Fatigue and Mechanical Damage Propagation
in Automotive PEM Fuel Cells

by

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Mechanical and Industrial Engineering Department
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Abstract

Polymer electrolyte membrane (PEM) fuel cells are generally exposed to high magnitude road-induced vibrations and impact loads, frequent humidity-temperature loading cycles, and freeze/thaw stresses when employed in automotive applications. The resultant mechanical stresses can play a significant role in the evolution of mechanical defects in the membrane electrode assembly (MEA). The focus of this research is to investigate fatigue challenges due to humidity-temperature (hygrothermal) cycles and vibrations and their effects on damage evolution in PEM fuel cells. To achieve this goal, this thesis is divided into three parts that provide insight into damage propagation in the MEA under i) hygrothermal cycles, ii) external applied vibrations, and iii) a combination of both to simulate realistic automotive conditions. A finite element damage model based on cohesive zone theory was developed to simulate the propagation of micro-scale defects (cracks and delaminations) in the MEA under fuel cell operating conditions.
It was found that the micro-defects can propagate to critical states under start-up and shut-down cycles, prior to reaching the desired lifespan of the fuel cell. The simultaneous presence of hygrothermal cycles and vibrations severely intensified damage propagation and resulted in considerably large defects within 75% of the fuel cell life expectancy. However, the order of generated damage was found to be larger under hygrothermal cycles than vibrations. Under hygrothermal cycles, membrane crack propagation was more severe compared to delamination propagation. Conversely, the degrading influence of vibrations was more significant on delaminations. The presence of an anode/cathode channel offset under the combined loadings lead to a 2.5-fold increase in the delamination length compared to the aligned-channel case. The developed model can be used to investigate the damage behaviour of current materials employed in fuel cells as well as to evaluate the alternative materials for the next generation of fuel cell development.
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<th>Description</th>
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</thead>
<tbody>
<tr>
<td>ANN</td>
<td>Artificial Neural Network</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>C</td>
<td>carbon</td>
</tr>
<tr>
<td>CCM</td>
<td>catalyst coated membrane</td>
</tr>
<tr>
<td>CDM</td>
<td>continuum damage mechanics</td>
</tr>
<tr>
<td>CFRP</td>
<td>carbon fibre reinforced polymer</td>
</tr>
<tr>
<td>CL</td>
<td>catalyst layer</td>
</tr>
<tr>
<td>DCB</td>
<td>double cantilever beam</td>
</tr>
<tr>
<td>DM</td>
<td>diffusion media</td>
</tr>
<tr>
<td>DMA</td>
<td>dynamic mechanical analyser</td>
</tr>
<tr>
<td>DOE</td>
<td>Department of Energy</td>
</tr>
<tr>
<td>DOF</td>
<td>degrees of freedom</td>
</tr>
<tr>
<td>ENF</td>
<td>end notch flexure</td>
</tr>
<tr>
<td>FE</td>
<td>finite element</td>
</tr>
<tr>
<td>GDE</td>
<td>gas diffusion electrode</td>
</tr>
<tr>
<td>GDL</td>
<td>gas diffusion layer</td>
</tr>
<tr>
<td>LEFM</td>
<td>linear elastic fracture mechanics</td>
</tr>
<tr>
<td>MEA</td>
<td>membrane electrode assembly</td>
</tr>
<tr>
<td>PEM</td>
<td>polymer electrolyte membrane</td>
</tr>
<tr>
<td>Pt</td>
<td>platinum</td>
</tr>
<tr>
<td>RH</td>
<td>humidity</td>
</tr>
<tr>
<td>UEL</td>
<td>user defined element</td>
</tr>
<tr>
<td>VCCT</td>
<td>Virtual Crack Closure Technique</td>
</tr>
</tbody>
</table>
# Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>crack/delamination length</td>
</tr>
<tr>
<td>$A$</td>
<td>amplitude of vibration</td>
</tr>
<tr>
<td>$A$ (section 3.1.4)</td>
<td>total damaged area</td>
</tr>
<tr>
<td>$A_c$</td>
<td>initial area exposed to damage</td>
</tr>
<tr>
<td>$A_d$</td>
<td>damaged area per element after N cycles</td>
</tr>
<tr>
<td>$C$ and $m$</td>
<td>empirical Paris’ law constants</td>
</tr>
<tr>
<td>$d$</td>
<td>scalar damage parameter</td>
</tr>
<tr>
<td>$d_{\text{quasi-static}}$</td>
<td>quasi-static damage</td>
</tr>
<tr>
<td>$d_{\text{cyclic}}$</td>
<td>damage generated due to fatigue</td>
</tr>
<tr>
<td>$D_{ij}^0$</td>
<td>initial stiffness tensor of the interface prior to damage initiation</td>
</tr>
<tr>
<td>$E$</td>
<td>Young's modulus</td>
</tr>
<tr>
<td>$J$</td>
<td>Jacobin matrix</td>
</tr>
<tr>
<td>$k$</td>
<td>initial interface stiffness prior to damage initiation</td>
</tr>
<tr>
<td>$K$</td>
<td>tangent stiffness matrix</td>
</tr>
<tr>
<td>$G$</td>
<td>energy release rate</td>
</tr>
<tr>
<td>$G_c$</td>
<td>critical strain energy release rate</td>
</tr>
<tr>
<td>$G_{Ic}$ and $G_{IIc}$</td>
<td>fracture toughness in normal direction (mode I) and shear</td>
</tr>
<tr>
<td>$\Delta G$</td>
<td>variation of energy release rate in each loading cycle</td>
</tr>
<tr>
<td>$G_{\text{max}}$</td>
<td>maximum energy release rate in each loading cycle</td>
</tr>
<tr>
<td>$N$</td>
<td>number of applied cycles</td>
</tr>
<tr>
<td>$q$</td>
<td>nodal deformation vector in the damage element</td>
</tr>
<tr>
<td>$RH$</td>
<td>relative humidity</td>
</tr>
<tr>
<td>$S_{ij}$</td>
<td>deviatoric stress tensor</td>
</tr>
<tr>
<td>$S^{\pm}$</td>
<td>upper ($S^+$) and lower ($S^-$) surfaces of the damage element</td>
</tr>
</tbody>
</table>
time

$t$

current temperature

$T$

reference temperature

$T_0$

Elastic Strain Energy

$U$

Greek Symbols

$\alpha$ coefficient of thermal expansion

$\delta_{ij}$ Kronecker delta

$\lambda$ interfacial separation displacement

$\lambda_m$ mixed mode separation displacement

$\lambda_m^0$ mixed-mode separation displacement corresponding to damage onset

$\lambda_m^f$ mixed-mode separation displacement corresponding to the final separation

$\varepsilon$ total strain tensor

$\varepsilon_{ij}^e$ elastic strain components

$\varepsilon_{ij}^{pl}$ plastic strain components

$\overline{\varepsilon}_{ij}^{pl}$ equivalent plastic strain

$\varepsilon_{ij}^{sw}$ swelling strain components

$\varepsilon_{ij}^T$ thermal strain components

$d\lambda$ scalar proportionality factor (plastic)

$\nu$ Poisson's ratio

$\rho$ density

$\sigma$ stress tensor

$\sigma_y$ yield stress

$\Theta$ rotation tensor
\( \omega \) vibration frequency

\( \tau \) interface traction (stress) tensor

\( \tau^0_m \) interfacial strength under mixed-mode conditions

\( \tau^0_n \) interfacial strength in the normal mode

\( \tau^0_{\text{shear}} \) interfacial strength in the shear mode

**Subscripts**

\( m \) mixed mode

\( n \) normal direction to the interface

\( s \) and \( t \) in-plane shear directions

\( I \) mode I of crack separation

\( II \) mode II of crack separation

\( III \) mode III of crack separation
Chapter 1

1 Introduction

1.1 Background and Motivation

The polymer electrolyte membrane (PEM) fuel cell has been recognized as a promising power technology with zero-local emissions for portable, mobile, and stationary applications. It has the potential to provide clean electrical energy with high power density, low operating temperatures, quiet operation, fast start-up and shutdown, and high overall efficiency [1]. The combination of these characteristics makes the PEM fuel cell a promising candidate to be used in transportation applications as the engine and/or for auxiliary power. However, prohibitive cost, poor durability, and mechanical degradations are still the major challenges that limit their commercial success. While it was expected to have fuel cell car prototypes widely commercialized in the market by 2015, the dynamic conditions present during the automobile operation make it very challenging to meet the 5000 h fuel cell life targeted by the U.S Department of Energy [2].

PEM fuel cells are generally exposed to high magnitude road-induced vibrations and impact loads in a range of 0.9 - 40 Hz when employed in transportation applications. These vibrations result in shear stresses between the PEM fuel cell layers and may initiate or exacerbate defects [3]. PEM fuel cells also experience a considerable amount of plastic strain due to humidity and temperature cycles (also known as hygrothermal cycles) during operation. The combination of these sources of mechanical stress can play an important role in the initiation and evolution of mechanical defects in the membrane electrode assembly (MEA) [4–10]. However, their impacts on PEM fuel cell mechanical degradations have yet to be fully investigated. Although
performance degradation is inevitable, an improved understanding of damage initiation and propagation mechanisms can be used to effectively control and minimize the degradation rate within PEM fuel cells.

