative humidity and temperature. Membrane swelling and contraction due to water sorption coupled with the constrained geometry of the membrane in between the catalyst layers, gas diffusion layers, and bipolar plates in the PEFC introduce mechanical stresses inside the membrane. During fuel cell operation, poor humidification and dry conditions result in the shrinkage and in-plane tension, while wet conditions lead to swelling and in-plane compression in the membrane.
In-situ fatigue testing.— The membrane electrode assemblies (MEAs) used in this work were fabricated using a previously reported procedure by coating catalyst layers containing carbon supported platinum and perfluorosulfonic acid (PFSA) ionomer on micro-porous layers covered gas diffusion layer (GDL) substrates to form gas diffusion electrodes (GDEs). Anode and cathode GDEs were hot pressed with a Nafion NR-211 non-reinforced PFSA ionomer membrane to obtain an MEA. Research-scale stacks consisting of five cells with 45 cm² active area were assembled in a standard test hardware. Minimum pressure drop and near-uniform conditions were ensured from inlet to outlet utilizing co-flow parallel straight channels. Prior to testing, the stack was conditioned for 20 hours in humidified nitrogen gas at 100% RH to ensure fully humidified cells.

In-situ fatigue degradation was induced using a custom-developed accelerated mechanical stress test (AMST) procedure based on the US Department of Energy accelerated stress test (AST) for mechanical membrane degradation. The AMST is designed to generate membrane fatigue by application of rapid, deep wet/dry cycles at relatively high temperature and ambient pressure. Two distinct AMST experiments were devised under slightly different testing conditions, as detailed in Table I and further illustrated in Figure 1. The first experiment (AMST-1) applied successive cycles of 2 min wet (90% RH) and 2 min dry (0% RH) states at 80 °C (Figure 1a), while the second experiment (AMST-2) was carried out using 1 min wet (100% RH) and 3 min dry (0% RH) states at 95 °C (Figure 1b). The latter experiment was subjected to harsher fatigue conditions due to higher temperature and larger wet/dry (stress) amplitude. The original AST protocol utilized air as the fuel/oxidant gas while in the present AMST, air was replaced by nitrogen in order to diminish any occurrence of chemical degradation. Besides applying nitrogen as the fuel/oxidant gas, electrochemical diagnostics such as in-situ leak tests, polarization and impedance measurements were avoided in order to ensure complete elimination of chemical stress and exposure throughout the AMST operation. During the wet phase, water was injected into the humidifier to preserve oversaturated inlet gas while a relatively dry state was obtained by simply terminating the flow of water. Lower gas flow rates were applied in AMST-2 due to the available constraints on the test station at elevated temperature. The stack temperature and outlet gas temperature were controlled according to the target values specified in Table I, while the inlet gas temperature was monitored to ensure that no excessively heated gas was fed into the stack. The inlet gas temperature was somewhat higher in the wet phase compared to the dry phases due to the concurrently high temperature and humidity. The wet/dry fatigue cycling was pursued until failure (crossover > 10 sccm per cell) or 20,000 cycles, whichever occurred first, while one cell was being extracted and replaced by a new cell every 4,000 cycles in order to find a novel, insightful bridge between the in-situ swelling and contraction due to hygrothermal swings and the ex-situ measured tensile properties.

The objective of the present work is to comprehensively investigate the microstructural and mechanical properties of in-situ fatigue degraded catalyst coated membranes. Contrary to the previous study on creep-recovery under mild humidity steps, the present work is focused on a custom-developed, aggressive fatigue based mechanical AST procedure that applies rapid cycling between fully wet and fully dry membrane states. In addition, the effect of accelerated mechanical stress testing (AMST) factors including wet/dry cycle frequency and operating temperature are thoroughly evaluated. Another novel element of the proposed in-situ AMST is to completely eliminate influences from chemical exposure and degradation by exclusive use of inert gas and by avoiding electrochemical diagnostics during the experiments. The obtained tensile and time-dependent hygrothermal properties are compared with the previously reported mechanical properties of CCMs subjected to combined chemical and mechanical degradation in order to elucidate the role of pure mechanical fatigue stress on the in-situ degradation of PFSA membranes in PEFCs.

Experimental
to obtain partially degraded MEAs for ex-situ characterization. The presence of through plane leaks across the membrane was evaluated qualitatively by performing a bubble jig test on the entire stack every 4,000 cycles by submerging each individual cell in water while air at 2 psig and atmospheric pressure was applied to each side of the cell. The corresponding crossover rate was calculated from the volume of air displaced at a certain time.

Ex-situ characterization.— Upon completion of the in-situ fatigue experiments, the microstructural and mechanical properties of the partially degraded MEAs were evaluated ex-situ. The locations of membrane leaks were determined on the end-of-test (fully degraded) MEAs using an FLIR T620 IR camera. At the IR benchmarked locations, surface analysis microscopy was conducted with a JEOL JSM-6360 scanning electron microscope (SEM) with integrated energy dispersive spectroscopy (EDS) analyzer. CCM samples for SEM surface analysis were cut from the MEA and the GDLs were removed from the sides of the samples. In addition to the surface analysis, SEM cross sectional backscattered electron (BSE) imaging at 20 kV was performed at the inlet, middle, and outlet positions of the end-of-test MEAs to evaluate the type and distribution of mechanical damage formed during the wet/dry cycles and to measure the level of the membrane thinning during the AMST. Cross sectional SEM samples were obtained by casting MEAs in epoxy pucks, followed by polishing with 120–1200 grit silicon carbide paper using a Struers TegraPol-11 polisher and carbon coating using an Edwards Scancoat Six Sputter Coater. The membrane thickness of the end-of-test MEAs was also measured using cross sectional SEM by taking the average of five measurements at different locations of each MEA. Finally, the platinum concentration in the membrane was measured by EDS elemental analysis.

Table I. Custom-developed accelerated mechanical stress test (AMST) procedures utilized in this work in order to generate in-situ membrane fatigue.

<table>
<thead>
<tr>
<th>Test</th>
<th>Crossover (&gt;10 sccm) or 20,000 cycles</th>
<th>Test II</th>
<th>Crossover (&gt;10 sccm) or 20,000 cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Duration</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td></td>
<td>95 °C</td>
<td></td>
</tr>
<tr>
<td>Wet/dry cycles</td>
<td>2 min dry state (∼0% RH) + 2 min wet state (∼90% RH)</td>
<td>3 min dry state (∼0% RH) + 1 min wet state (∼100% RH)</td>
<td></td>
</tr>
<tr>
<td>Fuel/Oxidant</td>
<td>N₂/N₂ on both sides</td>
<td>N₂/N₂ on both sides</td>
<td></td>
</tr>
<tr>
<td>Pressure</td>
<td>Ambient</td>
<td>Ambient</td>
<td></td>
</tr>
<tr>
<td>Flow rate</td>
<td>9.0 slpm</td>
<td>3.5 slpm</td>
<td></td>
</tr>
</tbody>
</table>

Figure 1. Schematic of the wet/dry fatigue cycles applied in the (a) AMST-1 and (b) AMST-2 experiments.
0% to 30%, 30% to 50%, 50% to 70%, and 70% to 90%. Similar to the thermal expansion, the time-dependent hygral elongations were captured by keeping the desired conditions constant for one hour.

Results and Discussion

The custom-designed accelerated mechanical stress tests (AMSTs) were applied on the research scale fuel cell stacks in order to investigate the in-situ hygrothermal membrane fatigue process and generate partially degraded catalyst coated membranes (CCMs) for subsequent ex-situ characterization of the microstructural and mechanical properties. The obtained damage and leak distribution of the end-of-test CCMs were determined with IR imaging while the cross sectional and top surface microstructure was analyzed using SEM. Furthermore, CCM tensile and expansion properties were measured at different levels of fatigue degradation from BOL to 20,000 fatigue cycles. From the obtained results, tensile stress-strain curves, elastic modulus, ultimate tensile strength, final strain, and hygrothermal expansion properties are derived and discussed.

**Accelerated mechanical stress tests - comparison.**— Two distinct AMSTs were examined in this work, as previously summarized in Table I and Figure 1. The first experiment (AMST-1) was terminated at 20,000 cycles, after which an MEA leak rate measurement of 14 sccm per cell was obtained, indicative of membrane failure. IR imaging of the AMST-1 end-of-test MEA further revealed membrane transfer leaks at the inlet region, as shown in Figure 2a. The inlet region of the cells was exposed to slightly higher gas temperatures compared to the middle and outlet regions, which resulted in more severe degradation at the inlet. This area of the MEA was therefore preserved for subsequent top surface SEM analysis. The analysis of the ohmic resistance of the cells indicated that although the inlet gas RH was 0% during the dry phase, the membranes did not reach a stable, fully dry condition within the 2 min hold time. The ohmic resistance of the stack was therefore scaled by exposing the cells to various fixed RH levels for one hour duration, thus equilibrating the ionomer wa-

<table>
<thead>
<tr>
<th>Relative Humidity (%)</th>
<th>Ohmic Resistance (ohm.cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.1111</td>
</tr>
<tr>
<td>10</td>
<td>0.0111</td>
</tr>
<tr>
<td>20</td>
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<tr>
<td>40</td>
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</tr>
<tr>
<td>60</td>
<td>0.00064</td>
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<tr>
<td>80</td>
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<td>90</td>
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</tr>
<tr>
<td>100</td>
<td>0.00033</td>
</tr>
<tr>
<td>120</td>
<td>0.00024</td>
</tr>
</tbody>
</table>

Table II. Ohmic resistance of the stack upon equilibration at fixed relative humidity levels.

**Microstructural analysis.**— The cross sectional and top surface microstructure of the end-of-test degraded CCMs (20,000 cycles) was analyzed using SEM. Cross sectional SEM was also utilized to track the membrane thickness during the tests. Figure 3 represents the average thickness of the AMST degraded membranes at the end-of-test normalized by the original membrane thickness at BOL. The results are also compared to the end-of-life membrane thickness after combined chemical and mechanical degradation via the cyclic open circuit voltage (COCV) AST previously reported by Lim et al. According to Figure 3, the average membrane thickness observed in the two AMSTs was ~4–5% and ~9%, respectively, while 48% thinning was measured for the COCV AST, notably due to severe chemical degradation which was completely eliminated in the present AMSTs. The small degree of membrane thinning detected in the AMSTs may have been

![Figure 2](image-url). IR images of AMST degraded MEAs after 20,000 cycles (end-of-test) in (a) AMST-1 and (b) AMST-2. The brightness is proportional to the local temperature; hence, bright regions indicate leak locations.
induced by in-plane visco-plastic deformation and residual stresses considering the dominant fatigue stress in this direction.\textsuperscript{46} In addition, the more significant thickness reduction observed for AMST-2 compared to AMST-1 could be correlated to the higher stress amplitude and temperature of the second experiment.

Cross sectional SEM images resembled the initiation and propagation of mechanical damage including cracks and delamination in the membranes and catalyst layers of the AMST degraded MEAs at the end-of-test, as depicted and compared with a BOL MEA image in Figure 4. The overall membrane damage was dominated by cracks. Major cracks generally extended from the membrane into the adjacent catalyst layers, indicating significant interaction between these two components, although the exact initiation sites cannot be verified by these images. Membrane leaks and failures were likely attributed to occasional, large cracks spanning the entire membrane thickness, such as the main crack identified in Figure 4d. Careful analysis of Figures 4c and 4d also revealed the formation of small micro-cracks inside the membrane, which is likely a result of material fatigue. Local delamination of membrane and catalyst layers, as observed here, is attributed to the fatigue stress combined with the differences in hygral expansion and contraction of the membrane and catalyst layers. Due to the loss of CCM integrity in these regions, it is likely that the local membrane stresses are exacerbated in the absence of the reinforcing effect otherwise known to occur.\textsuperscript{14,16} Qualitatively, larger and more frequent microstructural damage features were detected in the cross section of AMST-2 when compared to AMST-1, indicating that the AMST-2 MEAs were subjected to harsher conditions for mechanical membrane degradation.

