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Estimating the Durability of Polymer Electrolyte Fuel Cell Membranes Using a Fracture Percolation Model

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During fuel cell operation, the polymer electrolyte membranes are subjected to chemical and mechanical degradation that have an adverse impact on the membrane lifetime and thus overall durability of the fuel cell. To understand the synergistic effect of these two fundamentally different modes of degradation, it is therefore essential to consider both these effects when modeling membrane failure. A kinetic approach using a fracture percolation model is presented in this work that takes into consideration the hazard rates of chemical and mechanical degradation of the membrane incorporated into a two-dimensional membrane lattice network. While the chemical hazard rate is based on the rate of mass loss occurring during fuel cell operation, the mechanical hazard rate is evaluated based on a stress-induced, thermally activated process. The model captures the characteristic mechanisms of failure under the action of these fundamentally different modes, and converts the hazard functions into realistic time scale. The individual effects of the two modes are then incorporated in the model to predict in agreement with measured data, the time to fracture initiation in the membrane for a given combination of chemical and mechanical load.

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In the field of alternative hydrogen-based energy, polymer electrolyte membrane fuel cells (PEMFCs) are among the select few electrochemical technologies that are at the brink of large-scale commercialization. Over the years, there have been continuous improvements in this low-temperature, solid-electrolyte-based technology that have helped in increasing its technology readiness level (TRL) by enhancing its performance and durability, while bringing down the cost.¹ However, the field is still under active research to meet the renewed targets, and newer experimental materials and methods are being proposed to achieve these goals.^{2,3}

The durability of a polymer electrolyte membrane fuel cell depends in part on the operational stability of its solid electrolyte, which is typically a perfluorosulphonic acid (PFSA) ionomer membrane. In simple terms, degradation may compromise the ability of the membrane to separate the reactant gases, and therefore lead to lifetime limiting failure. The durability of fuel cells is usually benchmarked through accelerated stress tests in which the membrane, constrained within other components of the cell, is subjected to intensified operating conditions involving chemical and/or mechanical modes of loading.⁴ These types of tests save time when compared to characterization of durability through real-time field tests which may take several years.³ However, durability is a strong function of the specific operating conditions and duty cycles experienced in the field, and it is not possible to rely on accelerated stress testing alone in order to estimate durability.^{5,6} Hence, there is a need for both empirical and fundamental modeling tools that could further aid in bridging the gap between accelerated stress testing and use-level conditions in the context of durability. In this article, we introduce and discuss a fundamental modeling approach that is developed to estimate the time to failure initiation in a fuel cell membrane operating under the combined action of stressors.

Most commonly used fuel cell PFSA membranes consist of a phase-separated microstructure with a semi-crystalline hydrophobic backbone (with C-F bonds) providing structural integrity, and hydrophilic sidechains (with sulfate ions) assisting in the transport of protons and water.^{7,8} Due to metallic impurities entering the system,

hydroxyl radicals are formed and thus the polymer membranes are under attack from these chemical stressors. Modeling of chemical degradation due to these types of stressors has been a subject of various studies.^{9–12} The focus of these studies has been the modeling of transport and chemical rate kinetics of various species, and to quantify the effect of radical attack in terms of mass loss in the membrane. In addition to the chemical stressors, the membrane also endures mechanical stressors in the form of hygral strains produced due to the swelling (and shrinkage) of the constrained membrane under hydration-dehydration cycles. These cyclic strains lead to residual tensile stresses that are responsible for the development of cracks and/or pinholes in the membrane.^{13,14} Several numerical modeling techniques have reported in-situ stresses that develop in the membrane undergoing such hydration-dehydration or relative humidity (RH) cycling.^{15–19}

To investigate the combined effect of chemical and mechanical degradation, various experimental studies have been conducted,^{6,20–25} but very few modeling efforts have been reported in this field because of the challenges involved to couple the intricacies of these two fundamentally different modes of degradation acting at a range of length scales.²⁶ Some initial attempts to bridge these two degradation modes have proposed modified chemical rate equations to account for the resisting force experienced by molecular chains.²⁷ Synergistic effects of the chemical/mechanical degradation have been investigated by modeling the growth of pre-existing voids caused by humidity induced mechanical loading, and their effect on the chemical degradation was reported.²⁸ Recent investigation on membrane durability has demonstrated the importance of coupling the transport and mechanical modeling with the chemical degradation kinetics in a membrane.²⁹ These studies have suggested that the combined mode is the most severe mode of degradation, therefore to investigate durability, it is essential to simultaneously model the effect of these two dominant modes of degradation. In this work, we propose the use of the kinetic rate of chemical dissociation and the thermally activated mechanical failure rate induced by mechanical stresses to put forth a fracture percolation model for polymer membranes. Based on these two rates, the model can estimate the time to failure initiation in the membrane when acted upon by a combination of chemical and mechanical stressors.

The network percolation approach has been historically used for various other applications in which connectivity between the

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constituent elements of the network is considered, and a travel path through a random process is investigated. The constituent whose passage is studied could be neurons, electrical resistance, pathogens, and solvents etc.³⁰ This approach has also been used in the study of fracture of solids and for the predictions of time-to-fracture.^{31,32} In the fracture application, the percolation or the kinetic approach contrasts with the more common, static limiting-state theories (such as that of Griffith, Irvin) that are characterized by a critical breaking load. Alternately, the kinetic approach considers fracture as a developing process where elementary ruptures at the molecular scale lead to formation of submicroscopic cracks. These submicroscopic cracks then form clusters over time, and eventually coalesce into larger clusters paving way for macro crack propagation.³³

In the field of fuel cells, the network percolation approach has mostly been used to model transport through the porous network of gas diffusion layers and catalysts^{34–38} and water cluster distribution in the membranes.³⁹ Recently, Melchy et al.⁴⁰ used this approach to build a network failure model suitable for hierarchical materials such as PFSA membranes. They investigated the correlation between the size of the elementary unit (bundles), and the breaking events associated with them. This model however, did not distinguish between different modes of degradation, and used a net rate of bond breaking. In the present work, a membrane failure percolation network model based on the kinetic rates of chemical and mechanical degradation is developed. The model is introduced and the details of its formulation are discussed in Network Model section. The results from the simulations are presented and discussed in Results and Discussion section.

Network Model

Introduction.—To investigate the rate-limiting process of membrane failure, the ionomer membrane is modeled as a network of

bundles arranged in a two-dimensional regular lattice structure, $\mathbb{Z}^2$. Further, for each bundle in the network a sub-lattice of fibers ($\mathbb{Z}^2$) is defined, thus making a fiber the smallest computational unit in the model. This type of abstraction is motivated by the phase-separated structure of PFSA ionomer membranes, as shown by various experimental investigations.^{41,42} The proposed network modeling concept is illustrated in Figure 1.

It is to be noted that the model does not approach to solve the molecular dynamic behavior of each polymer fiber. The physical scale of the model is larger than for a typical molecular dynamic simulation, and consequently the fiber, represented as a polymer chain is defined as a single unit. Several fibers agglomerate and form a bundle, which then acts as a compound entity providing structural integrity to the membrane.^{43–45} The key attribute defined for each fiber is its instantaneous hazard rate, based on the two dominant modes of membrane degradation, as illustrated in Figure 1. The mechanical hazard function, λ_m relates the mechanical stresses, while the chemical hazard function, λ_c relates the chemical dissociation to the time to membrane failure.

