



Numerical evaluation of crack growth in polymer electrolyte fuel cell membranes based on plastically dissipated energy



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HIGHLIGHTS

- *In-situ* crack growth under relative humidity cycling is modeled.
- Crack growth is based on plastically dissipated energy.
- Crack growth is simulated by node release technology.
- Crack growth rate is directly obtained from finite element simulation.
- Numerical results capture experimental observations.

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ABSTRACT

Understanding the mechanisms of growth of defects in polymer electrolyte membrane (PEM) fuel cells is essential for improving cell longevity. Characterizing the crack growth in PEM fuel cell membrane under relative humidity (RH) cycling is an important step towards establishing strategies essential for developing more durable membrane electrode assemblies (MEA). In this study, a crack propagation criterion based on plastically dissipated energy is investigated numerically. The accumulation of plastically dissipated energy under cyclical RH loading ahead of the crack tip is calculated and compared to a critical value, presumed to be a material parameter. Once the accumulation reaches the critical value, the crack propagates via a node release algorithm. From the literature, it is well established experimentally that membranes reinforced with expanded polytetrafluoroethylene (ePTFE) reinforced perfluorosulfonic acid (PFSA) have better durability than unreinforced membranes, and through-thickness cracks are generally found under the flow channel regions but not land regions in unreinforced PFSA membranes. We show that the proposed plastically dissipated energy criterion captures these experimental observations and provides a framework for investigating failure mechanisms in ionomer membranes subjected to similar environmental loads.

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1. Introduction

As a clean energy-enabling technology, polymer electrolyte membrane (PEM) fuel cells have a wide range of potential applications from portable power sources and transportation to large-scale stationary power systems [1]. However, pre-mature failure of the membranes is one of the key challenges to wide-spread commercialization of PEM fuel cells [2,3].

PEM fuel cell membranes usually fail because of increased crossover of the reactant gases from through-thickness cracks or pinholes which are formed by a combination of chemical and mechanical degradation during fuel cell operation [2,4–7]. The initiation and propagation of cracks in polymer electrolyte membranes is not yet fully understood but it is generally considered to be caused by a combination of environmental and operational factors, such as hygrothermally induced mechanical stress [2,4,5,8]. Other typical failure drivers include: chemical degradation caused by attack from peroxide and hydroperoxide radicals produced from the side reactions during cell operation, defects from the membrane manufacturing process or membrane electrode assembly

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(MEA) fabrication process, and thermal degradation due to operating temperature around the glass transition temperatures of the perfluorosulfonic acid (PFSA) polymers [6,8]. However, the actual failure mechanisms in the cell are complex since a combination of chemical, mechanical and even thermal stressors results in synergistic effects accelerating the degradation [2,5,7,9–11]. One such synergistic effect is the chemical decomposition of ionomer causing local defects, which act as crack-initiation sites that can grow under mechanical stresses, leading to enhanced crossover and higher rates of chemical decomposition. Moreover, it has recently been shown that the defect-growth is a good metric to monitor the membrane's lifetime and fatigue behavior since there exists a correlation between the gas crossover and defect size in membranes [12,13]. Thus, investigation of crack-growth mechanisms due to mechanical stresses during RH cycling is of great interest for elucidating the factors controlling chemical/mechanical durability and developing strategies for improved membrane stability.

The mechanical stresses are associated with swelling and shrinkage of the membrane as a result of environmental changes inside the cell during operation. Hydration and heating lead to hygrothermal swelling strains in the membrane [14–17]. However, the membranes are generally constrained in the fuel cell system by gas diffusion layers (GDL), bipolar plates and gaskets, preventing the membrane from expanding. Consequently, significant compressive stresses can develop with increased temperature and swelling. If there are imperfections in the interface between the MEA and GDL, the MEA may buckle when subjected to compressive stress [18]. However, here we assume that the MEA and GDL are perfectly bonded, and there are no defects in the GDL. Therefore, potential buckling is not considered here. The stresses developed from humidity cycling frequently exceed the elastic limit of the membrane, resulting in permanent deformation of the membrane. If the stress exceeds the elastic limit during swelling, residual tensile stresses will likely develop during shrinkage in the membrane. In these cases, the membrane is subjected to cyclical compressive and tensile stresses during the cyclical hydration-dehydration and heating-cooling occurring during fuel cell operation [14–17]. Such loading encourages crack initiation and propagation, and is typically referred as fatigue loading. Thus, with the combination of the cyclic fatigue loading and the environmental factors, microcracks can easily initiate and grow into through-thickness cracks, increasing the gas crossover through the membrane and causing the eventual catastrophic failure of the PEM fuel cells [4].