Due to catalyst layer degradation under dynamic duty cycles, a Pt band is normally formed inside the membrane, which has been shown to enhance the membrane stability and lifetime.\textsuperscript{33,34} The presence of Pt inside the AMST degraded membranes was evaluated and compared to the ones degraded by the COCV AST. The results showed no distinct formation of Pt particles in either of the AMST-1 or AMST-2 end-of-test membranes (\textasciitilde0 ppm) while an average of \textasciitilde8,000 ppm Pt was detected in the end of life (EOL) COCV AST membrane,\textsuperscript{31} confirming that the Pt band is originated through chemical routes which were intentionally blocked in the present AMST experiments.

Complementary top surface microstructural analysis was performed on the severely damaged regions initially identified by IR imaging, located at the inlet of the end-of-test degraded MEAs. The SEM images in Figure 5 exhibit the BOL CCM surface as a reference and typical microstructural imperfections captured on the degraded CCM surface, including cracks and detachments of the catalyst layers as well as major cracks in the membrane. As represented in Figure 5,
cathode cracks and detachments are coupled with the cracks extended inside the membrane. This confirms the interaction between damage in the catalyst layers and membranes induced by the hygrothermal fatigue stress in the membrane. Cracks that span the entire membrane thickness are observed to extend substantially in the in-plane direction in the membrane. Similar to the cross-sectional findings, more severe damage was observed in AMST-2 compared to AMST-1 due to the higher fatigue amplitude and temperature. High operating temperature leads to lower mechanical strength of the membrane and thereby increases the impact of the fatigue cycles. Additionally, a longer dry phase induces larger membrane contraction and more aggressive tensile stresses in the membrane.

Tensile properties.— Tensile tests were conducted at 70°C and 90% RH on BOL and AMST degraded CCM samples at different stages of degradation. A graphical summary of the selected stress-strain curves is presented in Figure 6. Tensile properties of BOL CCMs were previously measured and indicated ductile behavior under a wide range of environmental conditions. After 4,000 cycles of AMST operation, the partially degraded CCMs still exhibited excellent ductile behavior similar to that of the BOL CCMs, reaching full elongation to the DMA maximum travel length without fracture. However, from 4,000 to 20,000 cycles, elongation and toughness (defined by the area below the stress-strain curve) diminished continuously and the CCM behavior gradually transformed from ductile to brittle identically in AMST-1 and AMST-2. Furthermore, the maximum tolerated stress at fracture was gradually reduced during the AMST operation. The decay in stress tolerance accompanied by the rapid drop in elongation and toughness indicates the ongoing formation and propagation of micro-cracks from BOL to 20,000 cycles due to the fatigue process. The decay in mechanical strength and ductility was relatively smooth when compared to the dramatic decay reported for the COCV AST. In the case of COCV AST, the rapid decay in mechanical strength was attributed to the highly aggressive underlying chemical degradation that disintegrated the ionomer molecular structure. Analogously, deterioration in mechanical properties (primarily elongation) was also observed under purely chemical degradation at constant RH. In summary, it is shown here that purely mechanical membrane degradation can independently reduce the mechanical strength of the CCM and ultimately generate membrane failure; however, chemical degradation can exacerbate the decay in mechanical strength and lead to rapid failure when subjected to mechanical stress.

The detailed mechanical properties (final strain, UTS, elastic modulus) of the AMST degraded CCMs obtained from tensile testing are displayed and compared in Figure 7 as a function of the number of AMST cycles. The total elongation (elastic and plastic) of the CCM is depicted in Figure 7a. As the BOL CCMs never reached the fracture point within the DMA travel length (330% elongation), the final strain was selected to represent CCM elongation instead of fracture strain. The final strain was reduced significantly from ~300% at 4,000 cycles to 20–55% at 20,000 cycles in both AMST experiments. The rate of decay in elongation was relatively high up to 12,000 cycles and then slowed down.
then slowed down until 20,000 cycles, suggesting that the initiation of micro-cracks inside the membrane in the early stages of the AMST had stronger influence on the ductility than the propagation of cracks in the later, more mature stages of degradation. In comparison, the EOL COCV AST resembled much lower final strain than the end-of-test AMST indicating a more advanced state of degradation obtained by the combined chemical and mechanical degradation mechanism. In addition, the relatively high variability in the final strain at each level of degradation indicates the highly localized nature of the mechanical degradation mechanism which is in agreement with the microstructural images represented in Figures 4 and 5. The high variability in the properties of the mechanically degraded CCMs is in contrast to the COCV AST degradated CCMs where more homogeneous decay in mechanical properties and microstructure was obtained due to chemical degradation.

The ultimate tensile strength (UTS) of the CCM as a function of AMST cycles is depicted in Figure 7b. It was found that UTS decreased gradually from BOL to 20,000 cycles with a decelerating decay rate where the changes were less pronounced beyond 12,000 cycles. Formation of micro-cracks in the early cycles produces preferred fracture nucleation sites. However, additional crack initiation sites formed at the later stages of the experiment would not be detected in the UTS trend due to the presence of more severe, pre-existing micro-cracks that are responsible for tensile fracture of the specimen. Although the present UTS decay trend is qualitatively similar to that of the previous reported COCV AST experiment, the mechanisms are entirely different, considering that the UTS decay during COCV AST was attributed to molecular changes caused by chemical degradation.

The elastic modulus of the CCM, representing the resistance to elastic deformation under applied stress, was calculated from the initial slope of the stress-strain curve and exhibited in Figure 7c as a function of the number of AMST cycles. No remarkable changes were observed in the elastic modulus during mechanical degradation, although high variability was present in the data. The nearly constant elastic modulus indicates that the deterioration in the ionomer molecular structure was insignificant during the fatigue process although localized changes may have occurred due to the presence of fatigue induced micro-cracks of various sizes.

Expansion properties.— The aforementioned results of tensile experiments provide useful insight into the ex-situ mechanical properties of the CCM and the state of degradation. However, under in-situ conditions, the MEA is continuously subjected to dynamic hygrothermal oscillations inducing essentially different types of stress in the CCM. A tensile test by its nature is incapable of capturing the time-dependent response of the membrane to hygrothermal changes when subjected to isolated chemical and combined chemical and mechanical degradation. Hence, hygral and thermal expansion experiments were performed.
utilized in order to evaluate the mechanical response of the degraded CCMs to the in-situ hygrothermal swings. Figure 8 exhibits the obtained time-dependent hygrothermal responses of the CCM to the stepwise rise in RH and temperature. Each data point in Figures 8a,8b resembles the average hygral elongation of the CCM at the desired RH with respect to the initial state at 0% RH in AMST-1 and AMST-2, respectively, while the temperature was fixed at 70°C. As anticipated, the in-plane expansion due to the membrane water uptake increased gradually with RH. It is noteworthy that the hygral expansion property of the CCM was substantially reduced during the MEA conditioning, after which the hygral expansion dropped to 65% of the BOL value at 90% RH. In contrast, from the conditioned state through to the end-of-test after 20,000 AMST cycles, the hygral expansion property remained unchanged independent of the degradation level. This finding is in stark contrast to the significant decay in hygral expansion during combined chemical and mechanical degradation which was mainly attributed to chemically induced changes in the ionomer.

Figures 8c,8d exhibit the average thermal expansion of the CCM from 20°C to the desired temperature at constant 90% RH in AMST-1 and AMST-2, respectively. The gradual expansion during the temperature rise was likely due to the increase in membrane water uptake capacity and molecular thermal expansion. In agreement with the hygral expansion results, the thermal expansion of the CCM was mainly affected by conditioning, due to which the thermal expansion property was reduced to 58% of the BOL value at 80°C. No remarkable changes in thermal expansion were observed during the hygrothermal fatigue degradation, which is again consistent with the hygral expansion results. The relatively fixed expansion properties during the mechanical degradation can be correlated to the obtained elastic modulus from the tensile tests. Although expansion experiments may induce both elastic and plastic strains, the hygrothermal expansion and elastic modulus resemble the ionomer molecular resistance and bundle strength against the dimensional changes. It is in agreement with the COCV AST results which led to reduction in hygrothermal expansion coefficients and increase in elastic modulus with respect to the COCV AST cycles, both indicating the elevation in membrane stiffness and resistance to elongation.

Conclusions

The evolution of microstructure and mechanical properties of catalyst coated PFSA membranes subjected to isolated mechanical fatigue degradation was investigated. Elevated hygrothermal stresses were applied to the membrane electrode assembly following two custom-developed accelerated mechanical stress test (AMST) procedures to create partially fatigue degraded CCMs for further mechanical and microstructural analyses. Cross sectional and top surface SEM images of the end-of-test CCMs revealed formation of mechanically induced damage including membrane and catalyst layer cracks as well as delamination as a result of cyclic tensile and compressive fatigue stress. The damage generated by the second AMST experiment was shown to be more severe than the first experiment due to the higher temperature and larger fatigue stress amplitude although the overall MEA leak rates were on the same order of magnitude, close to the membrane failure criterion. Tensile testing demonstrated that membrane fatigue can reduce the mechanical strength of the CCM in the absence of chemical stressors. In this manner, ultimate tensile strength, final strain, and fracture toughness were reduced significantly with similar trends in both experiments indicating the transformation in material behavior from ductile to relatively brittle due to the initiation
and propagation of micro-cracks. In contrast, the elastic modulus and hygral and thermal expansion properties were relatively constant during the fatigue process, except for a moderate reduction in expansion during MEA conditioning. This indicates that the mechanical fatigue does not alter the elastic behavior of the CCM and its response to hygrothermal fluctuations during dynamic fuel cell operation. Overall, the observed decay in mechanical strength and its linkage to the microstructural damage reveals the crucial role of mechanical fatigue degradation in the initiation and propagation of membrane failures. Development of mitigation strategies to limit the in-situ mechanical stresses is therefore essential for accomplishing the fuel cell durability and lifetime goals. Further analysis on the nature of crack initiation and subsequent crack propagation would also be useful in order to enhance the fundamental understanding of the mechanical membrane degradation phenomena.

Acknowledgments

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References

Appendix D.

*Ex-situ* Tensile Fatigue-Creep Testing: A Powerful Tool to Simulate *In-situ* Mechanical Degradation in Fuel Cells
Ex-situ Tensile Fatigue-Creep Testing: A Powerful Tool to Simulate In-situ Mechanical Degradation in Fuel Cells

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Abstract

An ex-situ tensile fatigue and creep based accelerated stress test (TFC-AST) is proposed to evaluate the mechanical stability of catalyst coated membranes (CCMs) used in fuel cells. The fatigue-creep action of the TFC test is analyzed by tensile and hygrothermal expansion measurements on partially degraded specimens supplemented by microstructural characterization using transmission electron microscopy, revealing significant decay in mechanical properties as well as morphological rearrangement due to the combined fatigue and creep loading. Through comparison with in-situ hygrothermally degraded CCMs, the TFC-AST protocol is demonstrated to be an economical alternative to the costly in-situ mechanical accelerated stress tests that can reduce the test duration by more than 99%. 
Polymer electrolyte fuel cells (PEFCs) are known as promising candidates to replace the internal combustion engines in automotive applications. Development of membrane electrode assemblies (MEAs) capable of meeting the automotive industry durability targets [1,2] is a key challenge facing the fuel cell industry. Deterioration of the perfluorosulfonic acid (PFSA) ionomer membrane due to chemical and mechanical degradation mechanisms during fuel cell operation is a prevalent failure mode. Chemical degradation is mainly originated from the attack of radical species (•OH and •OOH) while mechanical degradation is caused by hygrothermal fatigue and creep stresses due to fluctuations in relative humidity (RH) and temperature [3–6]. Development of mechanically stable PFSA membranes and catalyst coated membranes (CCMs) is crucial to keep the membrane intact and avoid unexpected failures during operation [7–12]. Mechanical degradation of PFSA membranes has primarily been investigated using accelerated stress tests (ASTs) that intensify the relevant stressors compared to the regular duty cycle conditions during field operation [13–17]. Lai et al. [16] studied the failure of PFSA membranes following the US Department of Energy mechanical AST protocol [18], i.e., 2 min/2 min wet/dry cycles at 80°C for 20,000 cycles. By varying the magnitude of the humidity swings from supersaturated conditions (150% RH) to 0%, 50%, and 80% RH, the initiation of membrane cracks was found to be postponed at the lower range of oscillation [16]. It is noteworthy however that modern fuel cell membranes such as those reinforced with ePTFE commonly do not reach failure within the assigned duration of the AST, and further (indefinite) extensions of the test duration are generally impractical for both planning and budgeting purposes (i.e., a test may take several months or even years and require a dedicated test station resource and technician). Hence, ex-situ mechanical test procedures with shorter duration are desirable. Aindow and O’Neill [19] proposed a strategy to map the stresses generated by in-situ RH cycling onto
mechanical stress that can more easily be replicated \textit{ex-situ}. An associated mechanical test was subsequently used to predict the durability of fuel cell membranes under humidity cycling using a stress vs. cycles-to-failure (S-N) curve. A similar experiment was utilized by our group to characterize the fatigue properties of PFSA membranes and catalyst coated membranes under a range of hygrothermal and stress conditions of relevance for fuel cells [9]. To date however, no attempt has been made to compare the relative action of \textit{ex-situ} mechanical stress and \textit{in-situ} hygrothermal stress in order to qualify the former approach for more general use. The objective of the present work is therefore to experimentally validate an \textit{ex-situ} tensile fatigue-creep (TFC) test in the context of \textit{in-situ} mechanical membrane degradation and to qualify its use as an alternative, low-cost mechanical AST protocol. The proposed \textit{ex-situ} approach utilizes the mechanical-hygrothermal stress analogy in order to apply stress at much higher frequency than conventional \textit{in-situ} tests. The proposed TFC test is evaluated against the previously reported \textit{in-situ} hygrothermal AST [20] through systematic investigation of the changes in mechanical, hygrothermal, and microstructural properties during the experiments.