Assumptions.—

- The membrane is approximated as a network of bundles and fibers with each representing a structural unit having finite strength.^{7,44,46}
- The bundle distribution in the network is assumed to be a regular 2D lattice. In semi-crystalline PFSA ionomer membranes, the arrangement of bundles may however lead to orientations in three dimensions, but the current form is chosen for the sake of computational efficiency.
- The lattice is uniformly weighted, that is all fibers (and bundles) are equally likely to fail for a given hazard rate. This also means

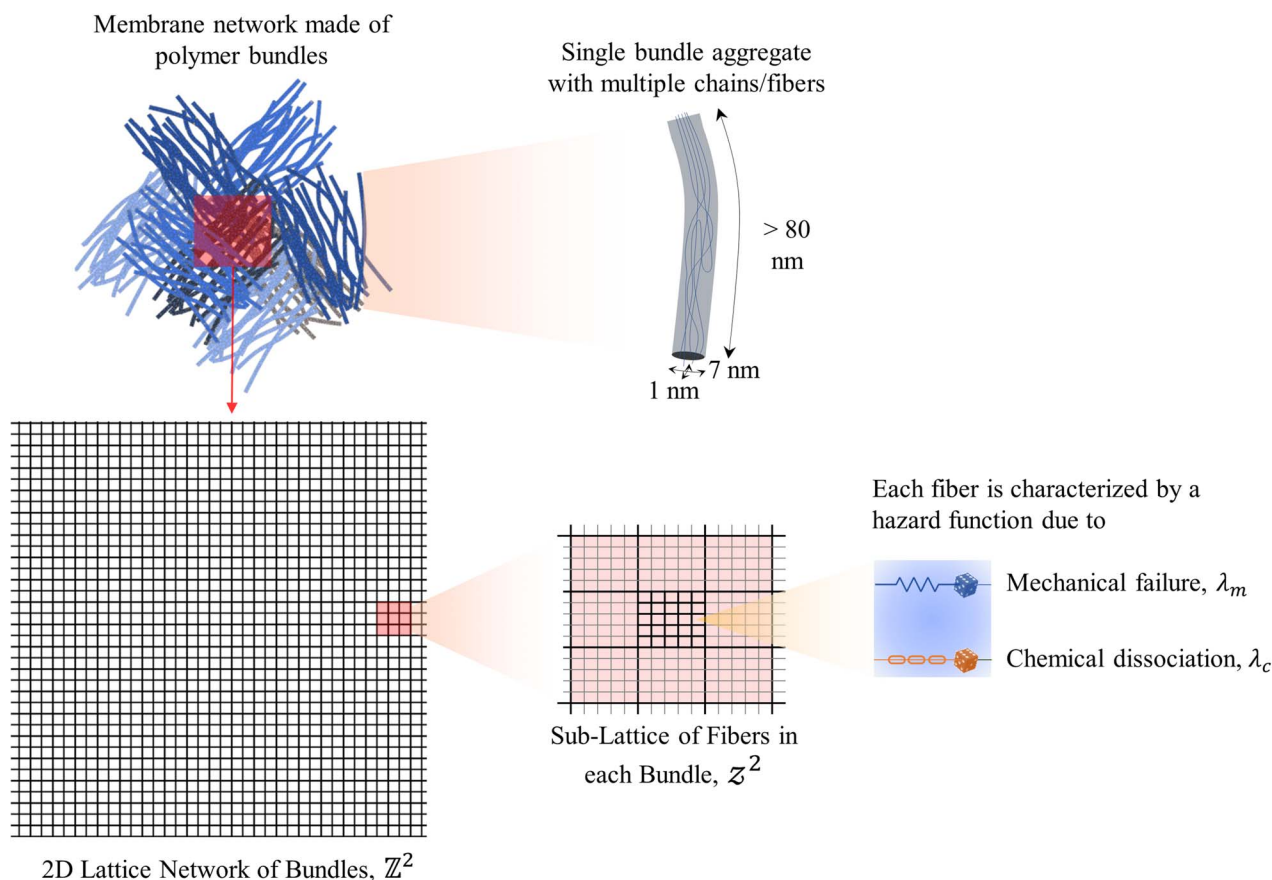


Figure 1. Illustration of the mathematical representation of the bundle and fiber network.

that the model assumes a pristine membrane to begin with, and that there is a uniform distribution of strength across the membrane. In addition, the persistence length and the aggregation number of each bundle is also assumed to be monodisperse in the network.

- iv. The fiber and bundle failure are assumed to take place only under tensile load. This is appropriate because the tensile (or the positive) stretch on the membrane alone may produce stresses in the membrane that lead to material disintegration.
- v. The mechanical hazard rate is influenced by the chemical hazard through the stress intensification, but the chemical hazard rate is assumed independent of the former.
- vi. Symmetry conditions are assumed at all the boundaries of the network.

Model formulation and equations.—The physical degradation mechanisms occurring in the membrane are modeled mathematically using the statistical concept of a hazard function. For a given mechanism of degradation (either due to chemical or mechanical stressors), the respective hazard function establishes the instantaneous degradation rate for the membrane fibers under the action of that stressor. These rates are then used to estimate the lifetime of a fiber, and hence the bundles, and subsequently the full network. The detailed explanation and derivation of the hazard rates is given in the following sections.

Chemical hazard rate.—Fuel cell membranes are subjected to attack by trace radical species that are formed during the cell operation. The mechanism of membrane degradation involving chemical dissociation and formation of various intermediate species begins with side-chain unzipping and eventually leads to main chain scission.¹⁴ The rate of overall membrane degradation due to chemical stressors is invariably measured using hydrogen fluoride release that is formed as a product of these reactions.⁴⁷ The amount of fluoride release is thus an indication of the total mass loss of the membrane. In this model, we use the membrane fluoride release rate to estimate the chemical hazard rate function, λ_c for the fibers in the network, given by

$$\lambda_c = \alpha \cdot \frac{d(\sum_v m_f)}{dt} \quad [1]$$

where $\sum_v m_f$ is the total percentage fluoride loss from the membrane and α is the ratio of main chain C-F bonds relative to the total C-F bonds in the membrane. α is used to account for the fact that the structural integrity of the membrane is predominantly provided by the hydrophobic backbone, represented by the main chain C-F bonds. The hazard rate, when calculated for the next instant of time after t , represents the instantaneous failure rate for the fibers that survive to time t . Or in other words, it is the conditional probability of failure in the next infinitesimally small time instant, given that the fiber (or the bundle) in question has survived up until time t . Thus, the hazard function is a measure of the risk of failure due to chemical radical attacks on the membrane. Moreover, because the hazard function is based on a measurable quantity, any change in test conditions or materials can be readily incorporated into the model.

Mechanical hazard rate.—During fuel cell operation, the membrane is constrained in compression on its two planar sides by other components including the gas diffusion media and corrugated bipolar plates. In addition to the mechanical compression, the sorption (and desorption) of water by the membrane leads to swelling (and shrinkage) of the membrane. These time-dependent dimensional changes in the membrane under constrained conditions give rise to the development of mechanical stresses in the membrane. Upon cyclic loading, the nature of these stresses alternates between compressive and tensile, while their magnitude depends on the local hydration and thermal conditions in the membrane. These mechanical stresses are responsible for the development of cracks and therefore, form the basis of mechanical hazard in this model.

