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

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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

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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.

Keywords: Polymer electrolyte membrane (PEM); Durability; Fatigue; Cyclic crack growth; Plastically dissipated energy; Numerical simulation

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 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 (MEA) fabrication process, and thermal degradation due to operating

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4 temperature around the glass transition temperatures of the perfluorosulfonic acid (PFSA)
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6 polymers [6,8]. However, the actual failure mechanisms in the cell are complex since a
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8 combination of chemical, mechanical and even thermal stressors results in synergistic
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10 effects accelerating the degradation [2,5,7,9-11]. One such synergetic effect is the
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12 chemical decomposition of ionomer causing local defects, which act as crack-initiation
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14 sites and could grow under mechanical stresses, leading to enhanced crossover and higher
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16 rates of chemical decomposition. Moreover, it has recently been shown that the defect-
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18 growth is a good metric to monitor the membrane's lifetime and fatigue behavior since
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20 there exists a correlation between the gas crossover and defect size in membranes [12,13].
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22 Thus, investigation of crack-growth mechanisms due to mechanical stresses during RH
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24 cycling is of great interest for elucidating the factors controlling chemical/mechanical
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26 durability and developing strategies for improved membrane stability.
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33 The mechanical stresses are associated with swelling and shrinkage of the
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35 membrane as a result of environmental changes inside the cell during operation.
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37 Hydration and heating lead to hygrothermal swelling strains in the membrane [14-17].
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39 However, the membranes are generally constrained in the fuel cell system by gas
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41 diffusion layers (GDL), bipolar plates and gaskets, preventing the membrane from
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43 expanding. Consequently, significant compressive stresses can develop with increased
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45 temperature and swelling. If there are imperfections in the interface between the MEA
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47 and GDL, the MEA may buckle when subjected to compressive stress [18]. However,
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49 here we assume that the MEA and GDL are perfectly bonded, and there are no defects in
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51 the GDL. Therefore, potential buckling is not considered here. The stresses developed
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53 from humidity cycling frequently exceed the elastic limit of the membrane, resulting in
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4 permanent deformation of the membrane. If the stress exceeds the elastic limit during
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6 swelling, residual tensile stresses will likely develop during shrinkage in the membrane.
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8 In these cases, the membrane is subjected to cyclical compressive and tensile stresses
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10 during the cyclical hydration-dehydration and heating-cooling occurring during fuel cell
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12 operation [14-17]. Such loading encourages crack initiation and propagation, and is
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14 typically referred as fatigue loading. Thus, with the combination of the cyclic fatigue
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16 loading and the environmental factors, microcracks can easily initiate and grow into
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18 through-thickness cracks, increasing the gas crossover through the membrane and
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20 causing the eventual catastrophic failure of the PEM fuel cells [4].
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26 Lai et al. [19] investigated the failure modes and crack morphology of membrane
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28 samples after RH cycling test using cross-sectional micrographs. Fig. 1, reprinted from
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30 Lai et al. [19], shows micrographs of three polymer electrolyte membranes removed from
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32 a cell after undergoing humidity cycling. A wide range of crack lengths were seen in each
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34 failed membrane sample, implying that the cracks in the membrane grew gradually
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36 instead of catastrophically. Most of the cracks extended from the electrodes into the
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38 membrane, suggesting that the cracks initiate in the electrodes and then propagate
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40 through the membrane during cyclic fatigue loading. Characterizing this fatigue crack
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42 growth under RH cycling is essential for understanding and improving the mechanical
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44 durability of PEM fuel cells.
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Figure 1 Representative postmortem cross-sectional micrographs of the three commercially available PFSA membrane (a) Nafion^{®†} NR-111 membrane, (b) Nafion[®] NR-111 membrane (c) Nafion^{®‡} N111-IP membrane (d) Gore-Select^{®‡} 57 membrane and (e) Gore-Select^{®57} membrane [19] (Reprint under permission from Wiley Books)

Currently, there is very little work on modelling *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

[†] Nafion[®] is a registered trademark of E.I. DuPont De Nemours & Co.