It was previously shown by our group that the mechanical behaviour of PFSA membranes is substantially altered when coated with catalyst layers to form a composite catalyst coated membrane (CCM) [11]. CCM specimens were therefore used in the present work in order for the results to be compatible with \textit{in-situ} fuel cell conditions. CCMs were prepared by removing the gas diffusion layers from the sides of membrane electrode assemblies (MEAs) [12]. Tensile specimens were cut in dog bone shape [9] (4 mm gauge length and 2 mm arc radius) to avoid premature fractures in the clamping area [9]. Tensile fatigue-creep experiments with 10 Hz frequency of sinusoidal cyclic load with 6.1 MPa mean stress and a minimum to maximum stress ratio (R) of 0.2 were applied to the CCMs at 80°C and 50% RH, which
represents the average environmental conditions during the RH cycling of the corresponding in-situ accelerated mechanical stress test (AMST) used for reference. A dynamic mechanical analyzer (DMA; TA Instruments Q800) equipped with an environmental chamber (TA Instruments DMA-RH Accessory) was utilized to perform the ex-situ TFC experiments. The baseline TFC lifetime was determined to be ~225 min on average, equal to ~135,000 cycles. This result can be compared to the standard in-situ AMST which is designed to perform up to 20,000 humidity cycles, equivalent to a test duration of ~8 weeks. Hence, the TFC test generated mechanical failure ~400 times faster than the in-situ test despite applying considerably milder stress (i.e., higher number of cycles to failure). It is noteworthy however that the TFC failure criterion represents fracture of a small tensile CCM specimen, while the in-situ AMST failure represents relatively large cracks and/or holes that carry significant convective gas leaks across the membrane. Hence, the TFC failure is deemed to represent crack initiation which leads to rapid specimen fracture under the applied tensile stress in contrast to the more mature cracks observed in-situ that would have propagated gradually under tensile-compressive hygrothermal load. Additionally, the tensile-tensile TFC load was observed to induce more severe creep than the in-situ tensile-compressive load although in both cases the mechanical degradation was a combination of fatigue and creep. The total specimen elongation during the TFC was ~120% on average. A rapid increase in strain occurred in the early stages of loading followed by a plateau region until failure [9], which indicates that creep action dominated the early stage of the experiment (similar to a conditioning effect) and that the fatigue action that dominated the later stages of the experiment was responsible for specimen failure by fracture initiation.

Next, partially degraded CCMs were prepared and extracted at certain fractions of the TFC lifetime (20%, 40%, 60%, and 80%) in order to analyze the progression of the mechanical
degradation and compare the mechanism to *in-situ* degradation. Tensile and expansion tests by dynamic mechanical analysis (DMA) and microstructural characterization by transmission electron microscopy (TEM) were conducted on the beginning of life (BOL; before and after MEA conditioning) and partially degraded CCMs. Prior to tensile and expansion tests, the width of the CCMs was carefully measured by optical microscope. Provided that the average width was reduced from 2 mm to about 1.4 mm in the central specimen section during the TFC process, a 7 mm gage length was used to avoid edge stress concentration. Tensile tests were performed at standardized fuel cell operating conditions (70°C and 90% RH) at a fixed strain rate (0.01 min⁻¹), and the key tensile properties were calculated from the obtained stress – strain curves, including elastic modulus, ultimate tensile strength, and final strain [15]. Hygral and thermal expansion tests were applied by measuring the specimen length at constant temperature (70°C) while the RH was elevated from 0% to 30%, 30% to 50%, 50% to 70%, and 70% to 90% and at constant RH (90%) while the temperature was raised from 20°C to 40°C, 40°C to 60°C, and 60°C to 80°C, respectively [15,20]. The microstructure of the membrane before and after TFC loading was measured using high-resolution TEM (FEI Tecnai Osiris). The CCM specimens were ion-exchanged by submersion in saturated lead acetate solution for 48 hours to enhance the image contrast, coated with epoxy, and sectioned into 70-90 nm strips using a Leica EM UC6 ultramicrotome. An end-of-test *in-situ* AMST degraded CCM was also characterized for comparison. TEM was performed using an accelerating voltage of 120 keV and micrographs were captured using a Gatan Ultrascan 1000XP-P CCD camera. The obtained micrographs were further analyzed using an open source image processing tool (ImageJ).

The obtained tensile properties of the BOL and partially degraded CCMs are presented in Figure 1. The BOL specimens remained intact until the maximum travel length (330%
elongation) of the DMA. The average final strain was reduced significantly in the early stage of degradation (first 20%) and then stabilized until close to failure (80%). This is believed to be an effect of creep, considering that the results are inversely proportional to the creep strain measured during the TFC experiment. The ex-situ fatigue-creep stress and the associated ~120% elongation resulted in work hardening and reduction in ductility of the membrane. More importantly however, the decay in final strain during the later stages of the TFC degradation was found to be consistent with the trend observed during the second half of the in-situ AMST degradation (12,000+ cycles) [20], which indicates that the initiation of microcracks due to fatigue action was progressing in a similar manner in both ex-situ and in-situ tests. It was previously shown that propagation of fatigue induced microcracks leads to specimen fracture under tensile test conditions for purely mechanically degraded CCMs [20]. The presence of microcracks provides local stress concentration which facilitates crack propagation and fracture at much lower strains compared to the BOL CCM. It should be mentioned that the equilibration of the CCM at relatively high temperature and RH (70°C, 90% RH) prior to tensile testing relieved a fraction of the recoverable creep strain, internal stress, and work hardening from the membrane. On the other hand, the creep stress beyond the CCM yield point [11] resulted in reorientation of membrane ionomer molecules along the stress direction, i.e., plastic deformation. This reorientation of molecules introduced anisotropy in the mechanical properties analogous to the observed anisotropy between the machine and cross-machine directions of the membrane manufacturing process [8]. Hence, the tensile strength increased along the stress direction, resulting in higher resistance to the applied tensile stress as exhibited in Figure 1b. The molecular alignment could also potentially generate crystalline order which provides further improvement to the tensile strength of the CCM. Lastly, the CCM resistance against elastic
deformation (i.e., elastic modulus) greatly diminished along the applied stress direction during the early stage of the TFC test, as presented in Figure 1c. This rapid reduction in elastic modulus can be correlated to the major creep strain during the TFC test and its relatively large recoverable portion that appeared again as elastic strain in the subsequent tensile test. During the fatigue dominated later stages of the TFC experiment a slight decay in the CCM elasticity was observed, similar to the corresponding trend during the in-situ AMST [20], which could be caused by disentanglement of molecular cross links due to the fatigue stress. It can be summarized from Figure 1 that the evolution in tensile properties during the fatigue dominated later stages of the TFC test were generally in fair agreement with the trends from in-situ hygrothermal fatigue although the large creep strain during the early stage of the test resulted in reductions in final strain and elastic modulus and an increase in tensile strength in the test direction.
The purported rearrangement of ionomer molecules along the TFC stress direction was further investigated using TEM micrographs of the 80% TFC degraded membrane, as shown in Figure 2. TEM micrographs of BOL and end-of-test *in-situ* AMST degraded membranes are also provided for comparison. The dark regions in these images represent the hydrophilic phase, i.e., sulfonic acid group rich domains, while the bright regions correspond to the hydrophobic phase, i.e., ionomer backbone rich domains. Although the *in-situ* AMST degraded membrane had similar morphological characteristics to those of the BOL membrane, the oriented morphology along the TFC stress direction indicated by the arrows in Figure 2c can be distinguished in the *ex-situ* TFC degraded microstructure. An elliptical mapping approach was utilized in order to highlight the morphological changes of the TFC degraded membrane by assigning ellipses (circles) to adjacent hydrophilic domains (dark regions). It can be observed from the elliptical maps in Figure 2 that the hydrophilic phase of the *ex-situ* TFC degraded membrane was elongated along the stress direction, which supports the findings from the tensile test results. This elongation was assigned to creep during the early stage of the test.
The viscoelastic-viscoplastic behaviour of PFSA ionomer membranes results in time-dependent response [12] to the dynamic hygrothermal oscillations during *in-situ* operating conditions. Therefore, transient expansion tests were conducted to capture the time-dependent characteristics of the degraded CCMs in the primary, tensile direction. Figure 3 represents the obtained hygrothermal expansion behaviour of the pristine and partially degraded CCMs to the discrete rise in relative humidity (Figure 3a) and temperature (Figure 3b). BOL and BOL-conditioned CCMs expanded gradually with increasing RH and temperature due to water sorption and thermal expansion, with the conditioned CCM expanding somewhat less due to the membrane swelling during MEA conditioning. Interestingly however, the *ex-situ* TFC degraded CCMs exhibited negative expansion, i.e., contraction, in response to the stepwise increase in both RH and temperature. These findings were in stark contrast to the results for CCMs degraded by *in-situ* hygrothermal AMST [20] as well as combined chemical and mechanical AST [15].
During *in-situ* AMST (and regular duty cycle operation) [20], the alternating compression-tension nature of the induced cyclic stresses and the relatively long duration of each wet/dry period provided the membrane with time to retrieve the stored strains. In contrast, the *ex-situ* TFC test utilized cyclic stresses exclusively in the tensile direction of the CCM [11] at considerably higher frequency, i.e., 600 cycles per minute compared to 0.25 cycles per minute for the *in-situ* AMST. The intermolecular bonds of the semi-crystalline clusters, formed during the fatigue and oriented along the stress direction (as presented in Figure 2), constrained the time-dependent recovery and left the membrane in a meta-stable state. The increase in membrane internal energy associated with the increase in temperature or relative humidity during the expansion experiments assisted the ionomer to retract toward the initial morphology before stretching [21,22]. In addition, the underlying elongation observed due to creep was higher than the elongation of the BOL CCM due to hygrothermal expansion; hence, retraction dominated the present results for the *ex-situ* degraded CCMs.
In summary, tensile fatigue and creep, capable of accelerating the mechanical degradation of catalyst coated membranes, was introduced as a low-cost and rapid *ex-situ* mechanical AST approach. Post-test mechanical analyses indicated rapid decay in fracture strain and elastic modulus accompanied by an increase in tensile strength, which was attributed to the creep portion of the TFC process during the early stage of degradation. The more advanced stages of the TFC process were dominated by the fatigue portion accompanied by mild decay in mechanical properties due to crack initiation leading to ultimate failure by fracture. Furthermore, an elongated, meta-stable morphological state was observed for the first time in the TFC degraded membranes, which was correlated to hygrothermally activated creep recovery during expansion tests. Nevertheless, the overall mechanical degradation of the CCM was dominated by fatigue, which was able to overcome the increased tensile strength manifested by the underlying creep strain. In conclusion, the proposed *ex-situ* TFC test can thus be utilized to evaluate the mechanical stability of CCMs in a fraction of the time and cost of a conventional *in-situ* mechanical accelerated stress test comprising of hygrothermal cycling. Due to the much smaller
sample size, however, several repetitions of each experiment are recommended in order to obtain statistically relevant results.

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References


Appendix E.