Considering the failure behavior of general polymeric materials from the thermodynamic standpoint, in the presence of mechanical

stresses, the thermal fluctuations in polymer chains are enhanced resulting in a reduction of the bond dissociation activation energy barrier.⁴⁸ Consequently, at the scale of each polymer chain, the two segments on the opposite side of a bond have enough energy to lead to scission of the bond. Therefore, the rate-determining step for a single chain involves the stress-induced thermally activated molecular motions occurring at temperatures below glass transition temperature, T_g leading to the failure of that chain.⁴⁹ These concepts formed the basis of the kinetic theory of fracture⁴⁸ which relates the lifetime τ , the stress σ , and the absolute temperature T with the following equation,

$$\tau = \tau_0 \cdot \exp\left(\frac{U_0 - \gamma \sigma}{kT}\right) \quad [2]$$

where τ_0 is the time corresponding, in order of magnitude, to the period of fluctuation in the atomic bonding, U_0 is the binding energy of the polymer, and k is the Boltzmann's constant. This equation has also been known in the literature by other names such as the *equation for polymer life*,⁴⁹ the *durability equation*,⁵⁰ and the *Boltzmann–Arrhenius–Zhurkov (BAZ) model*.⁵¹ Using Equation 2, the rate of failure due to mechanical stresses in each fiber of the network model can be deduced by the inverse relation given by,

$$\tau^{-1} = \tau_0^{-1} \cdot \exp\left(-\frac{U_0 - \gamma \sigma_f}{kT}\right) \quad [3]$$

where τ^{-1} is equivalent to the hazard (or the instantaneous failure) rate λ_m in the fiber. The stress in the fiber, σ_f , together with the structural parameter γ reduces the activation energy U_0 , thus increasing the failure rate. While the parameters U_0 , γ , τ_0 (prescribed for the polymer under investigation) stay constant during the simulation along with k , the stress in each fiber σ_f varies due to (i) RH cycling of the membrane and (ii) stress redistribution in the event of fiber or bundle failure.

Coupled hazard.—In an operating fuel cell, the membrane is exposed to both chemical and mechanical modes of degradation. The degradation mechanisms for these two modes are fundamentally different from each other, as discussed in the previous two sections. However, due to the inherent dependency of a current failure event on the damage history, both these modes influence each other. As a result, the current total hazard rate is dependent on the previous failure state caused by the combined effect of both modes. This also means that even if the modes occur simultaneously, sequentially, or in any other random or periodic pattern, the previous damage state caused by any type of load history determines the current failure risk, thus coupling the two modes of degradation.

Using the individual failure rates for the two modes defined using the hazard functions (Chemical Hazard Rate and Mechanical Hazard Rate sections), the damage in the membrane network is characterized by the failure of individual fibers. The arrival of a damage event is modeled as a non-homogenous Poisson type process with the non-homogeneity arising due to variation of the stressors with time. As the membrane is subjected to dual modes of degradation over the course of its entire load history, the failure process can be considered as a split Poisson process in which each fiber is subjected to two hazards λ_m and λ_c . The contribution from the two hazards is computed incrementally for the time step, yielding the total current hazard. The survival function $S(t)$ for a fiber is represented by the probability $P(T > t)$ of survival beyond a given time t , with T being the maximum survival time (or fiber lifetime). It is apparent that survival of a membrane fiber is related to the total risk (or hazard) it is subjected to. The elementary definition of a hazard function from statistics is given by

$$\lambda(t) = \frac{f(t)}{S(t)} \quad [4]$$

where $f(t)$ is the failure probability density function, defined as the derivative of the probability of failure $F(t)$ as

$$f(t) = \lim_{\partial t \rightarrow 0} \frac{F(t + \partial t) - F(t)}{\partial t} \quad [5]$$

The survival function, defined as $S(t) = 1 - F(t)$, is thus related to the hazard function through the following relation,

$$\lambda(t) = \frac{f(t)}{S(t)} = \frac{\frac{\partial}{\partial t} F(t)}{S(t)} = \frac{\frac{\partial}{\partial t} (1 - S(t))}{S(t)} = \frac{-\frac{\partial}{\partial t} S(t)}{S(t)} = -\frac{\partial}{\partial t} \log S(t) \quad [6]$$

which can be rearranged to write,

$$S(t) = e^{-\int_0^t \lambda(\tau) d\tau} \quad [7]$$

where the exponent represents the accumulated hazard, $\Lambda(t) = \int_0^t \lambda(\tau) d\tau$ up to time t . This is a measure of the accumulated risk: the greater the value of $\Lambda(t)$, the lesser the chance of survival or greater the risk of failure by time t . In the case of the membrane network, both the chemical and mechanical degradation contribute to this hazard and hence the risk of failure at any instant is enhanced by the presence of both modes.

Soon after the beginning of life (BOL) phase, the failure events occur according to the natural random process with individual fibers failing randomly in different bundles throughout the network. When a fiber failure occurs, the mechanical stress previously carried by that fiber must be redistributed among the surviving fibers within the same bundle to conserve the total force. There are various ways in which this redistribution could be achieved, most notably through global or local sharing. In the global sharing method, the stress in the failed fiber is shared equally by all the surviving fibers. This is unlikely in the case of fuel cell membranes because the hydrophilic domains will prevent such long-distance sharing, and thus the stress is shared among neighboring aggregates only. Therefore, the local sharing law of stress redistribution is used, with the assumption that the surviving fibers in the immediate vicinity of the failed fiber are more likely to take a larger portion of the stress that the failed fiber was carrying before failure. The magnitude of this redistributed portion of the stress is assumed to decrease as the distance from the failed fiber is increased. This redistributed stress is calculated using the inverse power law,⁵² and the new stress σ_i^{new} for the i^{th} surviving fiber is evaluated using the relation,

$$\sigma_i^{new} = \sigma_i^{old} + \sigma_f \cdot \frac{(d\langle n_f | n_i \rangle)^{-a}}{\sum_{i \neq f} (d\langle n_f | n_i \rangle)^{-a}} \quad [8]$$

where $d\langle n_f | n_i \rangle$ is the shortest distance between the failed fiber and the surviving i^{th} fiber in the network, and a is the power law exponent. The shortest distance $d\langle n_f | n_i \rangle$ is normalized using the sum $\sum_{i \neq f} (d\langle n_f | n_i \rangle)^{-a}$ to yield a weight factor with which the stress previously carried by the failed fiber σ_f is multiplied and added to the surviving fiber. If being a regular grid network, the shortest distance is calculated here by counting the number of fibers between the failed and surviving fiber, which is an approximation that represents an average distance when compared to the actual spatial distribution of fibers in the membrane.

As more and more fibers fail with time, collections or regions of failed fibers representing sub-microscopic crack formation begin to develop in the membrane network. When the number of failed fibers within a bundle is large enough, a spanning cluster may appear such that there is a continuous path of failed fibers from one end of the bundle to the other end. The bundle is said to have percolated in that case and therefore, it is taken out of the network. The stress carried by that bundle is then redistributed among the remaining connected bundles similar in manner to the one explained above. In this way, the chemical and mechanical stressors are coupled together because any failure previously caused due to either effect has a bearing on the next failure event.

