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Short communication

Ex-situ tensile fatigue-creep testing: A powerful tool to simulate *in-situ* mechanical degradation in fuel cells

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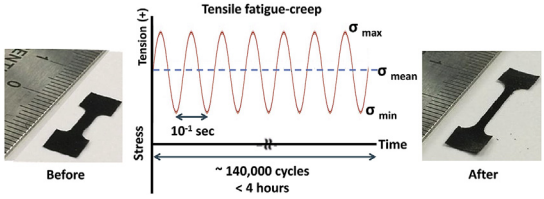
HIGHLIGHTS

- An *ex-situ* tensile fatigue-creep accelerated stress test (TFC-AST) is proposed.
- Fatigue induces work hardening and increased brittleness due to microcracks.
- Creep induces an elongated, metastable ionomer morphology.
- The TFC-AST is shown to be a rapid, economical alternative to *in-situ* tests.

GRAPHICAL ABSTRACT



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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

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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 due to their enhanced mechanical strength. 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 *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 *ex-situ* mechanical stress and *in-situ* hygrothermal stress in order to quality the former approach for more general use. The objective of the present work is therefore to experimentally validate an *ex-situ* tensile fatigue-creep (TFC) test in the context of *in-situ* mechanical membrane degradation and to qualify its use as an alternative, low-cost mechanical AST protocol. The proposed *ex-situ* approach utilizes the mechanical-hygrothermal stress analogy in order to apply stress at much higher frequency than conventional *in-situ* tests. The proposed TFC test is evaluated against the previously reported *in-situ* hygrothermal AST [20] through systematic investigation of the changes in mechanical, hygrothermal, and microstructural properties during the experiments.

Gas diffusion electrode (GDE) based membrane electrode assemblies (MEAs) were utilized in this work. Each anode or cathode GDE was fabricated by coating a catalyst layer on a gas diffusion layer consisting of a non-woven carbon fiber paper substrate and a carbon nano-particle and PTFE based micro-porous layer (MPL). 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 *in-situ* fuel cell conditions. CCMs were prepared by removing the gas diffusion layers from the sides of 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]. 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. After equilibration in the tensile fixture, the specimens were subjected to a 10 Hz sinusoidal cyclic load with 6.1 MPa mean stress and a minimum to maximum stress ratio (R) of 0.2. The tests were operated 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. 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 during the early stages of loading [9], which indicates that creep action dominated the initial phase of the experiment (similar to a conditioning effect). This was followed by a strain plateau region until failure, where fatigue action 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 analyzer (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}). 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%–50%, 50%–70%, and 70%–90% and at constant RH (90%) while the temperature was raised from 20 °C to 40 °C, 40 °C–60 °C, and 60 °C–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 h 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 Fig. 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