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Mechanical degradation of fuel cell membranes under fatigue fracture tests

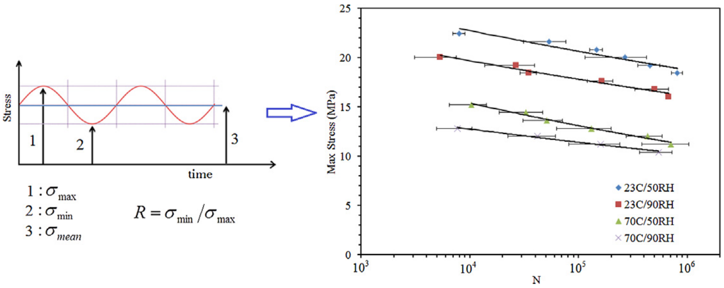
Ramin M.H. Khorasany, Alireza Sadeghi Alavijeh, Erik Kjeang*, G.G. Wang,
R.K.N.D. Rajapakse

School of Mechatronic Systems Engineering, Simon Fraser University, 250-13450 102 Avenue, Surrey, BC, V3T 0A3, Canada

HIGHLIGHTS

- An ex-situ tensile fatigue fracture test of fuel cell membranes is proposed.
- The membrane fatigue lifetime is a function of stress, temperature, and humidity.
- The effect of temperature on fatigue life is stronger than that of humidity.
- A critical level of elongation is shown to lead to membrane fracture.

GRAPHICAL ABSTRACT



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ABSTRACT

The effects of cyclic stresses on the fatigue and mechanical stability of perfluorosulfonic acid (PFSA) membranes are experimentally investigated under standard fuel cell conditions. The experiments are conducted ex-situ by subjecting membrane specimens to cyclic uniaxial tension at controlled temperature and relative humidity. The fatigue lifetime is measured in terms of the number of cycles until ultimate fracture. The results indicate that the membrane fatigue lifetime is a strong function of the applied stress, temperature, and relative humidity. The fatigue life increases exponentially with reduced stresses in all cases. The effect of temperature is found to be more significant than that of humidity, with reduced fatigue life at high temperatures. The maximum membrane strain at fracture is determined to decrease exponentially with increasing membrane lifetime. At a given fatigue life, a membrane exposed to fuel cell conditions is shown to accommodate more plastic strain before fracture than one exposed to room conditions. Overall, the proposed ex-situ membrane fatigue experiment can be utilized to benchmark the fatigue lifetime of new materials in a fraction of the time and cost associated with conventional in-situ accelerated stress testing methods.

1. Introduction

The polymer electrolyte fuel cell (PEFC) is a promising clean energy technology for converting chemical energy into electrical energy. PEFCs have a wide range of applications including uses in cars, heavy-duty vehicles, materials handling, and backup power systems. Widespread uses of this technology can be of a great benefit to the environment through reducing greenhouse gas emissions [1]. A typical PEFC consists of a membrane electrode assembly (MEA) situated between two flow field plates. The MEA is composed of an ion-conducting membrane flanked by two electrodes (anode and cathode) and two gas diffusion layers.

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* Corresponding author.
E-mail address: ekjeang@sfu.ca (E. Kjeang).

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Generating clean energy from hydrogen fuel cells has been the subject of numerous scholarly works ranging from low-power micro fuel cells [2] to high-power fuel cell stacks [3–5].

One of the major technical challenges of polymer electrode fuel cells is the durability of the MEA under dynamic operating conditions [1]. The stability of the MEA is commonly limited by the initiation of pinholes and micro cracks in the membrane, which may lead to undesirable hydrogen leaks, performance losses, and ultimate failure. Membrane damage can be initiated and propagated as a result of chemical and mechanical degradation mechanisms. Chemical degradation has been widely studied in the literature [5]. It has been reported that factors such as contamination of transition metal ion, reactant gas crossover, and variation in the temperature and potential have direct effect on the chemical degradation of commonly used perfluorosulfonic acid (PFSA) ionomer membranes [6,7]. Open circuit voltage (OCV) operation has been established as an in-situ accelerated stress test to accelerate the rate of chemical degradation [8,9]. A significant body of work is available on chemical membrane degradation mechanisms and mitigation strategies [10–18].