Material properties.—The hazard rates used in this work are calculated for a representative class of non-reinforced PFSA ionomer membranes commonly used in PEMFCs. The values for fluoride emission used for the determination of the chemical hazard rate are taken from our previous experimental work²¹ in which in-situ measurements were made by condensing anode and cathode gas exhausts and passing

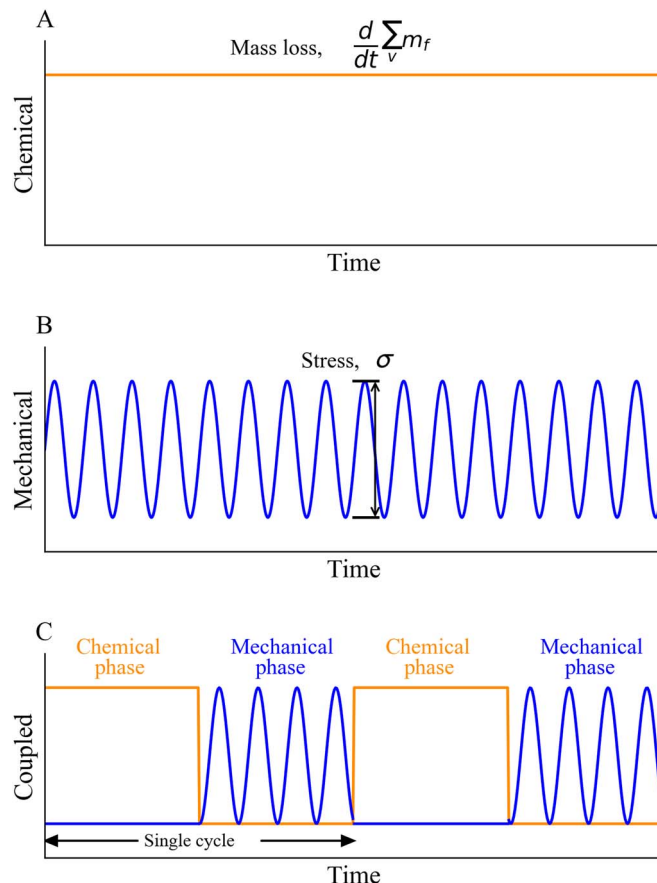


Figure 2. Load profiles for (A) pure chemical, (B) pure mechanical, and (C) alternating dual modes of degradation.

them through inline fluoride concentration meters during accelerated stress testing. The factor α , representing the ratio of the number of main chain bonds relative to the total number of bonds is around 0.7 for these membranes, and corresponds to the percentage of C-F bonds located at the backbone. The fuel cell operating temperature of 75°C is used for thermal activation and the average binding energy is taken to be 85 kJ/mol. The stress used for the calculation of mechanical hazard rate is estimated from previously reported numerical investigations.¹⁵ In that work, stress is determined in a constrained fuel cell assembly (consisting of catalyst coated membrane, gas diffusion layers, and bipolar plates) simulated under a similar range of humidity values as used here in this model. A nominal stress magnitude up to around 6 MPa is found based on temperature and humidity dependent mechanical properties for the membrane. The power law exponent for the local stress redistribution is taken to be 5.⁵³ The results obtained using these material properties are discussed in the next section.

Results and Discussion

In this section, we present the results obtained from the model simulated under three different types of accelerated stress conditions, featuring pure chemical, pure mechanical, and alternating dual modes of degradation, as graphically depicted in Figure 2. In the pure chemical case, the cell is held under open circuit voltage with hydrogen and air passed into anode and cathode respectively, at a constant relative humidity (30%) and temperature (75°C). In the pure mechanical case, the cell is subjected to relative humidity cycling with nitrogen on both sides. In the dual mode, the chemical and mechanical phases are applied alternately in a cyclic manner until the failure occurs. The typical choice of this type of dual cycle and the relative durations of each phase are motivated by our previously reported experimental work

investigating membrane lifetime under accelerated combined chemical and mechanical degradation.^{21,23,24,54} However, the model may be subjected to any other combination of loads as well.

The results correspond to a network of 50×50 bundles with each bundle consisting of 3×3 fibers in it, making it a network of 22,500 fibers. The load in the form of hazard rates is applied to each fiber of the network as a function of time. Symmetrical conditions are assumed at the boundary of the network. Each simulation is repeated 10 times to observe the variance of the process.

Chemical degradation.—The following results correspond to a simulated accelerated stress test conducted at open circuit voltage with a constant temperature of 75°C and 30% relative humidity. In such a steady state test, the membrane is subjected to pure chemical degradation alone with no RH cycling, hence no mechanical degradation. The chemical hazard function based on the fluoride release rate from the membrane is uniformly applied as an attribute to all the fibers in the network. As can be seen from the plots of the network at various stages of membrane failure shown in Figure 3A, there is a random distribution of failed fibers across various bundles in the network over time. This type of random distribution is due to radical attack occurring at multiple fronts within a fiber, notably the carbon-sulfur and ether bonds in the side chain and carboxylic acid end groups in the main chain.⁹ The side chain unzipping leads to main chain scission events,⁵⁵ the occurrence of which at various stages in fibers across the bundles gives rise to this random behavior. Such a failure process represents the distributed mass loss in the membrane leading to progressive thinning of the membrane over time.

The failure process is further characterized by the presence of large numbers of small disconnected clusters (defined here as regions of failed bundles) that are formed over the entire network. This failure distribution can be quantified and seen more clearly by measuring the size and number of these clusters as they are formed in the network over its lifetime, plotted at various fractions of bundle failure in Figures 4A–4B. The size of the two largest clusters in the network is shown in Figure 4A (after normalizing with the network size of 2500 bundles) while the total count of clusters of varied sizes is shown in Figure 4B. For a major part of the network life (and up to 30% of bundle failure), the size of all the clusters remains very small (Figure 4A), with the total number of clusters increasing because newer clusters are formed (Figure 4B). This amounts to random main chain scission events occurring in the fibers within the bundles across the network. Thereafter, disconnected clusters from throughout the network grow and start to coalesce with their nearest neighbors. The sharp jumps in the curves of Figure 4A correspond to the specific events when the two largest clusters at those instants coalesce to form a joint cluster, thus increasing the size of the largest cluster. The total number of clusters as a result starts to decrease as observed in Figure 4B. Although this process occurs randomly throughout the membrane network, bundles that are surrounded by regions of already failed bundles are more likely to fail and coalesce into a bigger cluster. This is also consistent with morphological membrane models featuring separate hydrophilic and hydrophobic domains.⁴⁴ With the loss of hydrophobic backbone, the hydrophilic domains cannot provide structural integrity in the adjoining region, and rather provide greater pathway for structural decay.

The evolution of bundle failure with time is shown in Figure 5A, along with the standard deviation obtained from different simulation trials. The timescale depicted here is the actual physical time defined from the rate functions described in Chemical Hazard Rate section. The fraction of failed bundles in the network increases with time. The rate of failure begins to increase at BOL and stabilizes to a steady value due to the application of a constant chemical hazard rate that was uniformly applied to all the fibers of the network, which is also the reason for low data scatter. The rate starts to decrease toward the end of the lifetime because the hazard rate (or the radical formation) is still present while the total number of surviving sites is reduced. In a 2D square lattice network, site percolation threshold occurs close to an occupation probability of 0.59.³⁰ Therefore, to be consistent while comparing various modes, a mean lifetime defined as the time when

60% of the bundles fail in the network is reported, as in Figure 5A. In this case, the obtained mean lifetime for the membrane to percolate, or the time to crack initiation is 285 hours.