Mechanical defects in PEM fuel cells such as pinholes, cracks, delaminations (separation of the layers) in the MEA, and fractures in the gas diffusion layer (GDL) can lead to fuel crossover, performance degradation, and reduced durability. This may ultimately result in operational failure in PEM fuel cells. These defects might remain at the micro-scale for a large fraction of the operation time; however, in the presence of other dynamic conditions, this damage may lead to severe crack propagation. Therefore, it is critical to identify and control the mechanisms that are involved in the defect initiation and propagation in PEM fuel cells and particularly under fatigue loading conditions.

Despite decades of research efforts, there is still a lack of fundamental understanding of the initiation and propagation of defects in PEM fuel cells. According to the available literature, there is no available study which has addressed the effect of vibrations on the mechanical damage evolution in PEM fuel cell and there are only few studies on the damage propagation under hygrothermal cycles. Therefore, there is a strong need for a theoretical or numerical model to investigate the effects of operation cyclic loadings and external vibrations on the initiation and propagation of damage in PEM fuel cells. Also, there is a need for models to simulate the damage and realistic loading regimes of working PEM fuel cells.
1.2 Structure of PEM Fuel Cells

A schematic of a PEM fuel cell is shown in Figure 1.2 (a). PEM fuel cells electrochemically convert hydrogen and oxygen from air into electricity, with heat and water as by-products, in the absence of combustion. Typically, a PEM fuel cell consists of an anode and a cathode, and a membrane electrode assembly (MEA) in the centre. The MEA consists of a polymer electrolyte membrane (PEM) embedded between two catalyst layers (CLs) and two carbon fibre gas diffusion layers (GDLs), as shown in Figure 1.2 (a).

The fuel (hydrogen) and the oxidant (oxygen) flow through the gas flow channels of bipolar plates and diffuse through the GDL to reach the catalyst layer, where the reactions take place. At the anode, hydrogen decomposes into hydrogen ions and electrons. The protons pass through the membrane and travel to the cathode CL. However, the electrons cannot pass through the membrane, but travel through an external circuit to the cathode (Figure 1.2 (b)). At the same time, at the cathode, oxygen reacts with the protons and electrons from the anode and produces water and heat. The overall mechanism is the reaction of hydrogen with oxygen to produce water and heat:

\[
\frac{1}{2}O_2 + H_2 \rightarrow H_2O + \text{Heat}
\]  

(1.1)
Single cells are often connected in series to form a PEM fuel cell stack to generate higher voltages. The integrity of the structure is maintained by the bolt assembly and rigid end plates providing uniform pressure between the components.

![Figure 1. 3. Reactions in the PEM fuel cell.](image)

### 1.3 Contributions

The work presented in this thesis resulted in two journal publications [13,14], and two manuscripts are currently under review state. The research contributions are summarized in the following list:

1. A numerical model for crack and delamination propagation in PEM fuel cells under fatigue loading was developed.
2. Damage properties used as model inputs for each PEM fuel cell component were provided.
3. The swelling and material property changes of the membrane and the generated plasticity under hygrothermal cycles in the MEA were modelled.
4. Effects of hygrothermal cycles on the defect propagation in the MEA were determined.
5. Impacts of external vibrations on the structural integrity of the PEM fuel cell were determined for the first time.
6. A range for critical amplitudes of vibrations and hygrothermal cycles resulting in severe damage propagation were provided.
1.4 Organization of the Thesis

This thesis is organized into eight chapters. The background and motivations are presented in Chapter 1, along with an overview of the contributions of the thesis. In Chapter 2, a literature review provides the background for the contributions of this thesis as well as the aspects that are missing in the current literature. The literature review also provides an introduction to the employed numerical method for modelling the damage and a background of this technique. Chapter 3 elaborates the theoretical details of the numerical modelling along with the validation process of the model. The details of the geometry and material modelling are stated in Chapter 4. Chapter 5 presents the effects of hygrothermal cycles on micro-scale mechanical defect propagation (cracks and delaminations). Chapter 6 presents the vibration-only simulations and their effects on defect propagation in the MEA. Chapter 7 combines the effects of both hygrothermal cycles and external vibration. Finally, conclusions and possible future plans of this research are presented in Chapter 8.
Chapter 2

2 Literature Review

Mechanical degradations of PEM fuel cell components have become a recent focus of attention over the last decade. Particularly, effects of humidity and temperature variations on the generated stresses in the MEA have been the focus of several studies. On the other hand, research concerning the effects of external vibration and micro damage propagation of PEM fuel cells is still in its infancy. In this chapter a literature review is provided for the effects of working conditions on fatigue and mechanical defects in PEM fuel cells. The literature review also encompasses evaluating membrane material properties as well as the limited number of studies focused on determining the membrane fracture properties. To conclude, the background for the employed numerical methodology for predicting effect propagation is presented.

2.1 Degradations due to Vibrations

Unlike internal combustion engines, fuel cells do not have moving parts, thus they are not a source of vibrations. However, fuel cells are subjected to road induced vibrations in automotive and transportation applications or vibrations from the environment. Passenger vehicles generally experience vibrations in the range of 8-16 Hz due to road unevenness and oscillations of the axel and wheel with the suspension system [15]. PEM fuel cells may also be employed to power auxiliary devices in semi-trailers, which typically experience vibrations in the range of 0.9-5.8 Hz due to uneven road conditions [16]. Others have suggested that auxiliary devices may be subjected to vibrations in the range of 17-40 Hz due to internal combustion engine vibrations
These vibrations result in shear stresses between the PEM fuel cell components which may initiate or exacerbate defects such as pinholes, cracks, and delaminations [3]. This may ultimately result in operational failure in PEM fuel cells.

Although the damage propagation under low-velocity impact loading is one of the most common types of failures in laminated composites (such as PEM fuel cells), the available studies in the literature have been mainly focused on the effect of vibrations on the power performance of the PEM fuel cell [18–21]. These studies include vibration tests on PEM fuel cell stacks, and their reports on the mechanical failure and damage were limited to qualitative descriptions of damage seen with the naked eye.

Rouss et al. [24, 25] conducted vibration studies for aircrafts applications. They developed a non-linear Artificial Neural Network (ANN) model based on their experimental data for monitoring the fuel cell under multi-axial vibrations. They exposed a five-cell stack (156 cm²) to three-directional vibrations with a frequency range of 6-2000Hz. Each test related to a specific vibration profile for 10-30 min and they investigated the nitrogen flow leakage rate through the fuel cell components. Only a slight lack of tightness and decrease of pressure at the anode side was detected. However, they stated that the result from a common fuel stack with higher number of cells would be probably different.

Rajalakshmi et al. [21] applied vertical and horizontal random-swept sine vibrations with a frequency range of 30-150 Hz for 90 min on a 500W PEM fuel cell 30-cell stack (330 cm²). Their post testing stack inspection showed minor torque release from 14 to 8 Nm; however, only a slight change in performance (from 425 W to 410W) was observed. In another study, Betournay et al. [18] investigated the effect of underground mining conditions, shock, and vibration on the performance of a 35W PEM fuel cell unit. The fuel cell was mounted over the rear wheel of a mine loader chassis and an accelerometer was used to measure the imposed shocks and vibrations. The data was recorded on two access ways in INCO’s Stobie Mine, Sudbury for 49 h. The fuel cell was then taken to the laboratory for visual inspection and performance checking. Neither the voltage-current nor the power-current curves showed a significant damage effect over the period of test time.
In the above mentioned studies [18–21], no visually detectable damage (cracks) or significant degradation in the power curves were observed during the test period. However, longer test times with start-up and shut-down considerations will provide valuable insight for PEM fuel cell lifetime estimations. Also, an understanding of damage generation at the microscale necessitates high resolution imaging that could be provided by microscopy techniques, such as scanning electron [22] and X-ray microscopy [23–25]. Furthermore, the tested fuel cells were not in operation during the test period which results in omitting a considerable amount of plastic strain generated by operation humidity and temperature loading cycles. A recent experimental study by Diloyan et al. [3] has shown that vibrations can considerably reduce the growth of platinum (Pt) particle agglomerations in the catalyst layer (CL). Loss of compression, thinning of the membrane, and degradations in PEM fuel cell components were also reported. They also found that increasing the vibration frequency and test duration had the most dominant impact on the results.