It is well known that the mechanical response of the membrane to dynamic operating conditions depends on the loading rate [19–21]. Furthermore, when the membrane is subjected to a constant strain, the stress relaxes over time [20]. On the other hand, the membrane also exhibits mechanical creep due to sliding of the polymer chains with respect to one another when subjected to a constant stress [21]. Ex-situ mechanical testing of the membrane has been widely used to determine its properties and ability to respond to applied stress [19,22]. The mechanical properties were found to vary with environmental conditions [23,24]. At elevated levels of environmental conditions, the elastic modulus and yield point of the membrane substantially decreased [22,25]. The creep and relaxation behavior of the membrane is also affected by the environmental conditions. At elevated levels of relative humidity, the stress relaxation time was shown to decrease due to the lower driving force [26]. Furthermore, the creep strain of the membrane increased with elevated temperature [27]. A previous experimental study by our group [19] revealed that catalyst coated membranes exhibit significantly different mechanical behavior than pure PFSA membranes, and would therefore respond differently under externally applied loads.

While chemical membrane degradation is one of the main stressors in membrane thinning and ultimate failure of the MEA, mechanical degradation is also considered to play a significant role in initiation and propagation of micro cracks and fractures inside the membrane. The membrane water absorption-desorption that occurs during typical fuel cell duty cycles causes swelling and contraction in the membrane [28]. As a result, dynamic stress patterns are created in the membrane that ultimately limit the membrane life due to fatigue and fracture. Ex-situ mechanical degradation has been studied by exposing the membrane to cyclic environmental conditions [29] or uniaxial mechanical loading [30]. In-situ mechanical accelerated stress testing was generally performed using wet/dry humidity cycles [9,31–34]. Lim et al. [35] applied an advanced accelerated stress test protocol to simultaneously study the effect of chemical and mechanical degradation mechanisms on the properties of the membrane.

Modeling the ex-situ and in-situ response of the membrane under hygrothermal and mechanical loadings is another challenge in further understanding the mechanical degradation process of the membrane [22,36,37]. In earlier attempts [34], linear elastic and plastic behavior with isotropic hardening was adopted for the response of the membrane. As stated earlier, due to time dependency of the response, such models cannot fully represent the mechanical behavior of the membrane [19]. It was shown that adopting an elastic-viscoplastic model cannot only capture the time-dependent response of the membrane but is also capable of predicting the response in different hygrothermal conditions [38]. These models were then used to study the effect of ex-situ biaxial tensioning on the membrane [39].

In previously published results, the mechanical stability of the membrane was found to be significantly affected by the cyclic change in the environmental conditions and in particular by cyclic changes in the relative humidity (RH) [29]. However, the membrane yield stress and yield strain did not change due to RH cycling. Conversely, with deep RH cycles, the strain to failure was found to significantly drop [29]. Two different approaches have been established regarding the failure determination of the membrane under mechanical cyclic loadings. In the first approach, the surface cracks on the membrane are monitored until a critical crack density is reached [40,41]. In the second approach, the failure of the membrane is defined as the mechanical rupture of the specimen [21,30,42,43]. Compared to the second approach [30], the first approach [29] predicts a significantly lower number of cycles to failure.

While mechanical degradation has been studied extensively using both ex-situ and in-situ techniques [16,44], as described above, the process of material *fatigue* leading to micro crack initiation and ultimate fracture propagation and failure is not yet well understood. For other more common materials such as metals, fatigue is a well-established concept and its role in material degradation and failure has been proven through comprehensive research and testing [45,46]. Hence, the main objective of the present work is to develop a comprehensive, fundamental understanding of the fatigue-fracture behavior of typical ionomer membranes during conditions relevant for fuel cell operation. An ex-situ tensile fatigue experiment is designed to characterize the effect of mechanically induced cyclic loadings on the fatigue lifetime of the membrane under a range of environmental conditions. A statistical design of experiments approach is employed to investigate the effects of relative humidity and temperature on the maximum stress and strain before the rupture. The proposed fatigue-fracture experiment is intended to shed light on the complex mechanical membrane degradation mechanism and can potentially be utilized as an ex-situ alternative to conventional in-situ accelerated stress tests for mechanical membrane durability.

2. Experimental technique

2.1. Materials

Commercially available Nafion® NR-211 perfluorosulfonic acid (PFSA) ionomer membrane specimens of 25 μm thickness were prepared from a single batch of material to warrant the consistency of the results. To reduce the effect of stress concentration in the clamping area, the specimens were cut in dog bone shapes, using the die shape illustrated in Fig. 1. The same geometry was previously used for a different type of membrane [30]; however, the

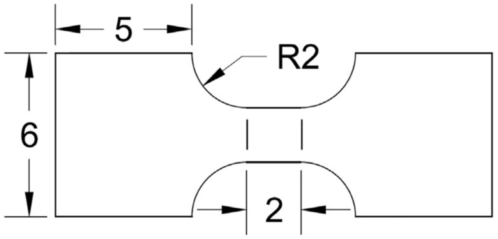

Fig. 1. Schematic of the specimen geometry with two marks to identify its straight portion (mm).