Mechanical degradation.—Another set of simulations is conducted in which the membrane is subjected to cyclic application of mechanical stresses (caused by RH cycling). This type of situation arises in accelerated mechanical stress tests conducted using nitrogen in the flow channels instead of hydrogen/oxygen to avoid any chemical degradation.⁵⁶ The resulting network state at various stages of membrane failure, highlighting failed and surviving fibers along with the stress in individual fibers is shown in Figure 3B. At the beginning of life, the fiber failure is randomly distributed similarly to the previous case of pure chemical degradation (compare the first plot of Figure 3A and Figure 3B). However, upon each fiber failure event, the mechanical stress carried by that fiber is redistributed to the adjacent fibers leading to an increase in the stress concentration around the failure location. These stresses are caused by the dimensional change due to water uptake in the hydrophilic domains of the membrane. The swelling ratio is dependent on the membrane type and is considered isotropic but can be anisotropic for certain membranes. Thus, the location where a failure would first appear is random, but once a cluster is formed, the failure tends to localize near that cluster due to higher local stresses in that region, as evident from the rest of plots in Figure 3B. Comparing the first and last plots in Figure 3B, one may see that the stress carried by a fiber at the periphery of the failed cluster is about 40 times higher than the corresponding value at BOL. This stress intensification is responsible for sub-microscopic crack initiation and its progression to microcracks in the membrane.

The cluster growth is quantified by observing the size of the largest cluster plotted as a function of failed bundle fraction, as shown in Figure 4C. As soon as a stress concentration site is formed, the failure cluster size begins to increase (at around 5% bundle failure) which is also the point when the total number of clusters (Figure 4D) begins to decrease. That is because the single largest cluster dominates the fracture growth from that point onwards. The cluster formation and growth in the pure mechanical degradation case is markedly different from the previously discussed case of pure chemical degradation. This is due to the fact that while radicals (chemical hazard) may act at any location across bundles, the stress (mechanical hazard) is dependent on the force each fiber within each bundle is experiencing. Once a fiber is no longer able to carry that force, it is distributed to neighboring fibers, resulting in localized failure progression. Thus, the total number of clusters is also smaller as compared to the previous case. A direct comparison of Figures 3A and 3B shows that the model captures the characteristic failure mechanisms occurring during the two fundamentally different modes of degradation.

The absence of chemical degradation leads to more isolated distribution of failure across the network, and instead longer time is spent in the development of a sub-microcrack and for the buildup of stresses around the crack periphery. This is demonstrated by the mechanism of failure as revealed by the simulations. Figure 5B shows that the failure rate in this case is relatively slow for the major part of membrane lifetime, marking the duration of development of sub-microcracks. However, once the locally elevated stresses reach a certain threshold, an avalanche effect can be seen, signaling a regime of development of a micro-crack which eventually grows very fast leading to network spanning membrane failure (Figure 5B). This process could occur with a single sub-microcrack that forms early on and grows until percolation. Alternatively, multiple sub-microcracks might form in the early stages that first grow in a synchronous manner and then coalesce with each other, as is the case in Figure 3B. Due to the competing effects of the dominant cluster growth, and formation of secondary fracture clusters, the deviation around the avalanche region is larger in this case. The mean lifetime, defined as the time when 60% of the bundles fail in the network, is longer in this case compared to the pure chemical degradation case. This is consistent with the experimental observations that the fuel cell membranes in general have longer lifetime under mechanical loading than under chemical loading.⁵⁷

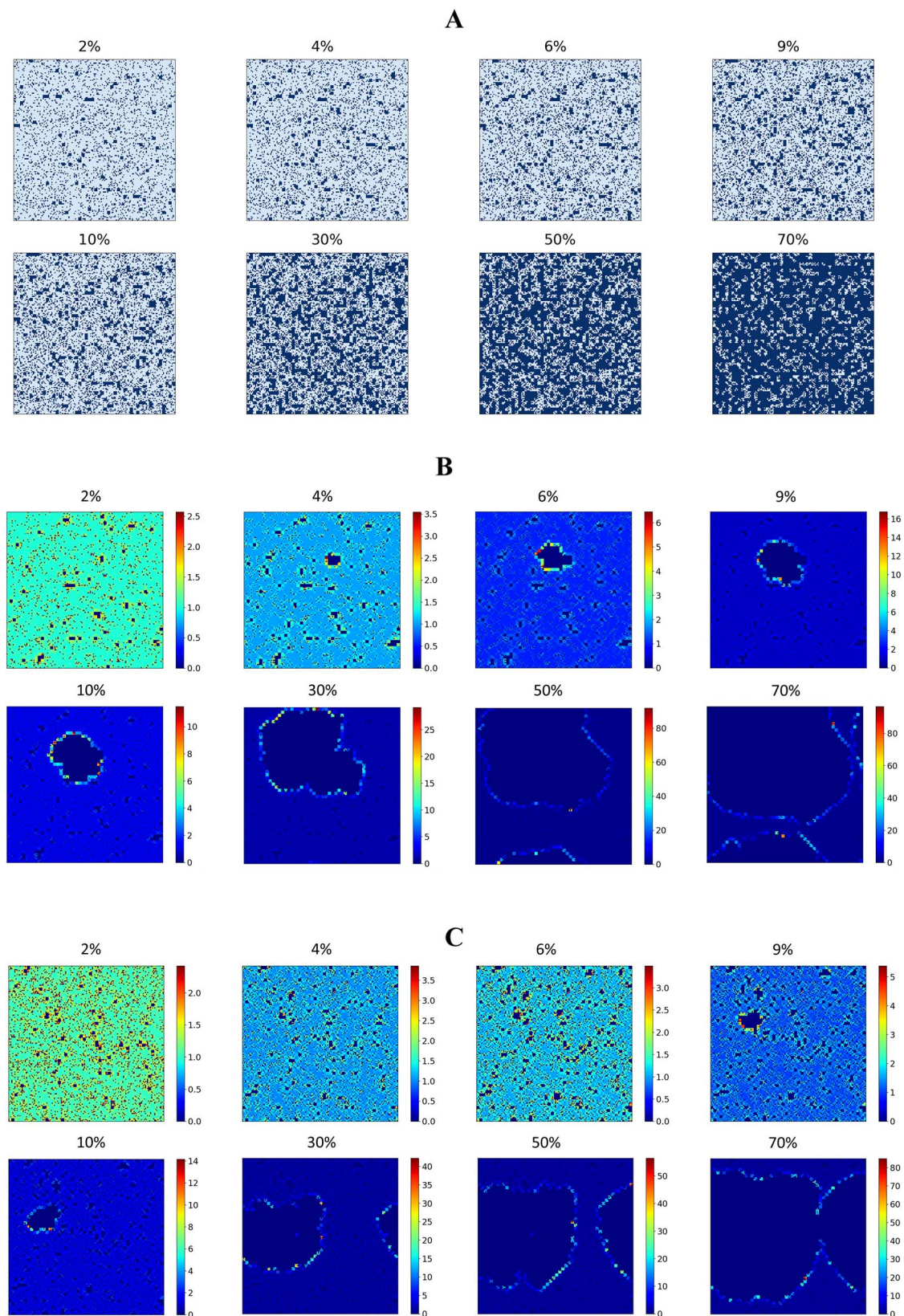


Figure 3. (A) Relative proportion of failed (dark colored) and surviving (light colored) fibers at various bundle failure fractions in the network subjected to pure chemical degradation, (B) pure mechanical degradation, and (C) coupled degradation. (The color scale in (B) and (C) corresponds to the stress in each fiber, with a failed fiber represented by zero stress).