Lai et al. [19] investigated the failure modes and crack morphology of membrane samples after RH cycling test using cross-sectional micrographs. Fig. 1, reprinted from Lai et al. [19], shows micrographs of three polymer electrolyte membranes removed from a cell after undergoing humidity cycling. A wide range of crack lengths were seen in each failed membrane sample, implying that the cracks in the membrane grew gradually instead of catastrophically. Most of the cracks extended from the electrodes into the membrane, suggesting that the cracks initiate in the electrodes and then propagate through the membrane during cyclic fatigue loading. Characterizing this fatigue crack growth under RH cycling is essential for understanding and improving the mechanical durability of PEM fuel cells.

Currently, there is very little work on modeling *in-situ* crack growth in polymer electrolyte membrane under relative humidity cycling in the literature. Previous mechanistic models on membrane deformation provided qualitative correlations between the stresses and lifetime but they either lacked a defect-growth mechanism [17,20] or modeled pinhole deformation *ex-situ* only [7]. Banan et al. [21] recently developed a cohesive zone model for crack growth in a PEM fuel cell under relative humidity cycling.

However, instead of modeling the crack growth through the thickness direction, which is the more general case observed in cell testing, they modeled crack growth in the in-plane direction using linear elastic-plastic material properties. Thus far, no attempt has been made to model *in-situ* crack-propagation in a membrane during cyclical hygrothermal loadings using time-dependent viscoplastic membrane mechanical properties, which is important for an accurate representation of damage accumulation with time.

However, considerable research has been devoted to modeling fatigue crack growth in other materials. Several useful methods have been proposed including damage mechanics [22,23], stress intensity factors [24,25] and energy criteria [26–30]. In 1967, Rice [26] first suggested the use of plastically dissipated energy as a criterion to study fatigue crack propagation. For ductile materials such as ductile metals and polymers, there can be significant plastic deformation at the crack tip during loading [26,31,32]. In metals, dislocation generation and motion are associated with plastic deformation, and in polymers shear banding and crazing are related with plastic deformation, both of which are directly associated with fatigue [26,33]. Following the work of Rice, there have been many analytical [27,34–36], experimental [37,38] and numerical [28,30] investigations into the application of plastically dissipated energy in predicting fatigue crack propagation.

Cojocaru and Karlsson [30] first proposed a numerical approach based on plastically dissipated energy to predict the fatigue crack growth rate directly from finite element simulations. In this method, the crack growth rate is the key result from the simulation. For example, with a two-dimensional (2D) plane strain model, changes in crack growth rate under negative load ratios and tensile overloads were simulated and the results were seen to be in qualitative agreement with experimental observations. With the same methodology, Nittur et al. [39] extended the technique and numerically predicted Paris regime crack growth rate (a power law relationship between the crack growth rate during cyclic fatigue loading and range of stress intensity factor [40]) based on plastically dissipated energy. Using this model they were able to predict the parameters used in the Paris Law and were able to produce a very good match between the numerically predicted and experimentally determined crack growth rates.

In the present work, we modify the numerical approach developed in Refs. [30,39] to study *in-situ* crack growth in the through-thickness direction under humidity cycling in a PEM fuel cell model. We will show that the plastically dissipated energy criterion can qualitatively capture a range of well-established experiment observations including crack propagation in unreinforced perfluorosulfonic acid (PFSA) membrane, crack propagation in expanded polytetrafluoroethylene (ePTFE) reinforced PFSA membrane, the differences between crack propagation under the channel and land regions in a typical flow channel architecture as well as the effect of fuel cell clamping pressure on membrane cracking.

2. Numerical framework

2.1. General concepts

The general numerical modeling concepts used in this work have been presented in the literature [30,39] but will be summarized here for clarity. This method is based on the fundamental assumption that, from a continuum perspective, fatigue cracks propagate because of progressive material degradation at the microscale in a small domain near the crack tip. Since plastically dissipated energy is a non-decreasing parameter directly associated with microscale deformation, it can therefore serve as a useful criterion for the prediction of fatigue crack growth [30].

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