[‡] Gore-Select[®] is a registered trademark of W.L. Gore Inc.

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4 direction using linear elastic-plastic material properties. Thus far, no attempt has been
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6 made to model *in-situ* crack-propagation in a membrane during cyclical hygrothermal
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8 loadings using time-dependent visco-plastic membrane mechanical properties, which is
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10 important for an accurate representation of damage accumulation with time.
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14 However, considerable research has been devoted to modeling fatigue crack
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16 growth in other materials. Several useful methods have been proposed including damage
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18 mechanics [22,23], stress intensity factors [24,25] and energy criteria [26-30]. In 1967,
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20 Rice [26] first suggested the use of plastically dissipated energy as a criterion to study
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22 fatigue crack propagation. For ductile materials such as ductile metals and polymers,
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24 there can be significant plastic deformation at the crack tip during loading [26,31,32]. In
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26 metals, dislocation generation and motion are associated with plastic deformation, and in
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28 polymers shear banding and crazing are related with plastic deformation, both of which
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30 are directly associated with fatigue [26,33]. Following the work of Rice, there have been
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32 many analytical [27,34-36], experimental [37,38] and numerical [28,30] investigations
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34 into the application of plastically dissipated energy in predicting fatigue crack
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36 propagation.
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43 Cojocaru and Karlsson [30] first proposed a numerical approach based on
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45 plastically dissipated energy to predict the fatigue crack growth rate directly from finite
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47 element simulations. In this method, the crack growth rate is the key result from the
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49 simulation. For example, with a two-dimensional (2D) plane strain model, changes in
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51 crack growth rate under negative load ratios and tensile overloads were simulated and the
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53 results were seen to be in qualitative agreement with experimental observations. With the
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55 same methodology, Nittur et al. [39] extended the technique and numerically predicted
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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 Ref [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

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4 associated with microscale deformation, it can therefore serve as a useful criterion for the
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6 prediction of fatigue crack growth [30].
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9 In this method, the accumulated plastically dissipated energy in a designated
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11 dissipation domain (Fig. 2a) around the crack tip is calculated as the summation of the
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13 plastically dissipated energy over all the elements in the domain and is denoted as W^p .
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15 This value is compared with a pre-determined critical value, W_{cr}^p . If the accumulated
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17 plastically dissipated energy in the domain exceeds the critical value, the crack will
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19 propagate and the domain will move accordingly to occupy the same region relative to
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21 the new crack tip. Thus, the rate of crack propagation is not prescribed *a-priori* but is
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23 obtained from simulations. The critical value, W_{cr}^p , is a material parameter, analogous to
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25 yield strength or critical stress intensity, which needs to be determined experimentally.
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27 Currently to the knowledge of the authors, no such values for this parameter are available
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29 in the literature for PFSA membrane. Therefore, in this work, the critical value of the
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31 plastically dissipated energy will be assumed to test the viability of the methodology. In
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33 the future, this value can be determined from experiments, and easily implemented in the
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35 methodology to provide accurate, quantitative investigations [39].
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Figure 2 (a) Illustration of dissipation domain in front of the crack tip [30]; (b) Illustration of the shape and size of dissipation domain used in finite element simulation

The current work differs from the previously cited numerical studies on fatigue crack growth, in that under typical fuel cell loading conditions, plastic energy is dissipated throughout a large portion of the PSFA membrane during any particular load cycle [14-17]. However, we have been able to show that there is significantly greater accumulation near the crack tip because of the stress concentration induced by the crack. Therefore, the dissipation domain in this study was chosen to capture the majority of the dissipated plastic energy increment around the crack tip, yet not to have that increment

obscured by the increase in dissipated energy in the rest of the membrane. A systematic investigation on the appropriate size of the dissipation domain is discussed in the Appendix.