Accelerated Membrane Durability Testing of Heavy Duty Fuel Cells

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Accelerated Membrane Durability Testing of Heavy Duty Fuel Cells

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Regular durability testing of heavy duty fuel cell systems for transit bus application requires several thousand hours of operation, which is costly and time consuming. Alternatively, accelerated durability tests are able to generate failure modes observed in field operation in a compressed time period, by applying enhanced levels of stress. The objective of the present work is to design and validate an accelerated membrane durability test (AMDT) for heavy duty fuel cells under bus related conditions. The proposed AMDT generates bus relevant membrane failure modes in a few hundred hours, which is more than an order of magnitude faster than for regular durability testing. Elevated voltage, temperature, and oxidant levels are used to accelerate membrane chemical stress, while relative humidity (RH) cycling is used to induce mechanical stress. RH cycling is found to significantly reduce membrane life-time compared to constant RH conditions. The role of a platinum band in the membrane is investigated and membranes with Pt bands demonstrate a considerable life-time extension under AMDT conditions, with minimal membrane degradation. Overall, this research serves to establish a benchmark AMDT that can rapidly and reliably evaluate membrane stability under simulated heavy duty fuel cell conditions.

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According to the World Health Organization, air pollution claimed seven million lives around the world in 2012.1 A major portion of this pollution was caused by road vehicles. Due to their zero emission operation, fuel cell buses offer a solution to air pollution in urban areas. Heavy duty fuel cell powered bus fleets in London, Hamburg, Cologne, Oslo, Whistler, and California are displaying long-term stability and durability in the field.2 A 2016 power plant life-time target of 18,000 hours was set for transit buses by the United States Department of Energy.3 Lab testing of fuel cell bus components and systems for such extensive periods of time is not feasible due to the high cost and long time involved. Therefore, major fuel cell developers turn to accelerated durability tests (ADTs) to estimate the durability of fuel cell systems and their components.

The membrane is a key component of fuel cells and is vital for fuel cell durability and performance. There are two main degradation mechanisms of perfluorosulfonic acid (PFSA) ionomer membranes under fuel cell operation:3 chemical and mechanical degradation. Chemical degradation of the membrane is caused by radical attack. Hydroxyl (HO•), hydroperoxyl (HOO•), and hydrogen (H•) radicals have been identified as potentially harmful to the membrane.4 Radicals can form in the catalyst layers or as a result of hydrogen peroxide decomposition in the presence of Fenton’s reagents in the membrane.5−8 Hydrogen peroxide forms electrochemically as a by-product of the oxygen reduction reaction (ORR) and chemically when crossover oxygen and hydrogen meet at the cathode or anode.9−12 Polymer side chain degradation in chemically stabilized PFSA membranes is predominantly due to HO• radical attack on the first ether bond in the α-OCF2− group.13 Attack by H• may occur to a smaller extent at the tertiary carbon C−F bond on both the main and side chains, while attack by HO• occurs solely on the side chain.14 Cell voltages close to the open circuit voltage (OCV) are known to lead to high levels of chemical degradation, resulting in a gradual loss of membrane material, observed as general membrane thinning and fluoride release in the effluent water.15 Adequate humidification of the membrane is crucial for membrane durability, since fuel cell operation at dry conditions leads to increased membrane degradation.16,17 Chemical stabilization of PFSA polymer end groups18 and use of additives, such as cerium and manganese radical scavengers are potential methods to mitigate chemical degradation.19,20 Chemical membrane degradation has a strong impact on mechanical membrane properties21 due to molecular weight reduction.

The resulting mechanical stress from frequent swelling and shrinking of the constrained membrane in response to changes in water content results in membrane creep, fatigue,22 and the formation of pinholes, cracks, and tears on the surface or in the bulk of the membrane.23 Membrane stiffness and strength was found to decrease when exposed to humidity cycling at high temperatures.24−28 The mechanical endurance of membranes can be enhanced by physical reinforcement of the membrane using a porous polymer matrix, fibers, or inorganic reinforcement.29

Coupled chemical and mechanical stressors have however been found to exacerbate membrane degradation compared to chemical and mechanical degradation applied separately.30−33 The impact of combined chemical and mechanical degradation on membrane durability was investigated in our group under Ballard Power Systems’ cyclic open circuit voltage (OCOV) AST protocol.34 Results of mechanical testing showed a rapid reduction in CCM ductility and fracture strain together with a significant decrease in ultimate tensile strength (UTS) as a function of AST cycles.35 During combined chemical and mechanical membrane degradation, mechanical stress can affect chemically weak regions of the membrane first, since they tend to be the least resistant to humidity changes and therefore more prone to damage. The failure modes of combined chemical and mechanical membrane degradation include localized membrane thinning (divots), pinholes with rough edges, tears, and microcracks.

The effect of platinum in the membrane on membrane durability is subject to debate. Platinum is known to be unstable at high voltages, and can hence dissolve, migrate out of the catalyst layer, and deposit in the membrane.36,37 The partial pressure of crossover H2 from the anode is relevant for Pt band formation, because H2 reduces Pt ions to form metallic Pt in the membrane.38 The location of the Pt band is determined by the local mixed potential distribution.39−42 Many authors believe that Pt in the membrane increases membrane degradation.41−47 Synthetic methods of planting Pt in the membrane have been shown to have a detrimental effect on the membrane,48,49 where platinum ions can act as a Fenton’s reaction promoter.50,51 However, in our group, field operated MEAs with a naturally grown metallic Pt band in the membrane were tested under CCOV AST conditions,

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and vastly outperformed freshly manufactured membranes in terms of durability.32

The objective of the present work is to develop an Accelerated Membrane Durability Test (AMDT) protocol for heavy duty fuel cells based on the characteristic duty cycle of transit buses. In contrast to generalized screening methods such as the COCV AST, the proposed AMDT conditions are much milder, yielding more realistic application oriented results, in this case for heavy duty bus fuel cells. Due to its close resemblance to bus conditions, the AMDT will provide an accurate evaluation of membrane stability for fuel cell bus operation. Additionally, the role of humidity cycling and platinum in the membrane will be investigated under AMDT conditions. This work is expected to aid the fundamental understanding of membrane degradation under fuel cell bus conditions.

**Experimental**

Membrane electrode assembly (MEA) fabrication.— Catalyzed gas diffusion electrodes (GDEs) were fabricated by coating a microporous layer made of polytetrafluoroethylene (PTFE) and carbon black on a non-woven carbon paper gas diffusion layer substrate, followed by coating a catalyst layer consisting of carbon-supported platinum catalyst and perfluorosulfonic acid ionomer.53 MEAs were prepared by hot-pressing a standard non-reinforced PFSA ionomer membrane with anode and cathode GDEs.

Stack assembly and test station.— MEAs were used to build a 10 cell stack with graphitic bipolar plates having co-flow parallel straight channels. A pressurized bladder ensured uniform compression between MEAs and bipolar plates. External and internal gas leak tests were done before installation of the stack on a test station. AMDTs were run on Ballard Power Systems’ fully automated standard test hardware. The stack was conditioned for 24 hours prior to the AMDT in order to equilibrate the membranes. The proposed AMDT test conditions are described in the following section.

**Accelerated Membrane Durability Test (AMDT)**

Baseline AMDT protocol.— Since the 2010 Winter Olympics, 20 fuel cell transit buses powered by Ballard HD6 modules operated in Whistler Resort Community in British Columbia, Canada for four years. This was the largest fuel cell hybrid bus fleet in the world, which successfully endured temperatures between −12°C to 27°C, snowfall from November to May, and a very challenging terrain with frequent up and down hill driving. The development of the AMDT for heavy duty fuel cell vehicles is based on a thorough characterization of the Whistler HD6 duty cycle for key stressors, their levels, and occurrence. The protocol uses constant and time dependent bus fuel cell stressors at elevated levels. All stressor levels were carefully chosen to avoid failure mode artifacts.

Buses often idle at traffic lights, stop signs, or bus stops, leading to extended periods at elevated voltage, which is known to chemically degrade the membrane. The baseline AMDT therefore applies chemical stress by maintaining the stack voltage at 9 V, simulating bus idling conditions. Due to regular acceleration and deceleration, transit buses have a highly dynamic duty cycle, which results in frequent humidity fluctuations. In the Whistler fleet, the humidity mildly dropped during acceleration and then quickly returned back to a fully saturated state once the level of demanded load was reduced. The amplitude of changes in humidity was smaller than 10% RH and short in duration, meaning that the membrane may not have experienced excessive swelling or shrinking, although its repetitive nature could eventually cause mechanical degradation over time. The baseline AMDT achieves RH cycling by bypassing the cathode humidifier for 66 seconds every 10 minutes, causing the RH to gradually dip to approximately 60% RH at the cathode. The total membrane RH during the dry cycle is estimated to drop to 80% RH, since the anode remains fully humidified, still generating more aggressive fluctuations in RH than in the bus. The ratio of the membrane resistivity measured during the wet and dry cycle was used to estimate the RH during the dry cycle, based on the corresponding conductivity and water content levels known for 100% RH.54,55

Idling and changes in humidity naturally occur in close proximity during driving. Therefore the baseline AMDT uses chemical and mechanical stressors simultaneously, simulating the real bus operating conditions. Additionally, elevated temperature and oxygen concentration are known to increase the rates of both chemical and mechanical membrane degradation processes without altering the failure modes. Buses generally use oxygen from the air in the surrounding environment as oxidant, which contains 21% oxygen. Increased oxygen availability allows for increased formation of radicals. To ensure rapid membrane failure the temperature and oxygen partial pressure used in the AMDT are 85°C and 45%, respectively, which are both elevated compared to bus conditions. Hydrogen and oxygen are used as reagent gases at flow rates of 5 and 10 slpm, respectively. These flows are intentionally high, considering the low load of only ~1 A, in order to ensure complete MEA surface coverage and avoid the formation of regions deficient of reactants. The backpressure is set to 0.1 barg, but generally fluctuates by around 0.03 barg during the test.

Complementary AMDT protocols.— Complementary tests with certain adjustments to the baseline AMDT protocol were designed to investigate the state of degradation at leak initiation and the effects of RH cycling and platinum in the membrane (PITM) on membrane durability. The temperature and oxidant levels were kept at 85°C and 45% O2 respectively, in all complementary testing. The early stage of membrane degradation was investigated in the initiation test, which applied the baseline AMDT conditions until initial hydrogen leaks across the membrane were detected by means of increased voltage fluctuation. Tests at 90% and 100% constant RH were performed to better understand the effect of RH cycling. The life-time difference between the tests at constant RH and the baseline AMDT is due to RH cycling, which is included in the baseline AMDT. The effect of PITM was studied using membranes with an artificially deposited Pt band tested under baseline AMDT conditions. Tests with PITM are considered to be more realistic, since a Pt band forms in membranes under bus operating conditions. The tests with PITM used a proprietary Ballard protocol to generate a Pt band in the membrane either before or during the baseline AMDT operation. The first test denoted by PITM-1 used Pt band generation prior to exposing the modified membranes to baseline AMDT conditions. The second test denoted by PITM-2 integrated the Pt band generation into the baseline AMDT protocol by running one Pt band generating cycle after every 6th RH cycle of the baseline AMDT. The baseline and complementary AMDT conditions are summarized in Table I.

**Diagnostic Methods**

External and internal gas leak tests were performed every 48 hours to assess the membrane condition. The stack was considered failed at an internal leak rate of 100 sccm, corresponding to the limiting leak rate through the membrane of 10 sccm per cell suggested by the US Department of Energy.56 After failure, the stack was disassembled and each MEA leak test and analysis under an Infra-Red camera (Kaiser RTI T620 FLIR) to identify the approximate location and size of leaks. In the IR camera test, hydrogen was supplied under bus operating conditions. Hydrogen and oxygen are used as reagent gases at flow rates of 5 and 10 slpm, respectively. These flows are intentionally high, considering the low load of only ~1 A, in order to ensure complete MEA surface coverage and avoid the formation of regions deficient of reactants. The backpressure is set to 0.1 barg, but generally fluctuates by around 0.03 barg during the test.