2.2 Degradations due to Humidity and Temperature Loading

Mechanical stresses induced by temperature and relative humidity (hygrothermal) cycles during PEM fuel cell operation play an important role in the initiation and evolution of micro-scale mechanical defects in the MEA [4–10]. The PEM fuel cell membrane experiences swelling and shrinking in response to the humidity and temperature variations during the cell operation. Being constrained by bi-polar plates, this behaviour results in developing in-plane compressive and tensile stresses in the membrane. These stresses can be significant enough to reach the yield state of the membrane and hence formation of mechanical defects, particularly after several hygrothermal cycles [5,7,26–29]. Ex-situ cyclic studies have shown that this fatigue failure is responsible for mechanical degradation (initiation and propagation of defects) in the MEA, even in the absence of electro-chemical effects [8,10,26,27].
2.2.1 Mechanical Stresses in Membrane under Hygrothermal Loading

Stresses and fatigue of MEA due to hygrothermal cycles have been widely investigated by several researchers [5,7,8,10,12,26–33]. Tang et al. [29] developed a finite element model to study the effect of membrane swelling on the stresses in the MEA. They showed that the in-plane stresses are the dominant stresses in the membrane. Huang et al. [34] showed that the RH cycles can cause micro cracks and defects in the membrane at the electrode/electrolyte interface. They found that hygrothermal cycle encourage the propagation of these defects along the membrane. They also showed that these damages were not present in only chemically aged specimens.

Bogrchev et al. [35] studied the evolution of stress and plastic strains during the start-up. They showed that the generated stresses are significant enough to initiate plastic deformation in the membrane. They also found that GDL/seal joint interface is the most vulnerable zone in the fuel cell.

The effect of the diffusion media (DM) material properties on the MEA damage under freeze/thaw cycles was studied by Kim et al. [11]. They found that the stiffness of the DM has a considerable effect on the damage mitigation. However, although material properties improvement could have significant effect, still water purging was found to be essential before shutting down the fuel cell. It was also found that damage occurs mostly under the channel not the land, due the assembly pressure applied by the land.

Kusoglu et al. [28] studied the mechanical behaviour of Nafion 112 under hydration–dehydration cycles. They performed a simulation using their previous experimental findings of Nafion® membranes, assuming a linear elasto-plastic constitutive behaviour for the membrane with isotropic hardening. They showed that membrane swelling has a dominant effect on the in-plane stresses in the MEA compared to effects of membrane thickness or the assembly conditions. They also suggested that the cathode side of the membrane is more prone to mechanical failure. They extended their work in a study by Khattra et al. [27], where they included the membrane viscoelasticity. Larger residual stress was observed compared to the previous study (without time and rate dependent properties). They found that slower feed and sorption rate lead to less generated stress. Also, uniform humidity feed across the membrane resulted in higher stresses compared to the non-uniform case.
Lu et al. [36] investigated the time-dependant behaviour of Nafion 211 under various strain rates for a range of humidity and temperature. They also postulated that the mechanical response of this type of membrane is more sensitive to variations of the stain rate and temperature than humidity changes. Their results also showed that Young’s modulus and the proportional limit stress both were increased with the strain rate increase, while they decrease with increasing the temperature and humidity. Shi et al. [37] experimentally studied the effect of hygrothermal aging on mechanical properties of the Nafion 212 membrane for different periods of testing time. They reported that due to the formation of cross links during longer aging processes the membrane will have a higher modulus and tensile strength. Furthermore, higher modulus and tensile strength were achieved for higher applied strain rates.

2.2.2 Material and Fracture properties of the Membrane

The membrane material properties show significant changes under the variation of humidity and temperature. Kusoglu et al. [38] studied the mechanical behaviour of Nafion 112 subjected to a hydration-dehydration cycle. They experimentally determined a range for the membrane Young’s modulus and yield stress at different humidities and temperatures. Li et al. [32] measured the fracture properties of the Dupant’s Nafion NRE-211 using three experimental methods (the double edge notched tension, the trouser tear test, and the modified knife test). They chose the knife test results to be more reliable, since less viscous and plastic dissipations were involved. A range of 0.15-0.6 kJm$^{-2}$ was reported for the membrane fracture toughness. Since the knife test considers the second mode of the fracture, these values can be used as $G_{IIc}$ of the membrane. Jia et al. [31] performed a double cantilever beam (DCB) test to quantify the fracture resistance of the membrane. They used a catalyst coated membrane (CCM) with a pre crack of 10 mm under 23 C° and humidities of 30%, 60% and 90%. The values of the first mode fracture toughness, $G_{Ic}$, and the fatigue parameters were generated by the author from Jia et al.’s work [31] to be used in this dissertation.
2.2.3 Membrane Life under Hygrothermal Loading

A limited number of studies have been conducted to investigate the effect of aging and working conditions on the life of the membrane. Aindow et al. [10] performed ex-situ fatigue tests in a dynamic mechanical analyser (DMA) to predict the membrane life in terms of the number of hygrothermal cycles that are experienced before reaching the yield state. They provided a failure curve which predicted the membrane life as a function of relative humidity (RH) cycling amplitude. Burlatsky et al. [8] developed a mathematical model for predicting the membrane life using molecular theory which included membrane non-linear viscoelasticity. Their model showed an exponential decrease in membrane life with increasing the RH cycling amplitude.

The effect of the strain rate on membrane Young’s modulus and the initiated crack density in the MEA were studied by Lu et al. [7] for a range of humidity and temperature. Their results suggested that the membrane is more resistant to cracking at higher humidities and strain rates. Also, the effect of temperature was found to be negligible on the crack initiation. However, these studies [7,8,10] did not include the propagation of micro mechanical defects, which will connect to create large critical defects after several loading cycles.

2.2.4 Damage Propagation under Hygrothermal Cycles

Damage evolution mechanisms in the MEA are still in the early stages of investigations [28]. To the author’s best knowledge, there are currently three studies available in the literature on the mechanical damage evolution in PEM fuel cells [4,6,9]. In all of these studies, the crack or delamination was modelled using the cohesive zone concept. The utilization of cohesive elements is a widely accepted method for the prediction of delamination/crack growth in composites subjected to static or cyclic loading [21]. Details of cohesive zone models will be explained in the subsequent sections.

Defect propagation in PEM fuel cells was first studied by Rong et al. [6] in 2008. They investigated the microstructure changes in the catalyst layer due to cyclic start-ups and shutdowns using a three-phase model including Nafion, a carbon/platinum (C/Pt) agglomerate and a pore. Their model was developed in ANSYS and included the rate-dependent material
properties for the Nafion. They showed that the delamination between Nafion and the C/Pt agglomerate initiated more readily under a higher frequency of start-ups and shut-downs (shorter cycle period), while yield failure and crack initiation in Nafion occurred more rapidly after longer cycles.

Poornesh et al. [4] investigated the crack propagation in the CL at the carbon fibre/CL interface. Their sandwich model consisted of an interlayer embedded between two catalyst layers. The interlayer had the material properties of a carbon fibre or the bulk properties of the CL. They showed how the fracture energy varies in the above mentioned layers and found that the damage propagation in the CL was highly influenced by the location of the crack.

Ma et al. [9] investigated the stresses induced by the capillary forces at the interface between a Nafion thin-film and two C/Pt particles. They showed that the capillary forces can be large enough to generate interfacial delaminations. The above mentioned studies [4,6,9] have provided valuable insight into the evolution of mechanical defects in idealized PEM fuel cells due to hygrothermal cycles; however, the evolution of mechanical defects in the MEA still requires a thorough investigation that includes the cracks and realistic loading regimes representative of operating PEM fuel cells.

2.3 PEM Fuel Cell Damage Modelling

Based on the limited number of studies on both vibrations and hygrothermal cycles effects on the damage propagation in PEM fuel cells, there is a strong need to investigate the damage propagation behaviours in PEM fuel cells. Since the PEM fuel cell can be considered as a layered composite structure, the available studies on delaminated composites under fatigue loading can provide insight into modelling damages in PEM fuel cells.

2.3.1 Damage Modelling Methodologies for Composite Structures

Methods developed for progressive failure in composite laminates in the fracture mechanics platform are mainly divided into two groups: linear elastic fracture mechanics (LEFM) methods
and continuum damage mechanics (CDM) methods. The available methods based on LEFM assumptions are the J-integral, Virtual Crack Extension Technique, and Virtual Crack Closure Technique (VCCT), where the VVCT method is the most commonly used one. VVCT method allows a good prediction for the crack growth in composite materials. However, an initial delaminated area must be predefined and a self-similar crack growth needs to be assumed. These assumptions limit the uses of the VVCT in some cases, particularly when the initiation of the cracks should be considered. Also, VCCT in each load increment needs to detect the delamination front, calculate the nodal values, and set the new boundary conditions, which includes the singularity at the crack tip. Therefore, the definition of the crack shape is very important for the accuracy of the results. With same reasons, the re-meshing should be performed at each step of crack propagation. This requires a complex algorithm to monitor the crack tip propagation by releasing constraints on duplicate nodes, particularly when more than one crack is introduced in the body [39]. The combination of all these characteristics makes the VVCT method inefficient and very time consuming for fatigue modelling, especially under high cycle fatigue conditions.

Another platform for modelling the composite laminates failure is to use continuum damage mechanics (CDM) theory. In CDM, based on the fact that delamination and cracks reduce the ability of the structure to carry loads (equivalent to degradation of the stiffness of the structure), a damage mechanics framework is defined by introducing a damage parameter into the material constitutive equations. In other words, the loss of stiffness can be physically considered as the macroscopic representation of a series of distributed micro cracks and micro voids [40–42].