2.2 Propagation Scheme

At the end of each loading cycle, the accumulated plastically dissipated energy in the dissipation domain is calculated and compared with the critical value W_{cr}^p . As noted earlier, this parameter is given an assumed value. If $W^p < W_{cr}^p$, the crack tip remains in its current location and another loading cycle is applied. If $W^p \geq W_{cr}^p$, the crack propagates along the pre-defined crack path. In this work the crack is assumed to propagate along a pre-defined straight line in the through-thickness direction. This crack path is based on experimental observations which suggest that through the thickness is the prevalent crack path for a fuel cell membrane under relative humidity cycling (for example see Fig. 1). In addition, from previous simulations [14-17], in-plane stress is the dominant stress in the membrane during humidity cycling. As a result, Mode I crack growth is the dominant crack growth mode for through-thickness cracks. The propagation of the crack is implemented by node release and consequently the introduction of a new increment of crack surface. Once the crack propagates, the dissipation domain is moved to correspond to the new crack tip location and the accumulated plastically dissipated energy is determined in the new dissipation domain. If the plastically dissipated energy inside the new domain is still above the critical value, another node is released and the dissipated energy is assessed again. This is repeated until the dissipated energy in the region is below the critical value, at which time the crack stops propagating for this load

increment and a new loading cycle is simulated. This algorithm is illustrated in Fig. 3. Following this procedure, a propagation rate, or the crack length as a function of cycle number, can be obtained from the finite element simulation.

Figure 3 Illustration of the node release algorithm for crack propagation analysis

3. Finite Element Model

3.1 Geometry

Two-dimensional plane strain models are created for representative unit volumes of a PEM fuel cell using the commercial finite element package ABAQUS [41]. The specific geometric models used in this study are adapted from our previous work [14-16,42] and a sample model is illustrated in Fig. 4a.

Repetitive lands and grooves of bipolar plates form the gas channels in a fuel cell unit volume. For this specific example geometry, the finite element model consists of two

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4 half lands and one whole channel. The right and left edges have symmetric boundary
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6 conditions applied to represent the repeating of the land-groove geometry. A fixed
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8 clamping displacement, to prevent any overall expansion in the thickness direction (y-
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10 direction in the FE model), is applied to the top surface in Fig. 4a, corresponding to the
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12 case where the fuel cell stack is clamped by relatively rigid bolts. A symmetry boundary
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14 condition is applied to the bottom surface. For the results and discussion in Section 4.1,
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16 4.2 and 4.3, the clamping displacement applied is zero, meaning that the top surface is
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18 fixed at no load during ambient conditions. In Section 4.4, the influence of different
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20 clamping displacements is discussed.
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Figure 4 (a) A two-dimensional representative model of a fuel cell unit with an initial crack under channel region (not to scale); (b) A two-dimensional representative model of a fuel cell unit with an initial crack under land region (not to scale); (c) Schematic of two types of MEA(not to scale).

Two types of membrane electrode assembly (MEA) are modeled and are illustrated in Fig. 4c. First, an MEA containing only unreinforced PFSA ionomer (u-PFSA) membrane is modeled as a three-layer sandwich structure with electrodes coated

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4 onto both sides of unreinforced PFSA [42]. Second, an MEA with core reinforced PFSA
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6 membranes is modeled as a five-layer structure with a layer of reinforced PFSA (r-PFSA)
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8 in the middle of the membrane region [43]. The electrodes, unreinforced PFSA (u-PFSA)
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10 and reinforced PFSA (r-PFSA) are all assumed perfectly bonded [41]. A pre-existing
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12 crack of length 13 μm is assumed, which extends through one electrode (12 μm thick)
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14 and 1 μm into PFSA membrane. The focus in this work is on the propagation of the crack.
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16 Initiation of the crack requires a different type of analysis and is not included in the
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18 current study.
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24 To compare crack growth in different regions of the membrane, the finite element
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26 model in Fig. 4a is also modified to include one whole land and two half channels as
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28 illustrated in Fig. 4b. The same initial crack length (13 μm) is assumed in the model
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30 under the land region.
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34 The structurally refined mesh along the crack path is composed of a uniform array
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36 of square, iso-parametric quadratic CPE4RT elements [41] with size 0.2 μm by 0.2 μm .
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38 This level of mesh refinement was chosen following a convergence study. This study
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40 showed that between mesh sizes of 0.2 μm and 0.15 μm , the accumulation of plastically
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42 dissipated energy for the same sized dissipation domain differs by only 6% and the
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44 average crack growth rate differs by 8%, thus showing fairly good mesh convergence.
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46 This mesh size also allows for crack growth through a significant portion of the
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48 membrane thickness during the simulation. Using this mesh, the crack propagates in
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50 increments of 0.2 μm each time the plastically dissipated energy in the dissipation
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52 domain reaches the critical value.
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3.2 Material Properties