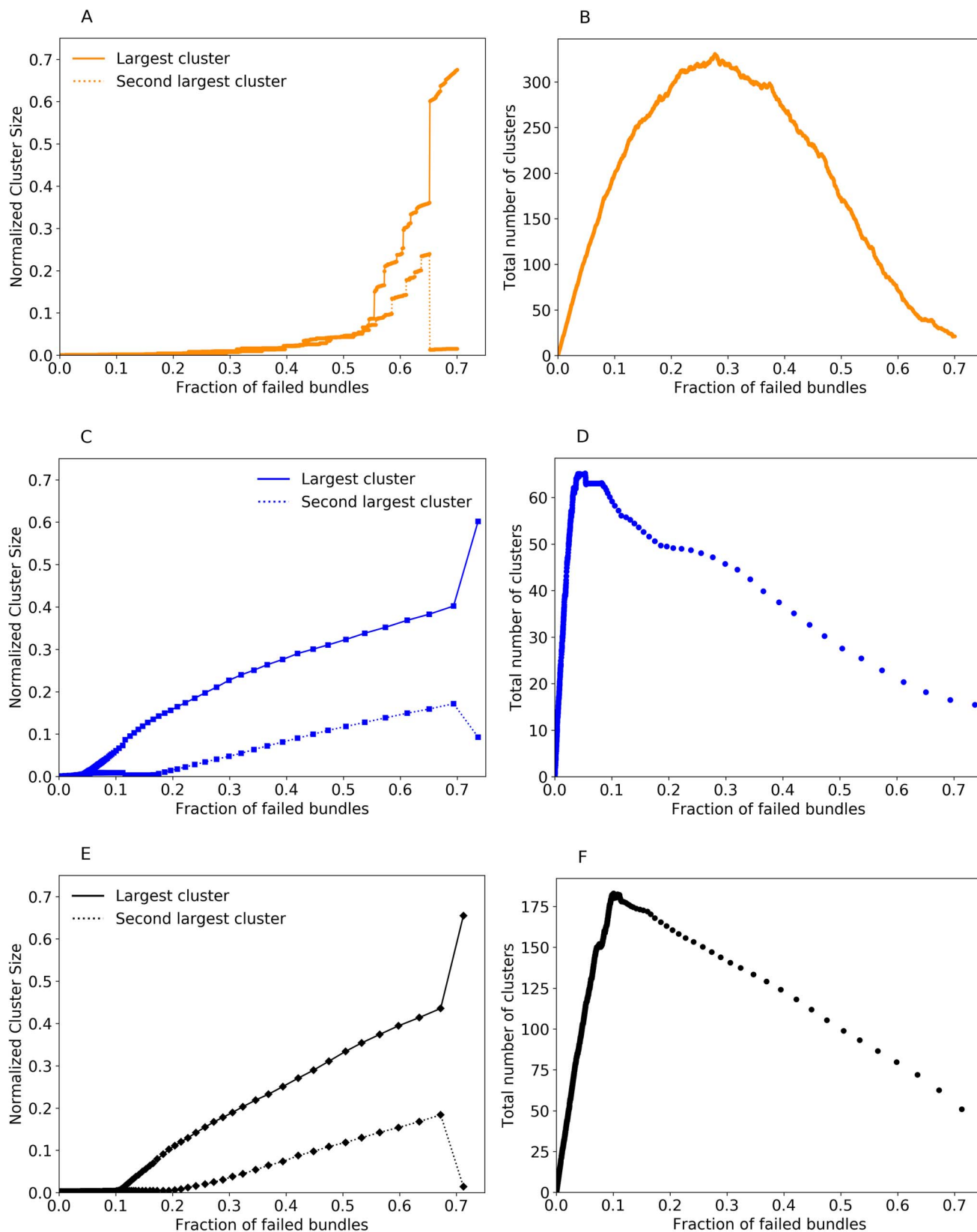


Figure 4. Cluster size (normalized) of the largest and second-largest clusters [left column figures] and Total number of clusters [right column figures] plotted as a function of the fraction of failed bundles for simulation invoking (A-B) pure chemical degradation, (C-D) pure mechanical degradation, and (E-F) coupled degradation.

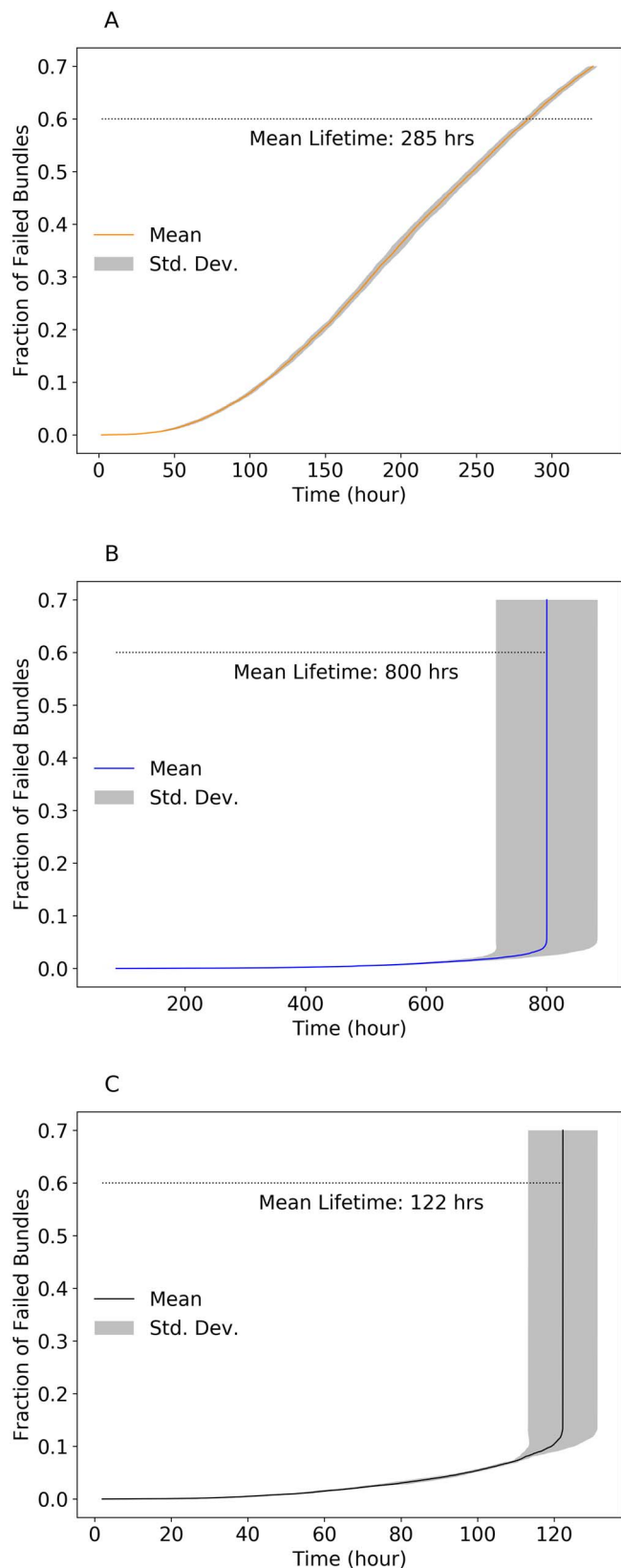


Figure 5. Fraction of failed bundles over time when subjected to (A) pure chemical degradation, (B) pure mechanical degradation, and (C) coupled degradation.