The limitations of the VCCT method are overcome by using hypothetical interface elements which are based on the concepts of CDM. Interface elements are separate finite element (FE) entities, which are placed between substructures of a composite material as a means of inserting a damageable layer for delamination modelling. Generally, interface elements function by connecting the two substructures and transferring all tractions across the interface, until a particular criterion is reached, at which point the element stiffness properties degrade. Cohesive elements are a type of interface elements that are employed in this thesis and will be introduced in the next section.
Although the limitations of the VVCT approach are overcome by the use of cohesive elements, the simulation of progressive delamination using these elements poses numerical difficulties as well. Cohesive elements require a fine mesh to remain accurate, and can become prohibitively inaccurate when larger mesh sizes are used, which must be considered in applications with large structures. Some of the other difficulties are related to the proper definition of the stiffness of the cohesive layer, the mesh sensitivity, and the convergence difficulties associated with problems involving material softening [41–43].

2.3.2 Cohesive Zone Model (CZM)

Cohesive elements are a type of interface elements that are increasingly being applied by researchers to model delaminations and debondings in composite structures. They treat the process zone ahead of crack tip as a continuous compliant layer (Fig.2.1). The progressive delamination/crack is then modelled by introducing a softening constitutive law named as the “cohesive zone model” that relates traction to the separation displacement at an interface where a Delamination/crack may occur. Delamination/crack is initiated or propagated whenever the inter-laminar traction attains the maximum interfacial strength. Details of cohesive zone modelling will be presented in the Chapter 3. A number of researchers have developed cohesive elements that utilize a variety of constitutional relationships, some of which are summarized in the work by Orifici et al. [3], where the different models are compared across a few categories including: type, approach to mixed-mode loading, whether additional constants or tests are required, and the types of analyzed structures.

![Figure 2. 1. Schematic of a cohesive zone model (CZM)](image-url)
2.3.2.1 CZM Background for Fatigue Analysis

The origin of cohesive zone models goes back to the work by Dugdale [16] in 1960, who introduced the concept of a generated thin plastic zone in front of a notch and postulated that the stresses in the surrounding material are limited by the yield stress. Barenblatt [17] in 1962 introduced cohesive forces on a molecular scale in order to solve the equilibrium problem in elastic bodies with cracks. These studies motivated Hillerborg et al. [18] who proposed a new formulation for the interface elements using the concept of tensile strength. Hillerborg’s model allowed the existing cracks to grow and as well it permitted the initiation of new cracks.

Xu and Needleman[44], Ortiz [45], and Yang and Ravi-chandar [46] incorporated a softening traction-displacement law which was defined based on the ultimate strength of the material. Their model allowed the debonding of materials under various loading conditions. They also suggested that a bi-linear relation between the traction and crack opening displacement is a better approach to describe the behaviour of a cracking material compared to a linear relation law which was used by that time. Their model also addressed the previous limitation of monotonic loading and was able to predict the damage behaviour under both loading and unloading conditions. However, it was assumed that the loading and unloading will be on the same path which was not able to address the hysteresis behaviour.

In a consequent study, Yang et al. [46] included the difference between the loading and unloading paths in a revised cohesive force law for quasi brittle materials. The new model was able to capture the damage behaviour under arbitrary loading conditions. Nguyen et al. [47] postulated that the loss of material stiffness is an effective representative of the irreversible material degradation during the unloading stage of each cycle. Two separate mechanisms for degrading the stiffness in the loading and unloading stages were considered in their work.

The concept of using a scalar damage parameter, $d$, in the damage model was introduced by Roe and Siegmund [48]. The scalar damage parameter accounted for accumulation of the degradation in the material during cyclic loading and had a range of 0-1 where $d = 1$ was representing the 100% damage state. The model was based on the cycle by cycle calculation which made it very time inefficient for high cycle fatigue. Robinson et al. [49] proposed a cycle-jump strategy to overcome this problem. Their model assumed an equivalent strain which was updated after a
certain number of cycles. Their model was capable to capture both initiation and propagation of the damage.

Turon et al. [31,50–52] improved the previous models by introducing a modified fatigue law which used the fracture and fatigue parameters directly obtained from fracture toughness experiments. Their model was later developed for high cycle fatigue and they also took the fracture mode mixity, cycle-jump strategy, and load ratio into consideration. They also provided an optimal value of the penalty stiffness of the cohesive element to overcome the convergence issues. Turon’s model was at the highest efficiency and accuracy for models with exciting pre-cracks assuming that the defects are always present due to manufacturing stage[39]. Turon’s model was later improved by May et al. [39,53] by introducing a variable fatigue damage initiation zone into the exiting model. Also, The estimation of the cohesive zone was further improved by Naghipour et al. [54] for mix-mode loading case. They used the improved model to predict the crack propagation in multidirectional carbon fibre reinforced polymer (CFRP) laminted composites. The model from Turon et al. [52] and Naghipour et al. [54] was employed in this thesis.
Chapter 3

3 Modelling of PEM Fuel cell Damage

The details of the MEA damage modelling are presented in this chapter. This model consists of two parts: (i) a damage model for predicting defect propagation, and (ii) a membrane model for simulating the swelling/shrinking behaviour of the membrane under humidity and temperature variations. An overview of how these modelling efforts are connected is provided in Figure 3.1. The author developed a package of user subroutines in ABAQUS 6.12 [50] to simulate defect propagation in automotive PEM fuel cells under realistic working conditions. At the end, the developed model is validated for a conventional composite and a PEM fuel cell unit. In this chapter, the equations of the cohesive element are obtained from [49,51,52].

Figure 3.1. Graphical overview of MEA damage modelling work.
3.1 Modelling of Damage Propagation

3.1.1 Kinematics of the Interfacial Element

An isoperimetric interface element is shown in Figure 3.1. The element consists of two surfaces with \( n \) nodes, which coincide with unreformed surface, at the unreformed state. The upper and lower surfaces are shown by \( S^+ \) and \( S^- \), respectively. The nodal displacement vector, \( q \), includes the coordinates of each node in the global coordinate system with \( X_i(\zeta, \eta) \) with \( i = 1, 2, \text{ and } 3 \).

Here, the coordinates of \( \zeta \) and \( \eta \) are the curvilinear coordinates on \( S^0 \) bounded by \(-1 \leq (\zeta, \eta) \leq +1\). The vector \( q \) starts with the degrees of freedom (DOFs) of the nodes on the lower surface and continues with the DOFs corresponding to the nodes on the upper one. Assuming \( n \) nodes on each surface with \( p \) degrees of freedom per node, the total number of DOFs on each surface will be \( 2pn \):

\[
q = \{q^-, q^+\}^T
\]

(3.1)

with \( q^- = \{q_1^-, q_2^-, q_3^-, \ldots, q_{pm}^-\}^T \), \( q^+ = \{q_1^+, q_2^+, q_3^+, \ldots, q_{pm}^+\}^T \).

It is assumed that the Cartesian coordinates \( x_i^\pm = x_i^\pm(\zeta, \eta) \) describes the deformations on \( S^\pm \).

![Figure 3.2. Deformation of the interface element](image)
A material point on the deformed surfaces, \( S^\pm \), is related to its original location on the unreformed surface, \( S^0 \), as follows:

\[
x_i^\pm = X_i + u_i^\pm
\]  \hspace{1cm} (3. 2)

The difference between the two states, \( u_i^\pm \), describes the deformation of the two surfaces in the global coordinates:

\[
u_i^\pm = N_{ik} q_k^\pm
\]  \hspace{1cm} (3. 3)

where \( N_{ik} \) is the related component of the shape function matrix, \( N \). Here, \( N \) has the dimension of \( n \times pn \) where \( n \) and \( p \) are both equal to 3 for the three-dimensional (3D) element, and are equal to 2 for the two-dimensional (2D) element. The shape function matrix is defined for the 3D and 2D elements as follows:

For 3D element:

\[
\psi_i^\pm = \frac{1}{4} (1 + \zeta \zeta_i) \ (1 + \eta \eta_i)
\]

\[
\psi_1^\pm = \frac{1}{4} (1 - \zeta) \ (1 - \eta), \quad \psi_2^\pm = \frac{1}{4} (1 + \zeta) \ (1 - \eta), \quad \psi_3^\pm = \frac{1}{4} (1 + \zeta) \ (1 + \eta), \quad \psi_4^\pm = \frac{1}{4} (1 - \zeta) \ (1 + \eta)
\]

\[
N = \begin{bmatrix}
\psi_1^e & 0 & 0 & \psi_2^e & 0 & 0 & \psi_3^e & 0 & 0 & \psi_4^e & 0 \\
0 & \psi_1 & 0 & 0 & \psi_2^e & 0 & 0 & \psi_3^e & 0 & 0 & \psi_4^e \\
0 & 0 & \psi_1^e & 0 & 0 & \psi_2 & 0 & 0 & \psi_3 & 0 & 0 & \psi_4^e
\end{bmatrix}
\]  \hspace{1cm} (3. 4)