<table>
<thead>
<tr>
<th>AMDT Name</th>
<th>Condition</th>
<th>Pt band protocol</th>
<th>Life-time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline</td>
<td>Baseline</td>
<td>-</td>
<td>298</td>
</tr>
<tr>
<td>Initiation</td>
<td>Baseline</td>
<td>-</td>
<td>131</td>
</tr>
<tr>
<td>90% RH</td>
<td>Baseline</td>
<td>90% RH</td>
<td>497</td>
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<tr>
<td>100% RH</td>
<td>Baseline</td>
<td>100% RH</td>
<td>643</td>
</tr>
<tr>
<td>PITM-1</td>
<td>Baseline</td>
<td>Prior to AMDT</td>
<td>405</td>
</tr>
<tr>
<td>PITM-2</td>
<td>Baseline</td>
<td>Integrated in AMDT</td>
<td>662</td>
</tr>
</tbody>
</table>
air when allowed to leak through holes in the membrane. The resulting heat generation was captured by the IR camera. The least and most damaged MEAs were further inspected by a Philips XL30 scanning electron microscope (SEM). Samples were prepared by casting MEAs in epoxy pucks, which were polished in a Struers TegraPol-11 polisher with 120–1200 grit silicon carbide paper, and then carbon coated with an Edwards Scancoat Six Sputter Coater. Micrographs were taken using a backscatter detector at 20 kV. The membrane thickness was measured in 12 different spots and the morphology of transfers was found in cross-sectional and surface images. Membrane thinning was considered present when the final membrane thickness was below three standard deviations of the initial thickness. The fluoride concentration was measured from effluent water and the total fluoride loss was calculated using a method described elsewhere.24

Ex-situ mechanical testing.— Ex-situ mechanical testing was done on the beginning-of-life (BOL) and AMDT degraded membranes. Tensile tests were used to compare the mechanical properties of samples degraded by combined chemical and mechanical degradation (baseline AMDT), isolated chemical degradation (constant RH), and in the presence of PITM. To ensure consistency, MEAs were cut into rectangular shapes (25 × 2 mm) along the transverse direction using a plotter cutter machine. The gas diffusion layers (GDLs) were removed from the MEA and the remaining CCM was stored between glass slides at ambient conditions to keep the samples straight before testing. Tensile tests were conducted using a dynamic mechanical analyzer (TA Instruments Q800 DMA) equipped with an environmental chamber (TA Instruments DMA-RH accessory). Tensile test samples were loaded with a 5:1 gauge length to width aspect ratio to prevent introduction of edge stress concentration.24 The rest of the sample length was gripped by lower and upper clamps. The average membrane width and thickness was measured using an optical microscope for all samples and SEM for representative samples, respectively. The exact sample gauge length was measured by the DMA prior to the tensile test initiation. After equilibration at the desired conditions, tensile tests were conducted at room conditions (23°C and 50% RH) and fuel cell conditions (70°C and 90% RH) at a low strain rate (0.01 min⁻¹) on BOL and AMDT degraded samples. The tensile test was continued until it either reached mechanical failure or the DMA maximum clamp travel length of around 26 mm (160% total elongation). The elastic modulus, ultimate tensile strength (UTS), and final strain were calculated from the stress–strain curves. The elastic modulus was determined from the maximum slope of a 5th order polynomial fit to the initial section between 0 and 0.5% strain.24 The UTS and final strain were calculated as the maximum tensile stress and total strain (elastic and plastic) tolerated by the CCM during the tensile test, respectively. Under each environmental condition and AMDT type, the average and standard deviation of three repetitive tests were calculated. The error bars on the curves represent ±2σ, which statistically covers 95% of inputs.

Results and Discussion

In order to accelerate membrane degradation, the baseline AMDT applied combined chemical and mechanical stress by using high voltage, temperature, oxygen concentration, and RH cycling. As a result, the life-time of membranes subjected to the baseline AMDT was reduced by more than an order of magnitude compared to real bus operating conditions. In contrast, the AMDT life-time was approximately twice as long as the average life-time obtained with the more aggressive COCV AST.24 Since the AMDT conditions were designed to closely resemble actual operating conditions, it successfully generated failure modes similar to those found under bus conditions. As expected there was a correlation between AMDT conditions and the length of the membrane life-time. RH cycling significantly reduced membrane life-time compared to constant RH conditions. A lower constant RH level also resulted in reduced membrane life-time compared to fully humidified conditions. PITM was found to visibly prolong membrane life-time under baseline AMDT conditions. A summary of the obtained membrane life-times at baseline conditions vs. complementary AMDT conditions is shown in Table I.

The baseline AMDT failed at 298 h due to coupled chemical-mechanical stress. In the absence of humidity cycling, the 90% and 100% constant RH AMDTs degraded the membrane in a purely chemical manner, resulting in longer membrane life-times than the baseline, 497 h and 643 h, respectively. This demonstrates that combined chemical and mechanical stress indeed enhances membrane degradation, not only by adding mechanical stress, but also due to the short periods of increased chemical degradation at low RH during the dry cycle. The difference in membrane life-time between the two tests at constant RH is evidence of a higher rate of chemical membrane degradation at lower RH due to increased rates of gas crossover and hydrogen peroxide formation,63–65 and thereby increased radical formation via Fenton’s reaction. Although it is known that the membrane gas permeability decreases at lower RH,10 there is a counteracting effect whereby the oxygen concentration increases due to the reduced water vapor pressure at a fixed absolute pressure. In the present case, the water vapor pressure at 85°C is 0.58 bar at 100% RH and 0.52 bar at 90% RH. With a 45% oxygen concentration in the dry gas, the oxygen partial pressures at 100% and 90% RH are 0.25 and 0.27 bar, respectively, which represents an 11% increase at 90% RH. Membrane permeability depends on the gas diffusion coefficient, which changes with humidity. By lowering the RH from 100% to 90%, the oxygen diffusion coefficient decreases by around 7%.66 Therefore, the effect of increased oxygen partial pressure dominates over the effect of reduced permeability by roughly 4%, which actually leads to increased oxygen crossover to the anode. Mechanical stress during RH cycling appears to have gradually exacerbated the effect of chemical degradation,66 causing chemically weak areas of the membrane to become more vulnerable to tearing and cracking. The presence of a Pt band in the membrane showed significant life enhancing effects on membrane durability by vastly outperforming the baseline AMDT by lasting 405 h and 662 h with the two PITM application methods, offering evidence that Pt in the membrane is capable of mitigating membrane degradation.

Hydrogen leaks and voltage decay.— Membrane holes were allowed to grow until the stack leak rate reached or exceeded 100 sccm in all AMDTs, except for the initiation AMDT, which was stopped at 131 h, when the first indicators of membrane damage occurred. Indicators of membrane damage include increased voltage fluctuations and voltage decay. The morphological changes present in the membrane prior to hole growth, which is mainly a thermal process, were studied in order to better understand the initial degradation process. Each test displayed different membrane leak rate development characteristics over time, as shown in Figure 1. The baseline showed

Figure 1. Hydrogen leak rate development during AMDT operation, showing slower leak growth at constant RH (green) and with PITM (red), compared to baseline (blue full). The initiation test (blue dashed) was stopped after leak initiation, in order to investigate the early stage of degradation.
short initiation and leak growth times. Chemically degrading conditions at 90% constant RH may have resulted in a shorter initiation time, but allowed for a relatively long leak growth time, eventually exceeding the baseline life-time. The 100% constant RH test had the mildest conditions, and as expected, displayed longer initiation and leak growth periods compared to the baseline and 90% RH runs. This pattern suggests the action of mechanical stress due to RH cycling as an accelerator for membrane rupture and leak growth. The initiation and leak growth periods of the tests with PITM resemble those of the constant RH tests, despite being exposed to baseline AMDT conditions, including RH cycling. The longer leak growth times at constant RH and with PITM confirm that MEAs are able to operate for a relatively long time despite the presence of small leaks, when the conditions are favorable; i.e., low mechanical stress in the case of constant RH and low chemical stress in the case of PITM.

The initiation AMDT was stopped at 131 h (Figure 1, insert) when the stack first started to exhibit increased voltage fluctuations and voltage decay, as shown in Figure 2. The initial voltage fluctuations in the beginning of the test may be due to different permeation rates of hydrogen through the healthy membranes during RH cycling. However, after the formation of leaks, the convective hydrogen flux to the cathode results in mixed potentials at the cathode, causing an increase in the amplitude of fluctuations, and the onset of voltage decay.

The formation and growth of new transfers over time resulted in further voltage drops, which can be correlated to the measured leak rate development seen in Figure 1. The baseline, for instance, exhibits a major voltage drop around 200 h in Figure 2b, which can be seen as the final largest increase in leak rate in Figure 1. The initiation, baseline, and PITM-1 voltages dropped significantly from 9.0 V to around 8.6, 8.3, and 8.4 V, respectively. The 90% RH had the most severe final voltage drop, reaching 8.0 V. On the other hand, the 100% RH voltage and PITM-2 stayed mostly above 8.8 and 8.9 V, pointing to a very small amount of MEAs with holes, which was later confirmed.

Similarly, open circuit voltage (OCV) decay is related to hydrogen leaks caused by membrane degradation and is therefore a good indicator of membrane health. The OCV can also drop due to increased hydrogen crossover rates through local regions of thinned membrane. The measured OCV results are provided in Figure 3 for the various AMDT runs.

The OCV decay curve can be separated into two parts. The first part represents the initiation time with a lower decay rate and the second part represents the leak growth phase with a much faster decay rate. As expected, the initiation and baseline AMDTs showed the fastest OCV decay, due to rapid leak formation and growth, causing all 10 cells to develop fairly large leaks in both cases. Interestingly, the 90% RH test showed an equally rapid decay rate as the first part...
of the baseline, indicating a similar level of membrane degradation to the baseline, suggesting that the initial phase of the baseline is dominated by chemical degradation. In later stages however, the effect of RH cycling gradually increased the degradation rate toward early failure for the baseline, while the 90% RH degradation rate remained constant during the entire testing period. At a later point in time the 90% RH OCV drop exceeded the OCV drop of the baseline, and similarly, all 10 cells were found to have developed leaks. The 100% RH test showed no signs of OCV decay in the first phase, in good agreement with its long initiation time, but once 3 out of 10 membranes developed leaks, the OCV decay rate mildly increased. The PITM tests experienced the lowest level of OCV decay rates and OCV drops, corresponding to long initiation times and few damaged cells. PITM-1 had 6 leaky membranes out of 10, while PITM-2 had only 2 leaky membranes despite having the longest test duration. This is a powerful indicator of the ability of the PITM to mitigate and reduce chemical degradation and thereby substantially extend the membrane stability and life-time.

Performance loss.— The performance of the AMDT stacks was periodically monitored by measuring polarization curves. Beginning of Life (BOL), Middle of Life (MOL), and End of Life (EOL) polarization curves are shown in Figure 4. The OCV decay observed here is consistent with the previous findings. The decay of the fuel cell performance is correlated to membrane degradation and observed consistently across all current densities. This decay can be attributed to increasing activation losses at MOL and EOL due to convective hydrogen crossover flux through the membrane. The voltage losses at non-zero current densities were however lower than at OCV; for
instance, the baseline had a performance loss of about 30 mV compared to an OCV loss of 100 mV.

Membrane thinning and fluoride loss.— Membrane thinning was prevalent in the AMDT degraded samples. Figure 5 shows the average membrane thickness loss in the different AMDT samples compared to the BOL membrane. It can be seen from Figure 5 that the baseline and constant RH samples experienced significant membrane thinning, while the membrane thickness in the PITM samples remained mostly unchanged. Membrane thinning is considered evidence of chemical degradation, which was effectively mitigated in the PITM samples. Although the constant RH samples exhibited more membrane thinning than the baseline, it should be mentioned that constant RH samples were exposed to AMDT stressors for a longer time before failure compared to the baseline samples; hence they experienced more chemical degradation, leading to general membrane thinning in all locations. The thinning level of the initiation sample was however similar to that of the baseline despite its shorter AMDT duration. Hence, the majority of the global chemical degradation is expected to occur during the initiation phase. The baseline membranes exhibited the most severe membrane thinning at the outlets, while membrane thinning was observed at both the inlets and outlets of the initiation membranes. The baseline AMDT thinning levels are roughly half of the COCV AST, which had a 48% membrane thickness loss in only half of the testing time. This is due to much milder AMDT conditions compared to AST conditions.