The material properties of the components in the finite element model are as follows:

1. The bipolar plates are linear elastic with elastic modulus of 10 GPa and Poisson's ratio of 0.25 [42]. Hygrothermal expansion is neglected.
2. The gas diffusion layers (GDL) are linear elastic and transversely isotropic with in-plane elastic modulus of 1500 MPa and out-of-plane elastic modulus of 9 MPa and Poisson's ratio of zero [42]. Hygrothermal expansion is neglected.
3. The electrodes are viscoelastic-plastic with material property parameters determined in Lu et al. [44]. Hygrothermal expansion is neglected.
4. The unreinforced PFSA (u-PFSA) is viscoelastic-plastic with material property parameters determined in Khattra et al. [42], with Poisson's ratio of 0.4 [45]. The PFSA membrane is the only component that experiences hygrothermal expansion and the hygrothermal expansion is assumed to be isotropic for simplicity.
5. When the model includes core reinforced PFSA membrane, the reinforced PFSA (r-PFSA) is viscoelastic-plastic with material property parameters determined in Khattra et al. [43].

3.3 Relative Humidity Cycling

To generate cyclic loading on the membranes, we use a relative humidity (RH) cycling test developed by W. L. Gore & Associates Inc. to assess the mechanical

durability of the membrane in the absence of chemical reactions [46]. This is a similar testing protocol to the one used in the experiments by Lai et al. [19]. The cycling test consists of forcing saturated air at 100% relative humidity (RH) through the flow channels on both the anode and cathode side of the MEA for 10s, followed dry air of 30% relative humidity (RH) for 50s, while the fuel cell is held at a constant temperature of 80 °C. This cycling test is simulated in the finite element models as follows:

1. *Initial condition:* $T = 25\text{ }^{\circ}\text{C}$ and 30% RH. The water content λ , defined as the number of water molecules attached to each sulfonic acid SO_3^- group [47], corresponding to 30% RH is $\lambda = 2$. (The clamping displacement is also set at this stage of the simulation.)
2. *Hydration:* $T = 80\text{ }^{\circ}\text{C}$ and 100% RH. The temperature and water content are increased to these values at a constant rate over 1s. The water content λ corresponding to 100% RH is 14 and is held for 10s, while the temperature is held at 80 °C for the rest of the simulation.
3. *Dehydration:* $T = 80\text{ }^{\circ}\text{C}$ and 30% RH. The water content λ is reduced to 2 over 1s and kept for 50s.

3.4 Dissipation Domain and Criterion

For the results that follow, the dissipation domain was chosen to be a rectangular region, extending 1.6 μm (8 elements) in front of, and 1.6 μm (8 elements) to either side of the crack tip (Fig. 2b). As described in the Appendix, a parametric study was performed to determine the domain geometry needed to capture the majority of the dissipated plastic energy increment around the crack tip, yet not to have that increment

obscured by the increase in dissipated energy in the rest of the membrane. The critical value for the plastically dissipated energy in a specific domain is assumed to be a material parameter that needs to be determined by experiments. However at present, such values, to the knowledge of the authors, are not available in open literature for unreinforced PFSA or ePTFE reinforced PFSA. Therefore, the criterion for this study is selected to be $2.0\text{E-}6 \text{ N}\cdot\text{mm}$ for both unreinforced PFSA and ePTFE reinforced PFSA to achieve crack propagation rates that allow the simulations to run for several hundred cycles. The following results are intended to demonstrate that the concepts and implementation give qualitatively meaningful results, but the numbers are not intended to be quantitatively accurate.