And for 2D element:

\[
\psi_i^e = \frac{1}{2} (1 + \zeta \zeta_i)
\]

\[
\psi_1^e = \frac{1}{2} (1 - \zeta), \quad \psi_2^e = \frac{1}{2} (1 + \zeta)
\]
The global separation displacement is then defined as

\[ [u_i] = N_{ik} (q_k^+ - q_k^-) \] (3.6)

where \( i = 1, 2, 3 \) and \( k = 1, 2, \ldots, pn \). A mid-surface, \( S \), is defined between the \( S^+ \) and \( S^- \) surfaces which coincide with \( S^0 \) in the unreformed configuration. The coordinates on the mid-surface is defined as

\[ \bar{x}_i = \frac{1}{2} (x_i^+ + x_i^-) = X_i + \frac{1}{2} (u_i^+ + u_i^-) \] (3.7)

The mid-surface displacement gradient, \( g_{ij} \), is defined as

\[ g_{ij} = \frac{\partial \bar{x}_i}{\partial \chi_j} \] (3.8)

where \( \chi_i = \zeta \) and \( \eta \). The local orientation of normal and the tangential vector unit of the element with respect to the \( S \) surface can be written as

\[ V_1 = \frac{\partial \bar{x}_i}{\partial \zeta} = \begin{bmatrix} g_{11} & g_{12} & g_{13} \end{bmatrix}^T \] \[ V_2 = \frac{\partial \bar{x}_i}{\partial \eta} = \begin{bmatrix} g_{21} & g_{22} & g_{23} \end{bmatrix}^T \] (3.9)

The rotation tensor, \( \Theta \), is defined using these local orthogonal coordinate vectors:

\[ \Theta = \{ \hat{V}_s \quad \hat{V}_t \quad \hat{V}_n \} \]

\[ \hat{V}_s = \frac{V_1}{\|V_1\|} \quad \hat{V}_t = \frac{V_1 \times V_2}{\|V_1 \times V_2\|} \quad \hat{V}_n = \hat{V}_s \times \hat{V}_t \] (3.10)

The separation displacement, \( \lambda \), is defined as follows using the rotation matrix \( \Theta \):
\[ \lambda_i = \Theta_{ji}[u_j] \]  

(3.11)

\[ \delta \lambda_i = \delta \Theta_{ji}[u_j] + \Theta_{ji} \delta [u_j] \]

\[
= [u_j] \frac{\partial \Theta_{ji}}{\partial q^+_k} \delta q^+_k + [u_j] \frac{\partial \Theta_{ji}}{\partial q^-_k} \delta q^-_k + \Theta_{ji} \frac{\partial [u_j]}{\partial q^+_k} \delta q^+_k + \Theta_{ji} \frac{\partial [u_j]}{\partial q^-_k} \delta q^-_k
\]

(3.12)

\[
= \{ \tilde{B}_{ik} - \tilde{B}_{ik} \} \delta q^-_k + \{ \tilde{B}_{ik} + \tilde{B}_{ik} \} \delta q^+_k
\]

where

\[
\tilde{B}_{ik} = \Theta_{ji}N_{jk}
\]

(3.13)

The dimension of both \( \tilde{B}_{ik} \) and \( \tilde{B}_{ik} \) matrices is \( n \times pn \). Assuming \( T_j = \sigma_{ij}n_i \) as the traction component acting on the mid-surface, the internal virtual work done by the interfacial traction is:

\[
\delta W^{\text{int}} = \int \int \tau_j \delta \lambda_j d\bar{S} = \int \int \tau_j \Theta_{ji} \delta [u_j] d\bar{S}
\]

\[
= \delta q^+_k \int \tau_j \Theta_{ji} \frac{\partial [u_j]}{\partial q^-_k} d\bar{S} + \delta q^-_k \int \tau_j \Theta_{ji} \frac{\partial [u_j]}{\partial q^+_k} d\bar{S}
\]

(3.14)

Substituting equations (3.6) and (3.13) into Equation (3.14), we have

\[
\delta W^{\text{int}} = (\int \tau_j \tilde{B}_{jk} d\bar{S})(\delta q^+_k - \delta q^-_k)
\]

(3.15)

Therefore, the internal force vector of the interface element is:

\[
F = \{ F^-, F^+ \}
\]

\[
F^\pm_r = \pm \int \tau_j \tilde{B}_{jk} d\bar{S}
\]

(3.16)

The tangent stiffness matrix of the element is defined as
\[ K = \begin{bmatrix}
\frac{\partial F^-}{\partial q^-} & \frac{\partial F^-}{\partial q^+} \\
\frac{\partial F^+}{\partial q^-} & \frac{\partial F^+}{\partial q^+}
\end{bmatrix} = \begin{bmatrix}
K^- & K^+ \\
K^+ & K^{++}
\end{bmatrix}
\]

(3.17)

\[ K_{rw}^{\pm \pm} = \frac{\partial F_j^z}{\partial q_w^z} \]

\[ = \pm \left\{ \int_S \left[ \hat{B} \frac{\partial \tau}{\partial \lambda} \frac{\partial \tau}{\partial \lambda} d\tilde{S} \right] + \int_S \left[ \hat{B} \frac{\partial \tau}{\partial \lambda} dS^0 \right] + \int_S \left[ \frac{\partial \tau}{\partial \lambda} d\tilde{S} \right] \right\}
\]

\[ = \pm \left\{ \int_S \left[ \hat{B} D \hat{B} + \hat{B} \frac{\partial \tau}{\partial \lambda} d\tilde{S} \right] + \int_S \left[ \frac{\partial \tau}{\partial \lambda} dS^0 \right] + \int_S \left[ \frac{\partial \tau}{\partial \lambda} d\tilde{S} \right] \right\}
\]

where \( D \) is a 3×3 matrix which is defined as \( D_{jr} = \frac{\partial \tau_j}{\partial \lambda_r} \), and will be explained further in the next section. The deformed mid-surface, \( \tilde{S} \), is related to the unreformed surface as follows using Jacobin matrix, \( J \):

\[ d\tilde{S} = JdS^0 \]

(3.18)

\[ J = \begin{bmatrix}
\frac{\partial \xi}{\partial x_1} & \frac{\partial \xi}{\partial x_2} & \frac{\partial \xi}{\partial x_3} \\
\frac{\partial \eta}{\partial x_1} & \frac{\partial \eta}{\partial x_2} & \frac{\partial \eta}{\partial x_3} \\
\frac{\partial \zeta}{\partial x_1} & \frac{\partial \zeta}{\partial x_2} & \frac{\partial \zeta}{\partial x_3} \\
\frac{\partial \gamma}{\partial x_1} & \frac{\partial \gamma}{\partial x_2} & \frac{\partial \gamma}{\partial x_3}
\end{bmatrix} = \begin{bmatrix}
g_{11} & g_{21} & g_{31} \\
g_{12} & g_{22} & g_{32} \\
g_{13} & g_{23} & g_{33}
\end{bmatrix}
\]

The tangent stiffness matrix and the internal force vector were obtained using the Newton-Raphson method. While this method requires an accurate calculation of the internal force vector, an approximation may be used for the tangent stiffness matrix [55,56]. Calculating the partial derivative of the rotation matrix, \( \frac{\partial \Theta}{\partial g} \), in Equation (3.17) is computationally expensive. Therefore, it can be assumed that \( \frac{\partial \Theta}{\partial g} \) and \( \frac{\partial (d\tilde{S})}{\partial g} \) can be neglected [55,56], which leads to
omitting the last two terms in Equation (3.17). Also, based on Equation (3.13), \( \bar{B}_{sw} \equiv 0 \). As a result, a linear tangent matrix can be written as:

\[
K^{\pm \pm} = \pm \pm \int_5 (\bar{B}_j D_j \bar{B}_{rw}) dS
\]

(3.19)

### 3.1.2 Cracked Bodies and Modes of Failure

Based on fracture mechanics theory, a macroscopic defect will propagate through three mechanisms (modes) of growth, as shown in Figure 3.2:

- **Mode I**: Opening mode (normal mode) where a tensile stress is applied normal to the plane of the crack.

- **Mode II**: Sliding mode (in-plane shearing mode) where a shear stress acts parallel to the plane of the crack and perpendicular to the crack front.

- **Mode III**: Tearing mode (out-of-plane shearing mode) where a shear stress acts parallel to the plane of the crack and parallel to the crack front. This mode normally happens in the presence of torsion.

![Figure 3.3](image1.png)

Figure 3.3. Schematic of damage growth modes: (a) opening (mode I), (b) in-plane shearing (mode II), and (c) out-of-plane shearing (mode III).

Although, mode I is commonly found in cracked bodies, generally a combination of these propagation modes is present, particularly under complex loading conditions. Therefore, a mixed-mode damage model is employed in this thesis, where a
combination of the normal and shear mode behaviours are considered. The details of this model are explained in the next section.