Fluoride release is another important indicator of chemical membrane degradation which was monitored periodically during the experiments. The cumulative fluoride release data in Figure 6 show that the AMDT fluoride loss was generally in good agreement with the thickness loss, which confirms the findings reported above. The relative rates of chemical membrane degradation can be assessed by comparing the slopes of the curves; the baseline had the highest rate followed by the 90% RH, 100% RH, PITM-1, and PITM-2 conditions, which is consistent with the relative severity of the chemical stressors in each case. The baseline thinning rate was approximately equal to its fluoride release. However, the constant RH runs showed higher thinning than fluoride release combined with a relatively large variability. The suppressed rate of fluoride removal from the degraded membranes in this case may be due to the absence of liquid water dynamics otherwise induced by RH cycling. The PITM runs showed very low fluoride release which is consistent with the thinning results. The effluent water of the initiation AMDT was not collected; hence there is no fluoride loss data available for this run.

Failure analysis.— Membrane holes and fracture sites are indicative of the regions exposed to the most aggressive levels of degradation. Figure 7 shows representative SEM images of the different failure modes observed in the AMDTs. The baseline AMDT generated membrane holes of 50–300 μm diameter with a hole count density of 2.9 holes per cm². The mechanical stress during RH cycling of the baseline AMDT is assumed to be responsible for the rough character of transfers seen as cracks and tears around the holes, shown in the SEM micrograph in Figure 7a. The initiation leaks had an average diameter of 200 μm with 1.3 holes per cm². The initiation MEAs exhibited divot and crack formation from both the anode and cathode sides (Figure 7b). The membranes also showed holes with rough edges similar to the baseline, as a result of combined chemical and mechanical degradation. Delamination between the membrane and catalyst layers was also commonly observed for both tests, presumably due to membrane degradation at the interfaces. Only one 40 μm hole was found in the 90% RH membranes (0.04 holes per cm²). The 100% RH membrane had an average hole diameter of 40 μm with 1.2 holes per cm². The surfaces around the holes were smooth in both AMDTs at constant RH, with areas of chemically eroded membrane, seen in Figure 7c. Due to the absence of mechanical degradation there were almost no cracks or fractures and all damage appeared to be chemical in nature. Only one divot was found in PITM-1, and 0.68 holes per cm² were identified. Only two cells failed due to large leaks in PITM-2 while the remaining eight cells were still in good condition. One divot and 0.33 holes per cm² were found. The character of holes in PITM-1 and PITM-2 was of combined chemical and mechanical stress, where the surrounding areas were irregular with rips and tears, similar to the baseline and initiation tests. Divots appeared in local regions without a platinum band, indicating lower chemical degradation mitigation capabilities in these areas, such as those observed in Figure 7d. It is anticipated that divots formed in these areas would eventually grow to holes such as those observed in Figure 7d due to combined chemical and mechanical degradation. This suggests that while the Pt band is effective in mitigation of chemical degradation, a complete coverage is essential in order to avoid local degradation and damage.

Pt band location and concentration.— The Pt concentration in the Pt band from inlet to outlet of the PITM membranes is shown in Figure 8. The membranes had the highest Pt concentration at the outlet and a lower concentration at the middle and inlet positions, in good agreement with the primary location of holes at the inlet. PITM-1 membranes displayed a wide Pt band located at a distance of 33% of the membrane thickness from the cathode interface, with Pt concentrations between 2,000 and 18,000 ppm in the band. In PITM-2, a Pt band was observed at a distance of 40% from the cathode, with Pt concentrations between 11,000 to 43,000 ppm. It is believed that the higher PITM concentration of PITM-2 was responsible for the life-time extension compared to PITM-1, in particular due to a better
coverage at the inlet region where gaps in the Pt band were found to allow local chemical degradation. The Pt concentration in the band also appeared to decrease in regions adjacent to large catalyst layer delamination sites, in good agreement with the locations of transfers.

Mechanical properties.— Tensile tests were conducted for AMDT degraded (EOL) catalyst coated membranes (CCMs) as well as fresh (BOL) CCMs in order to evaluate the effect of different AMDT stressors on the mechanical properties. Figure 9 illustrates the representative stress–strain curves of different AMDT samples at room and fuel cell conditions. The first curve represents the BOL and the rest are AMDT degraded samples. At room conditions (Figure 9a), BOL samples stretched well until the maximum traveling length of the DMA (∼160% strain). Among all AMDT samples, only the PITM samples resembled the ductile behavior of the BOL sample, while the baseline AMDT and constant RH samples fractured quickly, right after passing through the maximum strain.
their yield stress. It is suggested that polymer chain degradation and decrease in molecular weight resulting from chemical degradation reduces the chain entanglement and allows for easier chain detachment leading to a much lower fracture strain in the baseline and constant RH AMDTs.

At fuel cell conditions (Figure 9b), analogous to room conditions, BOL samples reached the DMA traveling length limit. On the other hand, the baseline AMDT and constant RH samples fractured at low strains after passing the elastic region. However, only the PITM-2 sample was able to endure the tensile test while the PITM-1 sample fractured at around 40% strain.

By comparing the plots in Figure 9, it can be summarized that chemical degradation had the strongest effect on the ductility of the EOL membranes since no brittleness was observed in the PITM samples, where chemical degradation was mitigated by introducing platinum into the membrane. Chemical degradation causes polymer chain disentanglement and membrane thinning in early stages of the AMDT which is accompanied by the formation of pinholes and divots prior to failure.

The two baseline AMDT samples exhibited similar tensile properties although the initiation AMDT was extracted from the stack well before failure. These results are evidence that chemical degradation in the first stages of the AMDT appears as polymer chain degradation and has the most crucial effect on membrane embrittlement during AMDT. This also indicates that the mechanical properties may primarily decay during the initiation phase, and that after hole formation, the hydrogen leaks generated may result in less severe conditions for chemical degradation and therefore limited further decay in mechanical properties. Another important observation is that once holes were formed, the mechanical properties remained the same, regardless of the size of the holes.

On the other hand, removal of mechanical degradation in constant RH AMDTs did not improve membrane ductility when compared to the ductility of the baseline AMDTs. The material’s ability to absorb energy before rupture is defined as material toughness and is determined by calculating the area below the stress – strain curve. Based on this definition, BOL and PITM EOL samples showed higher toughness and required much more energy to fracture compared to the baseline and constant RH EOL samples subjected to severe chemical degradation.

Figure 10a presents the final strain of the AMDT samples in mechanical tests at both room and fuel cell conditions. The main discrepancy between the room and fuel cell condition results was observed in the PITM-1 sample where testing at high temperature and water content led to much lower elongation. This may be due to the lower ability of the membrane in PITM-1 to absorb water compared to PITM-2, indicating a higher level of destruction of the water channels in the membrane due to chemical degradation. On the other hand, the water channel structure appeared to be highly preserved in the PITM-2 membrane. PITM-2 was found to have a much higher platinum concentration in the membrane, which suggests that increased PITM levels may result in a higher level of preservation of the membrane water channels and therefore mechanical properties.

The elastic modulus is an indication of the material’s resistance against elastic deformation and is another important mechanical property evaluated in this study, as depicted in Figure 10b. In agreement with the literature, the elastic modulus is a function of test conditions and was significantly reduced by increasing the temperature and relative humidity. The PITM samples exhibited a lower elastic modulus and less resistance against deformation, i.e., less stiffness, compared to the baseline and constant RH samples. High elastic modulus and the lack of ductility observed in the baseline and constant RH cases can more easily lead to crack initiation in highly degraded areas, where the membrane experiences high stresses due to local degradation. In contrast, high elastic modulus and stiffness can reduce membrane swelling and contraction and control hydrothermal cyclic stress induced during humidity cycles. In the baseline and constant RH samples, severe chemical degradation may lead to reduced water uptake in the membrane, as indicated by the minor stiffening effect (increased elastic modulus) observed at fuel cell conditions but not at room conditions.

The maximum stress tolerated by the CCMs during the tensile test, i.e., the ultimate tensile strength (UTS), is presented in Figure 10c. The UTS remained unchanged in the constant RH and PITM samples, which were mainly affected by chemical degradation and mechanical degradation, respectively. However, in the baseline AMDTs, the UTS decreased at room and fuel cell conditions. Polymer main chain degradation and membrane global thinning caused by chemical degradation

Figure 10. Tensile properties of BOL and AMDT degraded catalyst coated membranes at room (23°C, 50% RH) and fuel cell (70°C, 90% RH) conditions: (a) final strain; (b) elastic modulus; and (c) UTS.
accompanied with microcracks and mechanical defects resulted from mechanical degradation may have led to a compounded reduction in membrane tolerance against mechanical loading. However, more intermediate samples would be required to elucidate conclusive trends in UTS.

As a summary of the mechanical properties represented in Figures 9 and 10 it was determined that the decay in mechanical properties was largely dominated by chemical degradation where the membrane (in a CCM) was transformed from a ductile to a fragile material in the baseline and constant RH samples. In contrast, in the PITM samples where chemical degradation mechanisms were controlled to some extent, the ductility and toughness of the membrane were maintained. However, it is also evident that that mechanical damage generated during RH cycling may accelerate the decay in mechanical properties through nucleation of mechanical microcracks at chemically degraded sites.

Conclusions

A baseline accelerated membrane durability test (AMDT) protocol was established for heavy duty fuel cell applications along with complementary experimental investigations to elucidate the respective roles of chemical and mechanical stressors in the overall membrane degradation mechanism and their impact on membrane life-time. The proposed baseline AMDT successfully accelerated membrane degradation using combined chemical-mechanical stress and significantly reduced the time to failure compared to regular duty cycle operation, achieving membrane failure in less than 300 hours. The failure modes obtained with the AMDT were similar to those observed during field operation, comprising holes and cracks in the membrane accompanied by local thinning, which demonstrates the effectiveness of the test protocol. It was found that under baseline AMDT conditions, the majority of the chemical membrane degradation occurred during the leak initiation period, followed by a rapid growth of the leak rate caused primarily by mechanical degradation. The effects of RH cycling and Pt in the membrane were evaluated in complementary AMDT runs. The effect of RH cycling was visible when the tests at constant RH lasted significantly longer than the baseline, confirming that RH cycling indeed accelerates membrane degradation. RH cycling was found to gradually decrease the strength of the membrane due to the imposed mechanical stress, which was also found to exacerbate the effect of chemical degradation. The AMDTs at constant RH exhibited slower leak growth than the baseline, allowing the membrane life-time at 90% RH was shorter than at 100% RH, proving that the level of chemical membrane degradation increases with reduced humidity. The largest hole sizes and densities were found in the RH cycled samples, which also exhibited rougher damage structure indicative of mechanical degradation. Platinum band formation extended the membrane life-time and prevented decay in thickness and elongation which suggests mitigation of chemical degradation. As a result the AMDTs with PITM displayed up to a doubling of the effective life-time. The test with high PtM concentration resulted in the longest life-time, while the test with low PtM concentration was found to have areas with gaps in the Pt band that were prone to local chemical degradation and earlier failures. Tensile tests on AMDT degraded samples determined the deterioration of CCM toughness in samples subjected to chemical degradation, while in PITM samples where chemical degradation was controlled, the mechanical strength of the membrane was preserved. From these results, it can be concluded that PITM and constant RH operation result in enhanced membrane life-time under heavy duty fuel cell conditions. The baseline AMDT protocol developed and demonstrated in this work is recommended for rapid and reliable testing of membrane durability for heavy duty fuel cell applications.

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References

Appendix F.

*Ex-situ* Chemical Degradation of PFSA Membranes Subjected to Fenton’s Reagent test
Ex-situ Chemical Degradation of PFSA Membrane Subjected to Fenton’s Reagent test

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1. Introduction

Polymer electrolyte fuel cells (PEFCs) are known as one of the leading candidates to replace the combustion engines in automotive applications. Automotive industry durability targets require the development of durable membrane electrode assembly (MEA) for light duty and heavy duty vehicles [1,2]. Perfluorosulfonic acid (PFSA) ionomer membranes are the most prevalent type of membrane used in PEFCs due to high chemical stability and high proton conductivity at low temperatures [3]. Membrane degradation and failure during fuel cell operation is however one of the main lifetime limiting factors [3]. Accordingly, many efforts are directed to enhance the reliability and longevity of PFSA membranes through moderating the degradation stressors as well as developing more stable membranes [4].