4. Results and Discussions

4.1 Crack propagation in unreinforced PFSA membrane

As a first example and a baseline for comparison, we investigate crack propagation in an unreinforced PFSA membrane at the center of the channel, subjected to the relative humidity cycling protocol described in Section 3.3. Fig. 5 (solid line marked with squares) shows the crack length into the membrane as a function of the number of cycles. Note that the crack propagation is based on the scheme described in Section 2.2 and the result is a direct output from the simulation based on the plastically dissipated energy criterion. These are not prescribed beforehand. Since the initial crack length is $13 \mu\text{m}$ and the electrode is $12 \mu\text{m}$ thick, the initial value of crack length into the membrane is $1 \mu\text{m}$. When the crack propagates by $5.6 \mu\text{m}$ (the crack length into the membrane reaches $6.6 \mu\text{m}$), the simulation is stopped due to convergence and computational time

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4 issues. As is mentioned in Section 3, the structurally refined mesh through which the
5 crack propagates is composed of a uniform array of square, iso-parametric quadratic
6 CPE4RT elements with size $0.2\ \mu\text{m}$ by $0.2\ \mu\text{m}$. With the scheme illustrated in Fig. 3, the
7 crack propagates by $0.2\ \mu\text{m}$ each time the plastically dissipated energy in the dissipation
8 domain reaches the criteria. Therefore, a total of 28 elements are released during the
9 simulation.

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19 Initially, the plastically dissipated energy accumulates at a low rate per cycle and
20 it takes about 26 RH cycles before it reaches critical value for the first time. As the crack
21 grows, the plastically dissipated energy accumulates at a slightly higher rate. In addition,
22 there is already plastic deformation in the region around the crack tip region, which also
23 affects the mechanics and the accumulation of plastic energy. Therefore, it takes about 19
24 RH cycles before the second propagation increment of the crack. Subsequently, the
25 plastically dissipated energy and crack growth increase at a higher rate.
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Figure 5 Crack propagation in unreinforced PFSA membrane with crack under channel, core reinforced PFSA membrane with crack under channel and unreinforced PFSA membrane with crack under land

As discussed previously, Lai et al. [19] conducted similar humidity cycling tests on Nafion[®] NR111 membrane (25 μm thick unreinforced PFSA membrane) and showed the morphology of cracks at various stages of growth using cross-sectional micrographs. These are illustrated in Fig. 1a and 1b. From this experiment they showed that initially, when the crack was short, it was relatively sharp and blunted as it grew. This is qualitatively captured by the simulation as can be seen from “snapshots” of the model taken at the beginning and end of the simulation (Fig. 6a and 6b). It is worth pointing out that in the experiment, the MEA was sandwiched between two GDLs by clamping and it

may have been possible for the electrode surfaces to move relative to the GDLs during hydration and dehydration. In the simulation, however, perfect bonding between the electrodes and GDLs was assumed. Also, to obtain the micrographs in Fig. 1, Lai et al. [19] disassembled the fuel cells. These factors may explain why in the later stages of crack growth, the electrodes from the simulations look different than those in the experiments.

Figure 6 Crack morphology of unreinforced PFSA membrane and core reinforced PFSA membrane from simulation snapshots. (a) Initial crack opening morphology of unreinforced PFSA membrane, (b) Crack opening morphology of unreinforced PFSA membrane after 185 relative humidity cycles, (c) Initial crack opening morphology of core reinforced PFSA membrane, (d) Crack opening morphology of core reinforced PFSA membrane after 282 relative humidity cycles.