3.1.3 Constitutive equations

The elastic strain energy required for damage extension is defined as follows [56] for a damaged interface:

\[
U(\lambda, d) = (1 - d) \times \left( \frac{1}{2} \lambda_i \lambda_j D_{ij}^0 \lambda_{ij} + d \times \left( \frac{1}{2} \left[ \delta_{ij} H(-\lambda_3) \lambda_3 \right] \times D_{ij}^0 \times \left[ \delta_{ij} H(-\lambda_3) \lambda_3 \right] \right) \right)
\]

(3.20)

with \( D_{ij}^0 = \delta_{ij} k \) and \( \lambda \) as the interfacial separation displacement. Here, \( D^0 \) is the initial stiffness tensor of the interface before the presence of any damage, and \( k \) is the penalty stiffness which defines the interpenetration stiffness of the interface prior to damage initiation. \( d \) is the scalar damage parameter which increases from 0 (no damage) to 1 (complete separation) under varying loading conditions. The Heaviside function, \( H(\lambda) \), is used to prevent the interpenetration of interface surfaces and is defined as

\[
H(\lambda) = \begin{cases} 
0 & \lambda < 0 \\
1 & \lambda \geq 0 
\end{cases}
\]

(3.21)

The second term in Equation (3.20) is added to simulate the prevention of the interfacial penetration (\( \lambda_3 < 0 \)) due to contact. By differentiating the elastic strain energy with respect to the separation displacement, the constitutive equation of the element is achieved which incorporates a softening relationship between the interface traction (stress) vector, \( \tau \), and the interfacial separation displacement, \( \lambda \):

\[
\tau_i = \frac{\partial U}{\partial \lambda_i} = (1 - d) D_{ij}^0 \lambda_{ij} - d D_{ij}^0 \left[ \delta_{ij} H(-\lambda_3) \lambda_3 \right]
\]

(3.22)

Equation (3.22) can be rearranged in the matrix notation as
\[
\begin{bmatrix}
\tau_1 \\
\tau_2 \\
\tau_3 \\
\end{bmatrix} = 
\begin{bmatrix}
(1-d)k & 0 & 0 \\
0 & (1-d)k & 0 \\
0 & 0 & (1-d)k + dk H(-\lambda) \\
\end{bmatrix}
\begin{bmatrix}
\lambda_1 \\
\lambda_2 \\
\lambda_3 \\
\end{bmatrix}
\tag{3.23}
\]

where subscripts 1 and 2 correspond to the in-plane shear directions, while subscript 3 represents the normal direction to the interface. Figure 3.3 describes the relationship between traction, \( \tau \), and the interfacial separation, \( \lambda \), for a single mode case. As shown in Figure 3.3 (a), the delamination/crack is initiated whenever the interfacial traction attains the maximum interfacial strength, \( \tau^0 \). Figure 3.3 (b) shows how the material stiffness is degrading after damage onset. Based on the continuum damage, the released energy during damage evolution (highlighted in Figure 3.3 (b)) must be positive:

\[
U = \int_{t}^{t+1} (-\frac{\partial U}{\partial d} \frac{\partial d}{\partial t}) dt \geq 0
\tag{3.24}
\]

Figure 3.4. A bilinear constitutive behaviour for the cohesive element for: (a) a single mode, and (b) degrading the interface stiffness with increasing \( d \) [56].

Since generally a combination of the fracture modes is present in practical applications, a mixed-mode damage model is employed in this thesis. The mixed-mode model results in more accurate prediction for damage propagation, particularly under complex loading conditions. The applied approach for combing the normal and shear mode behaviours is shown in Figure 3.4. Here, the active mixed mode plane is shown in blue which is defined based on the mode ratio and the
interfacial strength under mixed-mode conditions, $\tau^0_m$. Interfacial strength in normal and shear modes are shown by $\tau^0_n$ and $\tau^0_{\text{shear}}$, respectively. The mixed-mode separation displacements corresponding to the damage onset and the final separation are presented by $\lambda^0_m$ and $\lambda^f_m$, respectively. The damage initiates when the interface traction reaches to $\tau^0_m$, and the material starts to degrade afterwards. The mixed-mode displacement at the crack tip, $\lambda_m$, is defined as

$$\lambda_m = \sqrt{\lambda_1^2 + \lambda_2^2 + \lambda_3^2} = \sqrt{\lambda_{\text{shear}}^2 + \lambda_{\text{normal}}^2}$$

$$\lambda_{\text{shear}} = \sqrt{\lambda_1^2 + \lambda_2^2}, \quad \lambda_{\text{normal}} = \lambda_3$$

$$\beta = \frac{\lambda_{\text{shear}}}{\lambda_{\text{shear}} + H(\lambda_{\text{normal}})}$$

where subscript $m$ refers to the mixed-mode condition. The damage will propagate after the energy release rate, $G$, reaches the critical strain energy release rate, $G_c$, in the material surrounding the damage. The value of $G_c$ is defined as (Benzegagh and Kenane [57]):

$$G_c = G_{lc} + (G_{llc} - G_{lc}) \left( \frac{\beta^2}{1 + \beta^2} \right)^\eta$$

where $\eta$ is the experimentally determined failure parameter. The critical strain energy release rates (also known as fracture toughness) for normal and shear modes are defined by $G_{lc}$ and $G_{llc}$, respectively. The value of $G_{llc}$ is generally assumed to be same as $G_{llc}$ due to the experimental difficulties in determining $G_{llc}$. 
In damage evolution due to fatigue, the state of total damage, $d$, in Equation (3.24) is defined as the sum of the damage created by quasi-static loads, $d_{\text{quasi-static}}$, and the damage created by cyclic loads, $d_{\text{cyclic}}$ [52]:

\[
\frac{\partial d}{\partial t} = \dot{d} = \dot{d}_{\text{quasi-static}} + \dot{d}_{\text{cyclic}}
\]  

(3.27)

where $t$ is time, and $\dot{d}$ denotes the variation of damage with respect to time. The quasi-static damage, $d_{\text{quasi-static}}$, at each time increment $\Delta t$ is defined as

\[
\dot{d}_{\text{quasi-static}} = \frac{\lambda'_m (\lambda_m - \lambda^0_m)}{\lambda_m (\lambda'_m - \lambda^0_m)}
\]  

(3.28)

The values of $\lambda^0_m$ and $\lambda'_m$ in equation (3.28) are defined as follows:
\[
\lambda_m^0 = \begin{cases} 
\lambda_n^0 \frac{1 + \beta^2}{\sqrt{\lambda_n^0} + \beta^2 (\lambda_n^0)^2} & \lambda_n > 0 \\
\lambda_n^0 & \lambda_n < 0
\end{cases}
\]

\[
\lambda_m^f = \begin{cases} 
\frac{2}{K\lambda_n^0} G_c & \lambda_n > 0 \\
\lambda_n^f & \lambda_n < 0
\end{cases}
\]

where \( \lambda_n^0 = \frac{\tau_n^0}{K} \) and \( \lambda_n^f = \frac{\tau_n^0}{K} \) and \( \lambda_n^f = \frac{2G_{ic}}{\tau_n^0} \).

The damage parameter with respect to subsequent cycles can be expressed as

\[
\dot{d}_{cyclic} = \frac{\partial d}{\partial N} \frac{\partial N}{\partial t} = \left( \frac{\partial d}{\partial A_d} \frac{\partial A_d}{\partial N} \right) \frac{\partial N}{\partial t}
\]

(3.30)

where \( A_d \) is the damaged area in front of the crack tip after \( N \) cycles. The term \( \frac{\partial d}{\partial A_d} \) is defined as follows:

\[
\frac{\partial d}{\partial A_d} = \frac{1}{A^c} \left[ \frac{\lambda_n^f (1 - d) + d\lambda_n^0}{\lambda_m^0 \lambda_n^0} \right]
\]

(3.31)

where \( A^c \) is the area of each cohesive element in the damage zone. Based on the approach proposed by Turon et al. [56], the crack growth can be defined as the sum of the damaged area growth rate in elements in front of the crack tip:

\[
\frac{\partial A}{\partial N} = \sum_{k_z} \frac{\partial A_d^c}{\partial N} = \frac{A_{cz}}{A^c} \frac{\partial A_d}{\partial N}
\]

(3.32)

where \( A_{cz} \) is the initial area exposed to damage at the front of the crack tip, which is modelled with cohesive elements. \( A_d^c \) is the damaged area of one element. Assuming \( A_d \) as the total damaged area after \( N \) cycles, the term \( \frac{\partial A_d}{\partial N} \) represents the mean value of the damage growth rate.
per cycle in an element. By rearranging Equation (3.32), \( \frac{\partial A_d}{\partial N} \) is defined as

\[
\frac{\partial A_d}{\partial N} = A^c \frac{\partial A}{A_c \partial N}
\] (3.33)