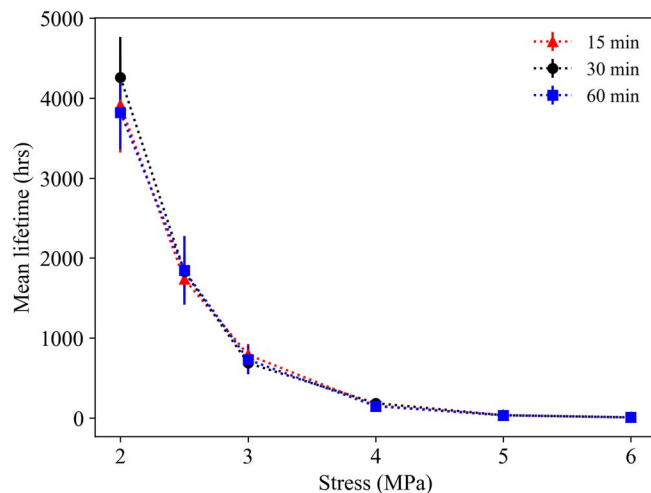


Figure 6. Variation of mean lifetime of the membrane with the amplitude of the mechanical stress for three different time periods of relative humidity cycling. Error bars indicate the standard deviation obtained from different simulation trials.

As discussed above, high stresses near failed fibers influence the development of failure clusters and eventually the lifetime of the membrane. It is therefore interesting to investigate the effect of the magnitude of the applied mechanical stress on the membrane. Figure 6 shows the variation of mean lifetime with the amplitude of applied cyclic stress, for different periods of hydration-dehydration cycling. The lifetime is strongly dependent on the magnitude of applied stress while the period of the hydration-dehydration cycle does not significantly affect the lifetime, especially at higher stresses. The reason is that for higher stresses above the membrane strength threshold, the sub-microcrack (or the dominant cluster) is formed promptly, soon after the application of mechanical load. Also, even though the trough period of the low-frequency hydration-dehydration cycle (i.e. when no tensile stresses act) may be longer, the high applied stress when further intensified at the crack tips causes the failure process to be biased toward the dominant cluster. This sub-microcrack then grows quickly to span the network, resulting in lower lifetime. This result shows that the determination of representative membrane stresses is important to make a good estimate of the lifetime.

Coupled degradation.—During fuel cell operation, both chemical and mechanical stressors act on the membrane and it is therefore imperative to investigate the failure process in the presence of both modes. A simulated cyclic open circuit voltage (COVC) accelerated stress test is used here to apply the chemical and mechanical stressors in an alternating pattern, as illustrated in Figure 2C. The failure process in this case exhibits a combination of the features observed in the two individual modes discussed in Chemical Degradation and Mechanical Degradation sections. While there is random distribution of failed fibers across all bundles in the network from the beginning to the end of life (as in the pure chemical case), a dominant fracture cluster is also formed that eventually triggers the final failure (as in the pure mechanical case), shown in Figure 3C. This translates to the presence of both membrane thinning and sub-microcracks in the membrane. The fibers that fail due to the action of chemical stressors act as sites of stress concentration, and in the presence of mechanical stress, this effect is amplified.

The size of the largest two (and hence all) clusters remains small up to about 10% of bundle failure fraction, as shown in Figure 4E. This number is in between the corresponding time taken in the pure chemical and pure mechanical case. It suggests that distributed failure and sub-microcrack formation are both occurring at the same time. Thereafter, the largest cluster (sub-microcrack) at that point becomes the dominant cluster due to stress redistribution and resembles the

cluster growth seen previously in the case of pure mechanical degradation (compare Figures 3B and 3C). The beginning of the dominant cluster growth is coincident with the onset of the decrease in the total number of clusters, as observed in Figure 4F. This is expected because more failure is occurring around the dominant crack, and thus no new clusters are formed.

The evolution of bundle failure with time is shown in Figure 5C. In this case involving both modes of degradation, the failure rate increases gradually in the beginning at about the same rate as that of pure chemical degradation, but the development of a dominant cluster overtakes this growth. Consequently, in the later stage of life the avalanche effect occurs, although much earlier than in the case of pure mechanical degradation. Hence, the mean lifetime in the case of coupled degradation is the lowest among the three cases discussed, which has also been established experimentally.^{54,57}

In the previous discussions, we have seen that there are two network characteristics that influence the fiber and bundle failure rate, namely the cluster count and the size of the clusters that eventually influence the lifetime. While the cluster count represents the distributed failure in the membrane, the size of the clusters signifies the extent of sub-microcrack development. These characteristics help in distinguishing different failure mechanisms in the membrane that arise depending on the type of stressor. These characteristics have thus far been mentioned heuristically in the literature on the basis of experimental observations.^{58–61} Here, we quantify these effects for various modes of loading. Figure 7A shows the comparison of the total number of clusters formed during several simulation trials for the three modes of degradation. From this graph, one might be tempted to conclude that the chemical degradation mode is the most severe of all because of the largest number of clusters formed during this mode. That is not correct however, because the lifetime predictions have shown otherwise (Figure 5). Although the number of clusters is large in the case of pure chemical degradation, their individual growth (or the size of each cluster) is limited. To properly characterize the formation of clusters in the network based on their numbers and relative sizes, a cluster dispersity index, $\mathcal{D}_C$ is used as given below,

$$D_C = \frac{\sum_i n_i s_i^2 / \sum_i n_i s_i}{\sum_i n_i s_i / \sum_i n_i} \quad [9]$$

where n_i represents the number of clusters of size s_i in the network. Using this index, the proportionate effect of larger clusters, albeit in small numbers can be readily seen as shown in Figure 7B for all the three modes considered. The dispersity index remains low in the case of pure chemical degradation due to the small size of clusters and only increases near the end of life when large scale coalescence of clusters takes place. For the pure mechanical and combined cases, the dispersity index increases as soon as a dominant cluster emerges. While for the pure mechanical case there is no further increase, in the combined case the additional action of chemical stressor continues and thus the index (and hence failure) keeps on increasing. The peak values of $\mathcal{D}_C$ for the three modes of degradation correspond well to the trend of predicted lifetime, as shown in Figure 5, suggesting that the combined mode of degradation is the most severe of the three modes.

No degradation.—The case in which the membrane network is subjected to neither mechanical nor chemical stressors is also simulated for reference. Due to the absence of radical attack, there is no mass loss resulting in zero chemical degradation. There are no mechanical stresses due to RH cycling, thus the term responsible for reducing the activation barrier in Equation 3 goes to zero. However, due to thermal activation, the membrane is subjected to a small mechanical hazard rate. This low rate results in a very long membrane lifetime of about 12.6 years which can be taken as infinite when compared with the lifetime for the other modes, as compiled in Figure 8. The plausible prediction in this reference case with no degradation mode also serves as an endorsement of the model in that the model is based on realistic physical rates of membrane degradation, and not just random failure events.