4.2 Crack propagation in core reinforced PFSA membrane

To improve mechanical durability, PFSA membranes using reinforcing agents such as polyvinylidene fluoride, expanded polytetrafluoroethylene (e-PTFE) fibrils and other polymers have been developed [48-53]. In particular, WL GoreTM has developed the Gore-Select[®] membrane, which is a three-layer composite membrane consisting of two layers of unreinforced PFSA on either side of a layer of ePTFE reinforced PFSA. Gore[®] Primea^{®§} Membrane Electrode Assembly (MEA), is the Gore-Select[®] membrane coated with catalyst electrodes. Gittleman et al. [5] conducted RH cycling tests on MEAs with Nafion[®] NRE211 membranes (unreinforced PFSA membrane) and Gore[®] Primea[®] Series 57. After RH cycling tests, through-thickness cracks were found in the membrane thickness direction of Nafion[®] NRE211 membrane while in the Gore[®] Primea[®] Series 57 MEA, the reinforcement improved the resistance against the crack propagation in the thickness direction. By measuring the H₂ crossover, Liu et al. [54] studied the lifetime of various PEM fuel cell membranes and found that the ePTFE reinforcement increased the lifetime. Li et al. [55] conducted biaxial cyclic loading test on various PEM fuel cell membranes using pressure-loaded blisters and found that the ePTFE reinforcement delayed the formation of cracks and crazes. Lai et al. [19] showed that compared with Nafion[®] NRE111 membrane, Gore-Select[®] 57 membrane had improved lifetime under RH cycling tests. A number of other studies [6,56-59] have reported increased durability with ePTFE reinforced PFSA membrane. This increased durability is generally attributed to the observations that ePTFE reinforcement improves the dimensional stability and reduces the in-plane swelling stresses developed in the membrane, both favorable for reducing the probability of failure, such as pinhole growth or crack formation [7,17,60,61].

[§] Gore[®] Primea[®] is a registered trademark of W.L. Gore Inc.

The morphology of cracks at various stages of growth in Gore-Select[®] 57 membrane (core reinforced PFSA membrane) from the RH cycling experiment test conducted by Lai et al. [19] are shown Fig. 1d and 1e. Crack morphologies from the simulations of reinforced membranes are shown in Fig. 6c and 6d. From the experiment micrographs (Fig. 1d and 1e) we can see that, similar to the crack in the unreinforced PFSA membrane (Fig. 1a and 1b), the initial crack is relatively sharp and as the crack propagates the crack tip becomes blunted. Also apparent from Fig. 1d and 1e is that the initially flat reinforcement layer becomes distorted in the out-of-plane direction. As seen in Fig. 6c and 6d, the simulation captures the crack propagation, the blunting of the crack tip, and the distortion of the ePTFE reinforced PFSA layer after humidity cycling. All of these features are directly obtained by probing the plastically dissipated energy in the dissipation domain ahead the crack-tip, assessing it as a criterion for crack propagation and propagating the crack via a node release technology once the criterion is satisfied.

Fig. 5 shows the crack length as a function of the number of cycles in the simulations for both the unreinforced PFSA membrane (solid line marked with squares) and core reinforced PFSA membrane (dash line marked with circles). The initial crack propagation behavior in core reinforced PFSA membrane is similar to the case of crack propagation in unreinforced PFSA membrane. Initially the crack grows slowly and as the crack becomes longer it grows faster. However, in the core reinforced PFSA membrane, as the crack propagates towards the ePTFE reinforcement (corresponding to the point where the crack length into membrane is 7 μm in Fig. 5), the influence of the ePTFE reinforcement becomes significant. The accumulation rate of plastically dissipated energy slows down and it takes more cycles to reach the critical value. As a result, the crack

propagation in core reinforced membrane slows as well. After about 185 cycles, the crack in the unreinforced PFSA membrane has grown from 1 μm to 6.6 μm and it appears that it will only take a few more cycles before the crack grows through the thickness. However, the crack in core reinforced PFSA membrane only grows from 1 μm to 4.4 μm after the same number of cycles. In total it takes about 282 cycles before the crack in core reinforced PFSA membrane reaches 6.6 μm .^{**} Therefore, the influence of the reinforcement on fatigue crack growth is qualitatively captured by the simulation based on the plastically dissipated energy criterion.

4.3 Crack propagation in unreinforced PFSA membrane under channel and under land

In cyclical RH experiments, as well as in actual PEM fuel cells, failures in the form of cracks and pinholes in the membrane are more commonly found in the regions under the flow channels than under the lands [5,19,55,62-64]. In this section, we investigate if the plastically dissipated energy criterion is able to capture this observation. For this, a second finite element model containing MEA with unreinforced PFSA membrane is created to have a full land and two half channels (Fig. 4b). An initial crack of the length 13 μm is assumed in the model with the crack under the land region. Propagation of the crack under the land is tracked and compared with propagation of the crack under the channel from the previous model (Fig. 4a).