The well-known Paris’ law [40] was used to describe the damage growth rate, \( \frac{\partial A}{\partial N} \), under fatigue loading. Paris’ law was originally proposed for predicting the crack growth in metals. However, its applicability to composite materials [39,52–54,58] and polymers [59] have been confirmed by several researchers. In the recent years, Paris-type damage accumulation laws have successfully been incorporated into interface elements formulations in composites [39,52–54]. The Paris law can accurately predict the crack behaviour in region II of the crack growth rate pattern (Fig. 3), where there is a linear relationship between the energy release rate and \( \frac{\partial A}{\partial N} \):

\[
\frac{\partial A}{\partial N} = C \left( \frac{\Delta G}{G_c} \right)^m \quad \Delta G < G_{\text{max}} < G_c
\] (3.34)

where \( A \) is the crack surface, and \( N \) is the number of cycles. Parameters \( C \) and \( m \) are empirical Paris law constants which are experimentally defined as shown in Figure 3.5. The maximum energy release rate, \( G_{\text{max}} \), in Equation (3.34) is defined as

\[
G_{\text{max}} = \frac{\tau_0^m}{2} \left( \delta_m^f - \left( \delta_m^f - \delta_m^{\text{max}} \right)^2 \right)
\] (3.35)

Considering the variation of energy release rate in each loading cycle, \( \Delta G \), as \( \Delta G = G_{\text{max}} - G_{\text{min}} \) with load ratio, \( R \), defined as \( R^2 = \frac{G_{\text{min}}}{G_{\text{max}}} \), the variation of energy release rate in a loading cycle can be written as

\[
\Delta G = G_{\text{max}} (1 - R^2)
\] (3.36)

Substituting Equations (3.31), (3.33) and (3.34) into Equation (3.30):
\[
d_{\text{cyclic}} = \frac{\partial d}{\partial N} = \frac{1}{A_c} \times \left[ \frac{\lambda_m^f (1 - d) + d \lambda_m^0}{\lambda_m^0 \lambda_m^f} \right] \times C \left( \frac{\frac{r_0^m}{2} \left( \lambda_m^f - \lambda_m^0 \right)^2}{G_c} \right)^m \quad G_{th} < G_{\text{max}} < G \quad (3.37)
\]

This CZM model was implemented in ABAQUS 6.12 [60] by developing a package of user subroutines to be used as a user defined element (UEL).

Figure 3. 6. General schematic of a Paris plot.

3.2 Modelling of the Membrane Nonlinear Behaviour

The membrane swelling and shrinking in response to humidity and temperature variations is modelled in this section. The material expansion due to humidity and thermal expansions are considered in the formulation as well as the resultant generated plasticity. Furthermore, the
changes of membrane material properties resulted from humidity and temperature working cycles are also considered in the model.

The above mentioned hygrothermal effects are incorporated into the membrane FE model using an uncoupled theory [5,6,28,29,38], which neglects the additional temperature variations due to the applied strain. The total strain tensor is expressed as

$$\varepsilon_{ij} = \varepsilon^e_{ij} + \varepsilon^pl_{ij} + \varepsilon^T_{ij} + \varepsilon^{Sw}_{ij}$$  \hspace{1cm} (3.38)

where $\varepsilon^e_{ij}$ and $\varepsilon^pl_{ij}$ are the elastic and plastic strain components, respectively. The thermal expansion and swelling strains are shown by $\varepsilon^T_{ij}$ and $\varepsilon^{Sw}_{ij}$, respectively. Assuming the membrane as an isotropic material [5–7,27,28], the elastic behaviour of the membrane is modelled using Hooke’s law,

$$\varepsilon^e_{ij} = \frac{1}{E(T, RH)} [\sigma_{ij} - \nu (\sigma_{kk} \delta_{ij} - \sigma_{ij})]$$ \hspace{1cm} (3.39)

where $\sigma_{ij}$ is the stress tensor and $\sigma_{kk} = \sigma_{11} + \sigma_{22} + \sigma_{33}$. Young's modulus, $E(T, RH)$, was defined as a function of temperature, $T$, and relative humidity, $RH$, using the experimental data provided by Kusoglu et al. [28,38]. $\delta_{ij}$ and $\nu$ are the Kronecker delta and Poisson's ratio, respectively. For the plastic strain, the J2 plasticity flow theory [61] is used as the yield function. Assuming incompressible plastic deformation [5–7,27,28],

$$f(\sigma_{ij}) = \sqrt{\frac{3}{2} S_{ij} S_{ij} - \sigma_{ij} (\overline{\varepsilon}^pl_{ij}, RH, T)} = 0$$ \hspace{1cm} (3.40)

where $\sigma_{ij}$ is the yield stress and is a function of humidity, temperature, and the equivalent plastic strain, $\overline{\varepsilon}^pl_{ij}$. $S_{ij}$ is the deviatoric stress tensor. The equivalent plastic strain is defined as

$$\overline{\varepsilon}^pl_{ij} = \int \sqrt{\frac{2}{3}} \frac{d\varepsilon^pl_{ij}}{d\varepsilon^pl_{ij}} \text{ with } d\varepsilon^pl_{ij} = S_{ij} d\lambda$$ \hspace{1cm} (3.41)
where $d\lambda$ is a scalar proportionality factor, and $d\varepsilon_{ij}^{pl}$ is the plastic strain increment tensor. During the integration procedure, first the Von Mises stresses are calculated based on purely elastic behaviour:

$$
\sigma_{ij}^{pr} = \sqrt{\frac{3}{2}} S_{ij}^{pr} S_{ij}^{pr}, \quad S_{ij}^{pr} = S_{ij}^0 + 2\mu \varepsilon_{ij}^{pl}
$$

(3.42)

where $\mu$ is the Lamé's second parameter or shear modulus. After solving the equations using backward Euler method, plastic flow will occur if the stress is larger than the yield stress. Next, the incremental equivalent plastic strain is calculated using the Newton-Raphson method:

$$
\bar{\sigma}_{ij}^{pr} - 3\mu \Delta \varepsilon_{ij}^{pl} = \sigma_y(\varepsilon^{pl})
$$

(3.43)

Using the generated value for $\varepsilon^{pl}$, the following parameters will be updated:

$$
\sigma_{ij} = \eta_{ij} \sigma_y + \frac{1}{3} \delta_{ij} \sigma_{kk}^{pr}, \quad \eta_{ij} = \frac{S_{ij}^{pr}}{\sigma_{ij}^{pr}}, \quad h = \frac{d\sigma_y}{d\varepsilon^{pl}}
$$

(3.44)

where $h$ is the plastic flow. Next, the plastic strain variation is calculated as

$$
\Delta \varepsilon_{ij}^{pl} = \frac{\bar{\sigma}_{ij}^{pr} - 3\mu \Delta \varepsilon_{ij}^{pl} - \sigma_y(\varepsilon^{pl})}{h + 3\mu}
$$

(3.45)

The swelling strain from humidity absorption, $\varepsilon_{ij}^{Sw}(T,RH)$, is defined using the experimental curves provided by Kusoglu et. al. [28] at various humidities and temperatures:

$$
\varepsilon_{ij}^{Sw}(T,RH) = \sum_{i,j=1}^{4} C_{ij} T^{i-j} RH^{4-i} \quad i, j = 1, 2, \ldots 4
$$

(3.46)

where $C_{ij}$ is the matrix of constants representing the swelling strain polynomial with its components presented in Table 3.1. The experimental curves achieved by Kusoglu et. al. [28] for the swelling strain are shown in Figure 3.6.
The thermal strain generated due to the temperature variation can be expressed as

$$\varepsilon_{ij}^T (T) = \alpha (T - T_0) \delta_{ij}$$ \hspace{1cm} (3. 47)$$

where \( \alpha \) and \( T_0 \) are the coefficient of thermal expansion and the reference temperature, respectively. The membrane behaviour is incorporated in the FE model with custom UMAT and UEXPAN subroutines developed in-house for use in ABAQUS 6.12 [62].
3.3 Validation of the Model

In this section, the details of the validation process of the developed model are presented. Since using cohesive elements is a common practice in composites, first the model is validated for damage propagation in a conventional composite. The ASTM standards were employed for this part of the validation. This step confirms if the damage model is developed properly, regardless of the unusual behaviours that are observed in PEM fuel cell membrane. Next, the model was examined for damage propagation in a PEM fuel cell to confirm the membrane modelling and the assigned fracture properties.

3.3.1 Validation of the Damage Model for a Conventional Composite

In order to validate the developed code for a conventional composite, simulations for the double cantilever beam (DCB) and end notch flexure (ENF) tests were performed. These static tests [63,64] are defined by the American Society for Testing and Materials (ASTM) to determine the fracture properties of the materials. As shown in Figure 3.7, DCB and ENF tests activate the first mode and the second mode of damage propagation, respectively. The material properties are from the work by Turon et al. [50] for a 102 mm AS4/PEEK carbon-fibre reinforced epoxy composite specimen with a 35mm-long crack. The developed cohesive element was used at the interface while for other areas ABAQUS three-dimensional elements C3D8I were used.

Figure 3.8 shows the load-displacement curves predicted by the present numerical model and the numerical and experimental data from Turon et al. [50]. Turon et al. [50] used the cohesive modelling approach in their numerical study. The maximum load in the graphs are compared with the numerical results provided by Ref [50] in Table 3.2. As can be observed from this table and Figure 3.8, there is a good agreement between the numerical and experimental results. Therefore, it can be concluded that the devolved code is reliable for damage analysis in a general composite structure.
Figure 3.8. Schematic of the testing setup for: (a) the end notch flexure (ENF) and (b) the double cantilever beam (DCB) tests.