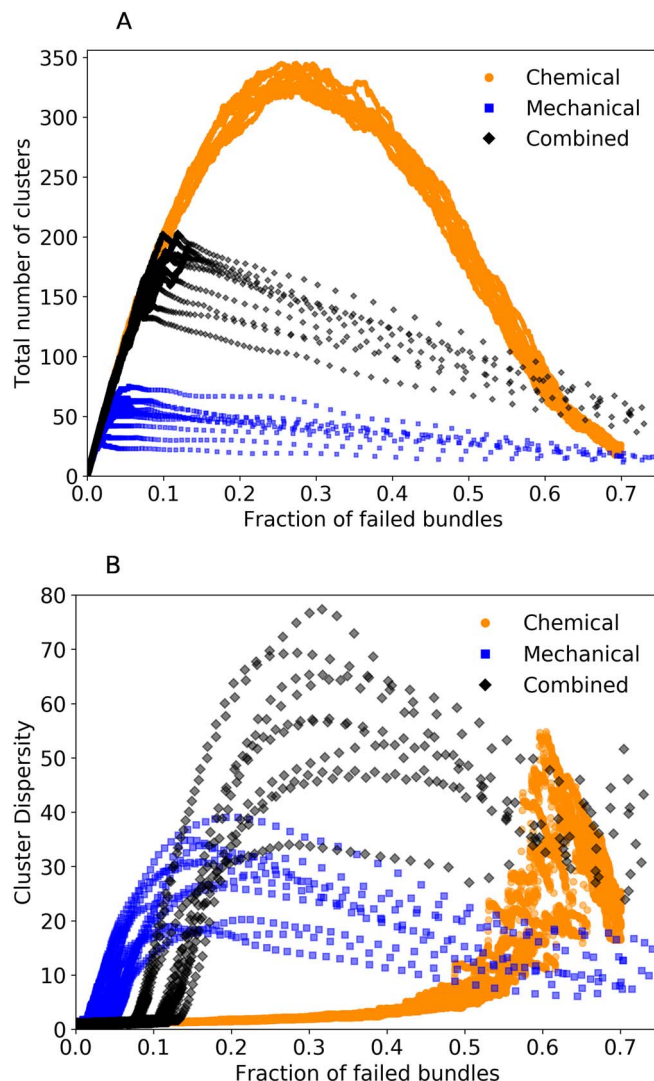


Figure 7. (A) Evolution of the number of clusters in the network and (B) Cluster Dispersity Index, $\mathcal{D}_C$, for the three modes of degradation.

Conclusions and Recommendations

A simulation method based on a fracture percolation network model is presented as a proof of concept for estimating the durability of polymer electrolyte fuel cell membranes under the action of combined chemical and mechanical modes of degradation. The membrane is approximated by a 2D regular lattice network, with each network

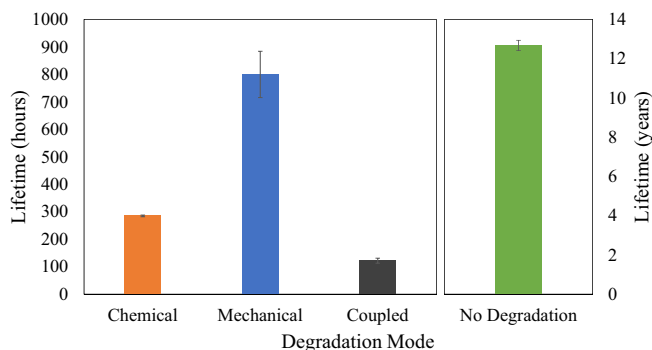


Figure 8. Predicted mean lifetime for various modes of degradation.

site corresponding to an aggregate bundle of polymer fibers, and each bundle consisting of a sub-lattice of individual fibers. The approach is based on well-established kinetic indicators of chemical and mechanical degradation, namely fluoride release rate and stress-induced thermally activated failure. By combining the hazard rates for these two modes, the failure mechanism under the action of both chemical and mechanical stressors is investigated. A key feature of this approach is the conversion of membrane degradation rates into real-time scale and thus the membrane lifetime is estimated from the network failure.

The 2D lattice network used in this work is motivated by the typical morphology of a fuel cell membrane in which the polymer fibers agglomerate to form a network of bundles. However, this approach can also be used for other such hierarchical materials. The important feature incorporated here is the identification of individual failure criterion for the membrane fibers based on the stressors acting upon them. Using this, the characteristic failure mechanisms under chemical and mechanical stressors are revealed during simulations. The chemical stressors are shown to lead to random fiber failure distribution throughout the network with no crack formation. Clustering of distributed failure sites is observed late in the lifetime due to coalescence of adjacent failed bundles. In contrast, under the action of mechanical stressors the random failure of certain fibers predisposes them to act as sites for further failure, owing to stress redistribution around them. Formation of a dominant cluster is consequently observed which grows catastrophically leading to percolation of the network. This resembles the initiation of sub-microscopic cracks that grow to become micro-cracks and/or pinholes, and are known to be the cause of failure under mechanical degradation. When both these stressors are applied together, the individual effects are amplified through coupling and hence the lifetime of the membrane is shortened, as observed by previous experimental investigations.

There have been many useful contributions in the literature that have observed crack formation in the membrane upon application of load, but the aspect of crack initiation has not been dealt with adequately. Such observations typically determine what type of macroscopic failure occurs at the end of life depending on the loading parameters, and others have modeled the growth of pre-existing cracks/voids. In this work, the failure initiation mechanism of fuel cell membranes at the sub-microscopic scale under the action of mechanical, chemical, and combined modes of degradation is investigated using the network percolation approach. This novel approach connects the physical degradation parameters to the failure initiation time of membrane fibers. As the degradation functions are based on the morphological features and the membrane material properties, the model could similarly be tuned for other types of membranes. The insights provided on the nature of failure processes and the quantifiable characteristics of the fracture formation along with the prediction of failure time are expected to be useful in estimating membrane durability in fuel cell applications.

The main limitations under which the current form of the model may be used and recommendations for potential model improvements are as follows:

a. During fuel cell operation, mechanical stresses develop in a cyclic fashion upon repeated hydration and dehydration of the membrane. The tensile stresses developed during dehydration in the constrained membrane are used as the mechanical stressor in this work. The compressive stresses are assumed to have no effect on the fiber failure, and hence neglected. Equation 2 is also only valid for positive (tensile) strain applied to the material. Although this is a reasonable assumption to make,⁶² however, if the compressive stresses are too large, there might be substantial stress redistribution, especially near a crack tip. Compression affects the water sorption in the membrane and increases the internal swelling pressures that could lead to change in morphology of hydrophilic domains.⁶³ These effects have not been quantified in literature and need more investigation. Once known, their contribution to the change in the activation energy may be added to the model to capture the influence on the time to fiber failure.

- b. In this approach, the effect of both the chemical and mechanical stressors has been implemented in a single model. The sites of mass loss due to chemical attacks become the stress concentration sites when acted upon by mechanical stress. However, the chemical hazard rate which is independently applied to the fibers can also be treated as dependent on the local mechanical stresses. That situation arises when the high local mechanical stresses influence the flow of reactants and may consequently alter the chemical reaction rates.⁷
- c. While the mechanical stresses are redistributed accordingly upon fiber and/or bundle failure, there is no such redistribution for the fibers failing due to chemical stressors. Chemical unzipping and splitting of main chain bonds, however, could conceivably induce localized distribution of orientation among the fibers and/or bundles. Through proper quantification, this chemical ‘stress’ may be added as an attribute and appropriately redistributed in the network.
- d. The failure approach used in this work corresponds to a uniformly weighted lattice network where all fibers and/or bundles are equally likely to fail at a given hazard rate. This approach can be extended to a heterogeneously weighted lattice graph for other applications where certain types of network constituents are more likely to fail than the others. This will enable to model to capture the failure mechanisms tailored to membranes with specific distribution of strength in their chemical structure. Moreover, spatial distribution of strength at mesoscale due to reinforcements/inclusions may also be modeled in that case.
- e. The bundle size and its associativity with the neighboring bundles is assumed to be uniform in the form of a regular square lattice. This assumption is reasonable when compared with the observed planar morphology of the fuel cell membrane at these length scales.⁴⁴ However, when considering the third dimension, the preferred orientation of the bundles may lead to non-uniform associativity with the other bundles in real-space. This may affect the arbitrary propagation of cracks in the planar versus the through-plane direction. To investigate this, a complete 3D network with a specific non-uniform distribution of bundle associativity (and/or size) is required.

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