In order to minimize the ohmic losses and improve the fuel cell performance the fuel cell industry aims to reduce the membrane thickness; thus, developing mechanically stable and durable membranes is essential. The mechanical properties of pristine Nafion® membranes were investigated by several research groups [5–7] summarizing the significant impact of temperature and relative humidity. Similarly, the mechanical properties of catalyst coated membranes
(CCMs) were investigated comprehensively by our group and compared to the corresponding PFSA membranes through experimental and modeling works [8–13].

Chemical and mechanical degradation mechanisms are recognized as the primary membrane failure mechanisms in PEFCs [3]. Chemical degradation is attributed to the chemical attack of hydroxyl (•OH) and hydroperoxyl (•OOH) radicals and their interaction with the vulnerable bonds in the polymer end groups [3,14,15]. The rate of chemical decomposition is intensified in the presence of the reactant gas crossover, Pt dissolution, and transition metal ion contaminants [16]. Membrane thinning, fluoride ion emission rate, loss of proton conductivity, and decay in cell performance are evidences exhibiting the rate of membrane chemical degradation [3,16]. Mechanical degradation, on the other hand, is caused by the mechanical stresses in the form of hygrothermal fatigue and creep originated from the fluctuations in temperature and relative humidity during the fuel cell operating conditions as well as start-up/shut-down. Inside the fuel cell, membrane hygrothermal swelling and contraction is constrained by the adjacent layers inducing mechanical stress to the membrane [3]. The lack of mechanical integrity caused by the mechanical degradation mechanisms leads to the initiation and propagation of microscopic cracks and subsequent failure.

Currently, accelerated stress testing (AST) is the dominant methodology to evaluate the durability of fuel cell components with the purpose of benchmarking new materials and diagnosing mitigation strategies. Chemical and mechanical stressors are applied at elevated levels beyond the regular operating conditions of fuel cells. Typical stressors intensified during the AST include operating temperature and relative humidity, cell voltage, and current density as employed by the US Department of Energy (DOE) AST protocols [17]. In the context of chemical degradation mechanisms, \textit{in-situ} chemical AST was extensively utilized via open
circuit voltage (OCV) to evaluate the membrane deterioration [18–22]. Under OCV conditions, in the absence of load current, the generation of hydrogen peroxide (H$_2$O$_2$) was intensified by the elevation of the gas crossover and hydrogen/oxygen reaction rate at the anode catalyst [15,23]. Decay in electrochemical and mechanical properties of CCMs subjected to the OCV degradations, independently or combined with mechanical degradations were evaluated by our research group [24–26]. The detrimental effects of individual degradation mechanisms were characterized indicating that the membrane failure rate under mechanical degradations was elevated significantly in the presence of chemical stressors [25–27].

Fenton’s reagent reaction, on the other hand, was utilized as an ex-situ AST technique to evaluate the chemical durability of fuel cell membranes [28–32]. Low concentrations of transition metal ion contaminants, iron cations in particular, in the MEA are adequate to activate the Fenton’s reactions [33]. Ex-situ chemical degradation of PFSA membranes via Fenton’s reagents was studied and compared to the in-situ approaches [28–30]. The Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) analysis reported by Tang et al. [28] indicated the initiation of the decomposition from the end of the main chain when Nafion® was subjected to the solution of H$_2$O$_2$ and metallic cations (Fe, Ni, and Cr). Furthermore, SEM micrographs of the Fenton’s treated membranes showed the initiation of small bubbles on the surface of the membrane which could create pin-holes in the later stages of degradation [28]. From NMR and mass spectrometry analytical results, Healy et al. [29] observed similar reaction products in both in-situ and ex-situ degradation analysis indicating the capability of Fenton’s reagent reactions in simulating the fuel cell chemical degradations. However, Gubler et al. [30] reported fundamental differences in the reaction pathways and radical concentrations between in-situ fuel cell test and ex-situ Fenton’s test. The detected
concentrations of •OH and •OOH radicals in the Fenton’s test were substantially higher than for the in-situ fuel cell test, while no traces of •H was found in the Fenton’s test in contrary to the in-situ results [30]. Kundu et al. [31] investigated and compared two distinct Fenton’s reagent tests on Nafion® 112 membrane, one with iron cations and peroxide in solution, and the other with doped Fe^{2+} ions inside the membrane prior to being submerged in H_2O_2 solution. Despite relatively similar chemical and mechanical characteristics obtained by these experiments, the approach with iron cations in solution resembled large bubbles inside the membrane while the doped Fe^{2+} ions approach resulted in small pores close to the surface of the membrane [31]. It was further revealed that Fe^{2+} ions decompose main and side chain at equal rate [32].

Although a few research articles were contributed to the context of mechanical properties of Fenton’s degraded ionomer membrane [28,31], however, the interactions between the characteristics of Fenton’s reagent test and membrane mechanical properties were not thoroughly understood. Therefore, the present work evaluates the decay in mechanical properties and mechanical failure of the chemically degraded PFSA membranes which coupled with the microstructural defects formed by the Fenton’s reagents. Furthermore, mitigation approaches in order to slow down the chemical degradation caused by Fenton’s reagents were proposed and investigated.

2. Experimental

2.1. Ex-situ chemical degradation

A baseline Fenton’s solution composed of 20% H_2O_2 and 10 ppm Fe^{2+} at neutral pH (~7) and 80°C was used in this study. PFSA ionomer membrane specimens were immersed in four different types of Fenton’s solutions, i.e. baseline (pH = 7 and Pt = 0 ppm), Pt in the solution (5 ppm), highly acidic solution (pH < 0), and combination of Pt and highly acidic solution.
Additional details on the experimental setup are provided elsewhere [34]. To ensure the desired concentration of $\text{H}_2\text{O}_2$ and $\text{Fe}^{2+}$, the Fenton’s solution was replaced every 12 hours. In order to characterize the evolutions in mechanical properties and microstructural characteristics, partially degraded membranes were extracted at three different exposure times (12, 36, and 48 hours), acid washed, immersed in distilled water for a few days, and carefully dried at ambient atmosphere in between low-lint wipes for a few days.

2.2. Microstructural characterization

The top surface microstructure of the partially degraded PFSA membranes was studied via optical microscope (Nikon Eclipse LV100) to determine any severe signs of degradation. The top surface and cross sectional microstructure of the pristine and severely degraded membranes (previously down-selected by optical microscope) was then investigated using scanning electron microscopy (SEM; FEI Dualbeam 235 FIB-SEM). Cross sections were prepared through brittle cut of the membranes in liquid nitrogen. A secondary electron (SE) detector was used to capture the signals extracted by the incidence of the 5 kV electron beam. Top surface SEM images were also acquired at the fracture surface of the mechanically tested membranes to examine the role of the *ex-situ* chemically degraded defects on facilitating the mechanical failure.

2.3. Tensile testing

Prior to the tensile tests, membrane samples were dried and cut into $25 \times 2$ mm rectangular shape along the transverse direction and stored in between microscope glass slides at ambient conditions for a few days. It should be noted that excessive damage was observed at the edges of the degraded samples due to the edge effect. Therefore, tensile samples were taken from the middle part of the Fenton’s reagent specimens to ensure consistency. Tensile tests were conducted at room conditions ($23^\circ\text{C} - 50\%\ \text{RH}$) on pristine and *ex-situ* chemically degraded
PFSA membranes. A dynamic mechanical analyzer (TA Instruments Q800 DMA) equipped with an environmental chamber (TA Instruments DMA-RH Accessory) was utilized to perform the tensile tests. Samples were loaded in the DMA tension clamp with a 5:1 length to width aspect ratio [11]. The exact sample gauge length was measured by DMA, while the average width and thickness of each sample were obtained by optical microscope (OM), and digital micrometer, respectively. Once equilibrated to the desired temperature and relative humidity (23°C – 50% RH) under small preload tension (0.003 N), the specimen was stretched with constant strain rate (0.1 min⁻¹) to the fracture point or the maximum DMA travel length of 26 mm (~ 160% elongation for 10 mm initial length). Typical tensile properties including elastic modulus, ultimate tensile strength (UTS), and final strain were characterized from the obtained stress – strain curves as reported in [26].

3. Results and discussion

3.1. Microstructural characterization

The top surface microstructure of the pristine and ex-situ chemically degraded membranes was studied using OM in order to determine the highly degraded membranes for the subsequent top surface and cross sectional SEM analysis. The top surface microstructure of the pristine PFSA membrane is depicted in Figure 1a. Among the degraded membranes studied by OM (four types of solutions at 12, 36, and 48 hours), only membranes treated in H₂O₂ + Fe for 36 and 48 hours revealed circular-shaped features distributed throughout the sample surface (Figure 1b). It should be noted that in these samples the visual appearance of the membrane was transformed from transparent to white opaque. In contrast, the membrane structure was retained in the highly acidic solutions and only small fractions of the circular-shaped features were
formed at the edges of the 48 hours treated membrane in \( \text{H}_2\text{O}_2 + \text{Fe} + \text{Pt} \) as illustrated in Figure 1c.

![Figure 1a](image1a.png) ![Figure 1b](image1b.png) ![Figure 1c](image1c.png)

**Figure 1.** Top surface microstructures of the pristine membrane (a), heavily degraded membrane (\( \text{H}_2\text{O}_2 + \text{Fe} \) treated membrane for 36 hours used as the representative of this group) (b), and slightly degraded membrane at the edge of the sample due to the edge effect (\( \text{H}_2\text{O}_2 + \text{Fe} + \text{Pt} \) after 48 hours treatment).

The thickness of the degraded membranes after being subjected to Fenton’s reagent was measured by digital micrometer prior to the tensile test and the average thickness normalized to the pristine membrane thickness is summarized in Figure 2. A significant increase in the membrane thickness was observed when subjected to \( \text{H}_2\text{O}_2 + \text{Fe} \) for more than 12 hours. At 48 hours treatment with \( \text{H}_2\text{O}_2 + \text{Fe} \), the membrane thickness had doubled compared to the original, pristine membrane thickness. The relatively small error bars in Figure 2 indicates that the damage was macroscopically uniform throughout the membrane (excluding the sample edges) during the *ex-situ* chemical degradation. However, the membrane thickness was preserved when Pt was introduced to the membrane and/or the solution pH was reduced to highly acidic expressing that the degradation and formation of circular-shaped defects were suppressed to a great extent.
Figure 2. Normalized membrane thickness measured after being subjected to different Fenton’s solutions at certain levels of degradation. Error bars represent two standard deviations.

The top surface SEM micrographs of the heavily degraded membranes corresponding to the OM microstructure in Figure 1b are represented in Figure 3. The formation of the bubble-shaped features was observed on the membrane surface similar to the ones reported by Tang et al. [28]. The observed increase in the membrane thickness is directly attributed to the presence of these bubbles. It seems that the bubbles were elongated until the membrane local fracture strain resulting in the formation of microcracks at the top of the bubbles [28,31]. It should be noted from Figure 3 that although the bubbles were initiated throughout the sample surface, only some of them were propagated and elongated to the fracture point. The microcracks formed at the top of the bubbles may become preferred locations for gas crossover resulting in the failure of the cell.
Figure 3. SEM micrographs of the ex-situ chemically degraded membranes treated in H$_2$O$_2$ + Fe solution for 36 hours (a), 48 hours (b), and 48 hours tilted by 60° from the sample surface (c).

Figure 4 exhibits the cross sectional SEM micrographs of the H$_2$O$_2$ + Fe$^{2+}$ degraded membranes, indicating that the bubbles nucleated from the middle of the membrane thickness...
and expanded spherically. The expansion continues until the bubble connects with the adjacent bubbles resulting in “unzipping” the membrane from the middle which is expected to be critically detrimental for the desired membrane properties including the proton conductivity. Additionally, the formation of large bubbles can be detected from the background of the cross sectional images as presented in Figure 4. The formation of bubbles can be attributed to the rapid and exothermic oxidation of membrane ionomer by the products of the Fenton’s reaction.