Fig. 5 shows that the crack under the channel (solid line marked with squares) propagates much faster than the crack under the land (dot line marked with triangles). When the crack under the channel has reached a length of 6.6 μm into the membrane, the

^{**} In this study, the crack has not reached the interface of PFSA membrane and ePTFE reinforcement. It is possible that after the crack reaches the interface, the crack continues to grow through thickness or continue to grow along the interface. This will be investigated in future study.

crack under the land is just 1.6 μm . After a relatively few more humidity cycles, the crack under the channel will likely develop into a through-thickness crack while the crack under the land will still be relatively short. These findings correspond with the experimental and in-field observations that through-thickness membrane cracks are generally only found under the channel regions and not under the land regions.

4.4 Crack propagation in unreinforced PFSA membrane under different clamping pressures

Within certain limits, increased clamping pressure has been observed to have a positive effect on the mechanical durability of the membranes [65]. In this section, the effect of clamping pressure on crack propagation in the membrane is investigated using the simulation. Within the framework of the models used here, clamping is controlled by fixing the vertical displacement of the upper surface in the FE model at ambient conditions and holding constant. The swelling expansion of the membrane therefore increases the clamping load during the hygrothermal loading in the simulations. Three selected ambient clamping displacement conditions are studied: 0.0 mm, 0.05 mm and 0.1 mm, corresponding to increasing clamping pressure.

Crack propagation under the selected clamping conditions is shown in Fig. 7. For the case where a 0.0 mm clamping displacement is applied (the baseline case discussed in section 4.1 and repeated here for clarity) after about 185 cycles, the crack has grown by 5.6 μm (the crack length into the membrane is 6.6 μm). However, when a 0.05 mm clamping displacement is applied, after 185 cycles the crack has grown only by 1.6 μm (the crack length into the membrane is 2.6 μm). It takes a total of about 259 cycles before

this crack propagates by 5.6 μm (the crack length into the membrane is 6.6 μm). For the case of clamping displacement 0.1 mm, the crack has only grown by 1.2 μm (the crack length into the membrane is 2.2 μm) after 335 cycles. Further simulation was not conducted in the case of 0.1 mm clamping because of the time and computation cost involved. In summary, fatigue crack simulation based on the plastically dissipated energy criterion agrees qualitatively with observations from experiments, suggesting that increased clamping pressure reduces the crack propagation rate, thus increasing the durability of membrane.

Figure 7 Crack propagation in unreinforced PFSA membrane under three selected clamping displacements, where higher clamping displacement corresponds to increased clamping pressure

5. Concluding Remarks

Using finite element simulation of fatigue crack growth based on plastically dissipated energy as a propagation criterion, we have investigated fatigue crack growth in PEM fuel cell membranes under relative humidity (RH) cycling. The accumulation of plastically dissipated energy in a region ahead of at the crack tip (dissipation domain) is compared with a user-selected critical value. Once the critical value is reached, the crack is made to propagate via a node release algorithm. Given the proper critical value for the plastically dissipated energy the crack growth rate could be obtained from the simulation.

To test the viability of the plastically dissipated energy criterion, crack propagation in PEM fuel cell membranes under RH cycling was simulated in 2D plane strain representative PEM fuel cell models created in the commercial finite element package ABAQUS. It is well-established experimentally that during RH cycling, the crack tip will blunt and that ePTFE reinforced PSFA membrane offers better durability than unreinforced PFSA membrane. In addition, experimental and in-field observations shows that, through-thickness membrane cracks are generally found in the regions under the channel but not in the regions under the land. Moreover, within certain limits, increasing clamping on the fuel cell improves the mechanical durability of the membrane. These conditions were all investigated within the context of the finite element model and the proposed plastically dissipated energy criterion captured all of these observations qualitatively. Thus, the proposed scheme may be a useful tool to numerically characterize crack propagation in PEM fuel cell membranes under RH cycling. The possibility exists