![Figure 4. Cross sectional SEM images of the 36 hours H₂O₂ + Fe²⁺ degraded membrane. The bubbles initiated from the middle of the membrane thickness and joined the adjacent bubbles, thus forming large cavities in the membrane.](image_url)

3.2. Tensile properties

Tensile tests were conducted on the ex-situ degraded PFSA membranes and the principal tensile properties including elastic modulus, ultimate tensile strength (UTS), and final strain were extracted from the obtained stress – strain curves as presented in Figure 5. The mechanical properties of the membrane were significantly reduced after treatment in the solution of H₂O₂ + Fe²⁺. The decay in tensile properties originated from the early stages of degradation resulting in slight reduction in the elastic modulus and UTS after 12 hours of treatment. After 48 hours of treatment, the elastic modulus, UTS, and final strain were reduced with the same rate to 24%,
23%, and 26% of the pristine membrane. The comprehensive reduction observed in tensile behaviour can be attributed to the formation of bubbles during the chemical degradation tests (Figure 3). In addition, membrane molecular deterioration due to the Fenton’s treatment may also contribute to the loss in membrane ductility and facilitate breakage of ionomer fibrils. Further investigations on the fracture surface of the H₂O₂ + Fe²⁺ degraded membranes after 36 and 48 hours revealed that the final fracture resulted from the propagation and connection of the previously formed microcracks at the top of the bubbles, as illustrated in Figure 6. When subjected to tension, the microcracks are expected to expand perpendicularly to the direction of the tensile stress and join the adjacent microcracks to form larger cracks. The crack propagation continues until the critical tolerable crack length of the degraded membrane and final fracture are obtained. In summary, membrane molecular dis-entanglement accompanied with the microcrack formation due to the ex-situ chemical degradation may facilitate the failure of the membrane at lower UTS, fracture strain, and fracture energy.

On the other hand, the deterioration in mechanical properties was remarkably mitigated by the presence of Pt in the solution and/or with increasing the acidity of the solution, where the calculated mechanical properties were comparable to the ones for pristine PFSA membranes as indicated by dashed line in Figure 5. It should be noted that the majority of the tensile tests were terminated at ~160% strain due to the DMA maximum travel length limit and never reached the actual fracture point, as shown by the arrows in Figure 5c.
Figure 5. Typical mechanical properties of the *ex-situ* chemically degraded membranes obtained at 23°C – 50% RH: (a) elastic modulus, (b) ultimate tensile strength (UTS), and (c) final strain. The dashed line exhibits the pristine membrane mechanical properties. Error bars represent two standard deviations.
Figure 6. (a) Propagation and connection of two adjacent microcracks in the 36 hours H$_2$O$_2$ + Fe$^{2+}$ in-situ degraded membrane subjected to tensile stress. (b) Fracture obtained when the connected microcracks reached the critical crack length.

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Appendix G.

Fuel Cell Durability Enhancement with Cerium Oxide under Combined Chemical and Mechanical Membrane Degradation

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Fuel Cell Durability Enhancement with Cerium Oxide under Combined Chemical and Mechanical Membrane Degradation

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A CeO2 supported membrane electrode assembly (MEA) was fabricated by hot-pressing CeO2-coated electrodes and a PFSA ionomer membrane. Upon application of a combined chemical and mechanical accelerated stress test (AST), the CeO2 supported MEA showed six times longer lifetime and 40 times lower fluoride emission rate than a baseline MEA without cerium. The membrane in the CeO2 supported MEA effectively retained its original thickness and ductility despite the highly aggressive AST conditions. Most of the cerium applied on the anode migrated into the membrane and provided excellent mitigation of joint chemical and mechanical membrane degradation.

In a polymer electrolyte fuel cell (PEFC), it is imminent to achieve extension of membrane lifetime for enhancing durability and hence cost-competitiveness of the PEFC system. Hydroxyl radicals, generated from hydrogen peroxide through the Fenton reaction,1 are known to be responsible for chemical degradation of perfluorosulfonic acid (PFSA) ionomer membranes used in PEFCs.2 One approach of mitigating the attack of hydroxyl radicals is to incorporate the Ce3+/Ce4+ redox system as a regenerative radical scavenger into the membrane3–6 or catalyst layers7–9 which has been shown to reduce the fluoride emission rate during low humidity and open circuit voltage (OCV)-hold condition. Although uniform incorporation of Ce3+ by ion-exchanging of protons represented the most powerful scavenging effect on the attack of hydroxyl radicals,7,10 it can also introduce tradeoffs such as loss in high power performance due to the associated reduction in membrane conductivity.10 Moreover, cerium initially present inside a membrane was observed to migrate toward the catalyst layers during an accelerated stress test, where its mitigation function may not be preserved.8 The objective of the present work is to demonstrate the effectiveness of cerium under combined chemical and mechanical membrane degradation, representative of the actual membrane degradation mechanism during field operation of PEFCs.

Catalyzed gas diffusion electrodes (GDEs) were fabricated by coating a micro-porous layer onto a non-woven carbon paper gas diffusion layer (GDL) substrate, followed by coating a catalyst layer (CL) consisting of carbon-supported platinum catalyst and PFSA ionomer. A baseline MEA was prepared by hot-pressing a standard PFSA membrane with anode and cathode GDEs. A CeO2-MEA was prepared in the same way with CeO2-coated anode and cathode GDEs. The CeO2-coated GDEs were fabricated by spray-coating a mixture solution consisting of a commercial cerium oxide powder (Alfa Aesar, 20–150 nm) and 5% PFSA ionomer solution (Ion Power Inc., 1100 EW) on top of the anode and cathode GDEs. The CeO2 loading of the anode was controlled to be higher than for the cathode. The total loading of CeO2 was about 7 mol% of the total number of sulfonic acid sites in the membrane.

A stack consisting of five MEAs having active area of 45 cm2 per cell was subjected to a cyclic open circuit voltage (OCOV) accelerated stress test (AST) protocol,11–13 designed to induce combined chemical and mechanical membrane degradation. Prior to applying the OCOV-AST procedure, the stack was subjected to a beginning of life (BOL) conditioning procedure for 12 hrs. Fig. 1a represents the obtained trends in open circuit voltage and high frequency (HF) impedance as a function of AST operation time for a baseline MEA and a CeO2-MEA. Whereas the AST lifetime of the baseline MEA was determined to be 186 hours based on a threshold H2 leak rate,14 the lifetime of the CeO2-MEA was remarkably extended to 1,244 hours, demonstrating a six-fold enhancement in lifetime. Fig. 1b shows cumulative fluoride loss profiles concurrently obtained during the AST from the baseline and the CeO2-MEA. Whereas the cumulative fluoride loss of the baseline MEA reached 82 μmol F·cm−2 at 186 hours, that of the CeO2-MEA was only 2 μmol F·cm−2 at the same number of hours and reached 9 μmol F·cm−2 at the EOL of 1,244 hours. Correspondingly, whereas the membrane thickness of the baseline MEA at EOL was determined by scanning electron microscopy (SEM) to be 52% of that at BOL, the membrane thickness of the CeO2-MEA at EOL was about 90% of that at BOL. It is known that the Ce3+/ion scavenges the hydroxyl radical by reducing it to water and Ce4+, and is regenerated from Ce4+ by reacting with hydrogen peroxide or hydroperoxyl radical.9 The decrease in hydroxyl radical concentration inside the membrane might reduce the radical attack toward the polymer chains, resulting in reduced FER in the CeO2 supported MEA as shown in Fig. 1b. It is emphasized that the chemical-mitigated CeO2-MEA failed four times earlier than the FER-predicted lifetime of 7,630 hours. Considering that the CeO2-MEA was exposed to more hydration cycles of the AST during the extended lifetime, it is believed that the CeO2-MEA must have accumulated more mechanical fatigue damage than the baseline MEA. In fact, from postmortem failure analysis by SEM, the CeO2-MEA revealed about 25 μm wide pinholes with higher population, leading to progressive increase of hydrogen leak rate, than the baseline MEA having 100 μm wide pinholes leading to sudden increase of hydrogen leak rate. It was reported that the MEA, which experienced more mechanical fatigue damage of hygrothermal cycling, exhibited formation of gas-leak initiating pinholes at less membrane thinning of chemical degradation.14

In practical point of view, a mitigation strategy of membrane degradation should meet the practical need of high power performance. During the AST operation, the HF impedance of the CeO2-MEA was evaluated to be about 0.26 Ω·cm−2 which is 1.5 times higher than the baseline (0.18 Ω·cm−2) as shown in Fig. 1a. Polarization curves were measured intermittently during the OCOV-AST on different MEAs. Fig. 2 shows the evolution of cell voltages at different applied current densities obtained from the polarization curves of the baseline and the CeO2-MEA. While the cell voltages of the CeO2-MEA at high current densities (0.66 and 1.38 A·cm−2) were initially lower than those of the baseline MEA due to the higher ohmic resistance, the former eventually outperformed the latter at the onset of hydrogen leaks across the membrane. In our result, the addition of CeO2 on the anode and cathode CLs not only extended the membrane durability but also stabilized the high power MEA performance as a consequence.

References

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of mitigating the membrane degradation and the performance losses induced by hydrogen leaks.

The mechanical properties of the membrane were previously shown to play an important role in the combined chemical and mechanical degradation process and were therefore evaluated at BOL and EOL in the present experiments using the same procedure. The obtained stress–strain curves of the baseline and CeO2-MEAs are depicted in Fig. 3 and the extracted properties are summarized in Table I. Both BOL MEAs exhibited similar tensile curves with ductile behavior and elongated to the maximum traction length of the instrument (~160% strain) without fracture. In contrast, the baseline MEA at EOL was fractured quickly at low levels of strain (2.3%), indicating that the membrane experienced severe embrittlement as a result of the degradation process. However, the CeO2-MEA at EOL still exhibited good ductility up to the strain limit of the instrument, revealing that the CeO2-MEA retained much of the original ductility of the BOL membrane even after being exposed to a considerably longer period of AST operation. The elastic modulus of the baseline MEA was increased by 25% from BOL to EOL, indicating a stiffening effect, while that of the CeO2-MEA remained constant. Similarly, the ultimate tensile strength (UTS) of the baseline MEA diminished by 70% upon AST operation, while the UTS of the CeO2-MEA was effectively preserved. In addition to fluoride release and general thinning, the decay in the intrinsic mechanical properties represents evidence of changes in the polymer structure and morphology under the AST conditions. On the other hand, the preserved mechanical properties of the CeO2-MEA at EOL demonstrates that the addition of CeO2 effectively mitigated the chemically induced degradation of the polymer while substantially preventing the loss in mechanical strength and ductility, otherwise known to be a precursor to mechanical failure under COCV-AST conditions.

The distribution and concentration of cerium in the CeO2-MEAs were determined by neutron activation analysis (NAA). Fig. 4
The CeO₂ supported MEA, mainly representing the ohmic resistance, most of the cerium originally situated at the anode was dissolved and was in the anode and cathode catalyst layers, leaving little cerium across the MEA shown by X-ray fluorescence (XRF) spectroscopy. The cerium concentration in the membrane obtained by NAA. The cerium was determined to occupy 3.0 mol% of the total number of sulfonic acid sites in the membrane at BOL state and migrated further into the membrane up to 5.1 mol% at EOL state. Albeit the present result is promising, the stability of cerium in the MEA is subject to further research.

In summary, upon subjecting to a combined chemical and mechanical accelerated stress test, the CeO₂ supported MEA showed six times longer lifetime and 40 times lower fluoride emission rate than a baseline MEA without cerium. The EOL membrane in the CeO₂ supported MEA was observed to retain its thickness and ductility comparable to the BOL membrane. The CeO₂ applied on the electrodes is believed to be dissolved into Ce ions which migrate into the membrane and reduce the rate of chemical degradation through hydroxyl radical scavenging. This action was shown to be effective under combined chemical and mechanical degradation conditions, which suggests that mechanical failures can be delayed by mitigation of chemical degradation and avoidance of the associated loss in mechanical strength.

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table

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<thead>
<tr>
<th>Properties</th>
<th>Baseline CCM</th>
<th>CeO₂-CCM</th>
</tr>
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<tbody>
<tr>
<td>Elastic modulus (MPa)</td>
<td>142 (± 9)</td>
<td>177 (± 17)</td>
</tr>
<tr>
<td>Ultimate tensile strength (UTS, MPa)</td>
<td>6.4 (± 0.3)</td>
<td>2.0 (± 1.1)</td>
</tr>
<tr>
<td>Final strain (%)</td>
<td>160 (limit)</td>
<td>160 (limit)</td>
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Figure 4. Cerium concentrations determined by Neutron Activation Analysis (NAA) at anode catalyst layer, membrane, and cathode catalyst layer from BOL, BOL-conditioned, and EOL MEAs where CeO₂ was initially coated on the electrodes.

References