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4 of expanding the methodology to simulate other materials, other fuel cell designs and a
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6 wider range of loading conditions (including field operation).
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9 The critical value for the dissipated plastic energy is a material parameter that
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11 must be determined from experiments. In the current investigation, the critical value was
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13 not known and therefore we assumed values to obtain reasonable overall simulation times
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15 and to test the viability of the proposed methodology. Calibration and further
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17 development of the proposed plastically dissipated energy criterion will require
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19 experimental measurements. This will be addressed in future work.
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51 **Appendix – Dissipation Domain**

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54 In references [30,39], during the loading cycle, the material ahead of the crack tip
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56 yields in tension because of the stress concentration induced by the crack. This forms a
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58 region known as the forward plastic zone [30,39]. Due to the permanent deformation
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4 associated with this yielding, compressive stresses are introduced during unloading and
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6 therefore compressive yielding typically develops in a smaller region known as the
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8 reversed plastic zone [30,39]. As the structure is continuously cycled, the material within
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10 the reversed plastic zone undergoes forward and reversed yielding and there is continuous
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12 accumulation of plastically dissipated energy [30,39]. Therefore, the reversed plastic
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14 zone is chosen as the dissipation domain and the size is approximated by analysis based
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16 on References [66,67].
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21 Simulations show that under typical fuel cell loading conditions, the entire PFSA
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23 membrane yields [5-8], so there is no such distinct forward plastic zone or reversed
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25 plastic zone in the PFSA membrane as in [30,39]. Because of the yielding, plastic energy
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27 is dissipated throughout the PFSA membrane during any particular load cycle. However,
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29 we show here that there is significantly greater accumulation near the crack tip. Therefore,
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31 to create a robust simulation, in this work we postulate that the dissipation domain should
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33 encompass a region around the crack tip where the accumulation in plastically dissipated
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35 energy is significantly greater than the average increase in the membrane after a few RH
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37 cycles. Thus, the following scheme is used.
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43 First, the plastically dissipated energy density in a typical element far away from
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45 the crack tip (the crack length is 13 μm) is calculated. The ratio of the plastically
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47 dissipated energy density in the elements near the crack tip to that in the element far away
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49 from the crack tip is calculated. Elements along three representative angles, 0°, 45° and
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51 90°, are chosen as illustrated in Fig. 2b. The elements are all of the same size of 0.2 μm
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53 by 0.2 μm (based on the convergence study discussed previously). The first element in
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55 front of the crack tip (Element 0) is chosen as the origin. An element-wise distance is
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defined as the number of elements away from the origin along each angle. Thus, Elements 1⁰ labeled in Fig. 2b has an element-wise distance of 1, while the element next to it along 0° will have an element-wise distance of 2. The same element-wise distances are defined along 45° and 90°.

The ratio as a function of element-wise distance along different angle is plotted in Fig. A1 which shows that element 0, which is the one that is closest to the crack tip, has a very high ratio of about 341. However, as we select elements farther away from element 0, the ratio drops significantly. For an element-wise distance of 7, the ratio is very close to 1, meaning that the plastically dissipated energy density in this element is close to the far-field value.

Figure A1 Ratio between each element as defined in Fig. 2b and the far field element, as a function of element-wise distance as defined in Fig. 2b.

In this qualitative study, a constant dissipation domain is used through the simulation to investigate the variability of using the plastically dissipated energy as a criterion to study the general experimental observations. Therefore, we select the dissipation domain in the simulation as a 8 by 8 elements rectangle domain on either side of the crack, which is a 1.6 μm by 1.6 μm square domain on either side of the crack as is illustrated in Fig. 7. In this way, the dissipation domain is able to capture the majority of the dissipated plastic energy increment around the crack tip, without having that increment obscured by the increase in dissipated energy in the rest of the membrane. Once we have quantitative experimental results, a thorough study will be conducted to determine the appropriate dissipation domain size as the crack grows, since this will have an impact on the quantitative results.

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