Figure 3.9. Predicted and experimental load-displacement curves for: (a) DCB test and (b) ENF test.

Table 3.2. Comparison of the numerical results for maximum loads

<table>
<thead>
<tr>
<th></th>
<th>$F_{\text{max}}$ (Present Work, N)</th>
<th>$F_{\text{max}}$ (Turon et al. [50], N)</th>
<th>Percentage Difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Double cantilever beam test</td>
<td>153.6</td>
<td>152.4</td>
<td>0.79</td>
</tr>
<tr>
<td>End notch flexure test</td>
<td>688.1</td>
<td>698.6</td>
<td>1.50</td>
</tr>
</tbody>
</table>
3.3.2 Validation of the Damage Model for PEM Fuel Cells

Although the fracture properties of the membrane have been recently under the attention [31,32,38], there is still a lack of experimental studies focused on the mechanical damage propagation in a fuel cell unit. Therefore, the model validation for the PEM fuel cell was performed through two separate procedures: (i) the membrane swelling and material properties variation under hygrothermal cycles and the resulting stresses in the MEA, and (ii) the assigned fracture properties and the ability of the model to capture the MEA damage propagation.

For the first part, a numerical study from Kusoglu et al. [28] was used, where a unit of fuel cell with no damage was exposed to hygrothermal cycles. For the second part, an experiment from Jia et al. [31] was used to validate the damage model for crack propagation in the membrane. The first part proves that stresses, deformations, and material property changes are correctly captured by the model, while the second validation part accounts for the damage model and the employed fracture properties for the CLs and membrane.

3.3.2.1 Validation of the Membrane Swelling Behaviour and Variation of Material Properties

The numerical study from Kusoglu et al. [28] was employed to validate the membrane behaviour modelling. The computational domain used for this simulation is shown in Figure 3.9 (a). Cyclic hygrothermal loading was applied to a PEM fuel cell unit, in which humidity and temperature started from ambient conditions (of 30% RH and 20 °C) and reached the maximum loading conditions of 95% RH and 85 °C. The employed dimensions and material properties can be found in [28]. As explained earlier, the swelling and shrinking of the membrane induces in-plane stresses in the MEA. Validating these stresses can be an indicator of the accuracy of the modelling. For this purpose, the location shown in Figure 3.9 (a) is chosen to investigate the in-plane stresses.

Figure 3.9 (b) illustrates a comparison between the resultant in-plane stresses at the membrane/gas diffusion electrode (GDE) interface from the present model with the reference
This interface is particularly important since the present study considers the damage propagation at this vicinity. As it is shown in the figure, results are in a good agreement with the values from [28]. For the first peak, a 1.12% difference was observed between the result from [28] (5.14 MPa) and the current model (5.08 MPa); while for the consequent maxima a 2.18% percentage difference was observed. Therefore, the model effectively simulates the stresses, deformations, and material property changes under hygrothermal cycles. Hence, the validation indicates that stresses, deformations, and material property changes were sufficiently captured in the model used in this work.

![Figure 3.10](image)

Figure 3.10. (a) Schematic of the computational domain in Ref [28] - (b) Comparison of in-plane stresses in the MEA at the specified location.

### 3.3.2.2 Damage model at a Specific Temperature and Humidity

An experimental study by Jia et al. [31] was used to validate the damage model and the assigned fracture properties for the PEM fuel cell. They performed a DCB test on a catalyst coated membrane (CCM) specimen under ambient conditions (25°C and 30% RH). A schematic of this experimental setup is shown in Figure 3.10 (a). Their set up consisted of a CCM embedded between two polycarbonate layers. The in-plane dimensions were 10mm×40mm with an initial
delamination length of 10 mm. The thickness of the Nafion layer, catalyst layers, and polycarbonate layers were 25 µm, 10 µm, and 3 mm, respectively. In this experiment, Jia et al. [31] applied a cyclic load on the pre-cracked specimen and provided a graph which related the applied load to the displacement at the tip of the specimen (Figure 3.10 (b)). The displacement of the specimen tip is directly related to the crack length and is used as an indicator of crack propagation in DCB tests [63].

A similar loading condition to Jia et al. [31] was applied to the simulated specimen using the present damage model, and the results are compared with the experimental data from [31] in Figure 3.10 (b). As Figure 3.10 (b) shows, a good agreement was achieved between the current numerical model and the experiment in [31]. For the first peak, the difference between the numerical (7.899 N) and experimental results (7.78 N) is 1.53%. Since the CCM specimen includes the membrane/CL interface where the defect in this study was investigated, it can be concluded that our damage model is capable of predicting the damage in this part of the fuel cell. Also, this section validates the employed fracture properties for the CLs and membrane.

Figure 3. 11. (a) The schematic model of the double cantilever beam test specimen - (b) Comparison of the numerical load-displacement curve with the DCB test results.
3.4 Summary

The detailed formulation for the damage model was presented in this chapter. This model consisted of two parts: (i) a damage model based on continuum damage mechanics theory for predicting the defect propagation, (ii) and a membrane model to simulate the non-linear behaviour of the membrane under humidity and temperature variations. The model was validated for a conventional composite and a PEM fuel cell unit, and a good agreement was achieved between the present model and the literature. This model was implemented as a package of user developed subroutines in ABAQUS 6.12 [60] written in FORTRAN programming language platform. Both 2-D and 3-D elements are developed and validated in this chapter. The 2-D element is employed in the following chapters to study the damage behaviours in the MEA. Two-dimensional models have been utilized extensively in the literature to investigate the stresses, plastic strains, and damages of PEM fuel cells [4–8,26–29,35,38,65–68], and they can provide valuable insight at reasonable computational costs.
Chapter 4

4 Numerical Model and Simulations

The numerical domain for the PEM fuel cell is presented in this chapter. The two-dimensional (2D) cohesive element model is employed to simulate the evolution of defects in the PEM fuel cell. This chapter includes the simulation steps as well as the details of geometry, boundary condition, and material property assumptions. These assumptions are particularly important and have not been explicitly reported in the literature prior to the work from this thesis.

4.1 Geometry and Boundary Conditions

The current 2D finite element (FE) model of the fuel cell included two bipolar plates, two GDLs, two CLs, and a Nafion membrane, as shown in Figure 4.1. Three locations for an initial defect were considered: a delamination at the membrane/CL interface and two cracks in the membrane. The delamination was placed at the cathode membrane/CL interface under the channel, since this interface has been reported as one of the most vulnerable areas for the initiation of defect due to mechanical fatigue resulting from RH cycles [6,8,9,11,26,28,69]. The cracks were placed in the membrane along its thickness as shown in the simplified illustration in Figure 4.1: at the centre and at a distance of $L = \frac{t_{\text{membrane}}}{4}$ from the membrane/CL interface, where $t_{\text{membrane}}$ is the membrane thickness.
In order to model the assembly pressure, a fixed displacement was applied to the upper bipolar plate, while the clamped boundary condition was applied on the lower bipolar plate [28]. The value of the applied displacement was 0.00115 mm, which was calculated as the result of applying an assembly pressure of 1 MPa to an undamaged fuel cell. A symmetry boundary condition was applied to the left edge. A linear constraint of $u_x^1 - u_x^i = 0$ was applied to the right edge of the model to ensure its uniform movement [28], where $u_x^1$ and $u_x^i$ are the displacement in the $x$-direction of node 1 and node $i$, respectively. Node 1 is the first node at the bottom of the left edge, and node $i$ denotes the remaining edge nodes with $i = 2 \ldots N_e$, where $N_e$ is the total number of edge nodes.

The developed cohesive element, with zero thickness, was employed for modelling the damage zone in front of the delamination/crack tip. For modelling the other layers, The ABAQUS built-in four-node coupled temperature-displacement generalized plane strain elements (CPEG4T) were used. In the $x$-direction, 200 elements were placed to satisfy the maximum acceptable
length of the cohesive element \( l_{\text{max}} = \frac{2}{3\pi} \frac{E_G}{\ell(\tau^0)^2} \) at the maximum temperature and humidity. For GDLs, CLs, and membrane, 10, 2, and 8 element layers in the thickness direction were considered, respectively. The initial delamination length was chosen to be \( a = 0.025 \text{ mm} \) (25 \( \mu \text{m} \)), which is consistent with experimental findings from literature [7,11].

### 4.2 Material and Fracture Properties

The material properties and the thickness of the PEM fuel cell layers employed in this simulation are listed in Tables 4.1 and 4.2. The membrane and CL were assumed to be isotropic [4,6,27–29], while the GDL was modelled as an orthotropic material. The equivalent orthotropic material properties of GDL were obtained from the experimental study by Yi et al. [68]. The GDL porosity can have a noticeable effect on the propagation behaviour of a fracture in GDLs or delaminations at the GDL/CL interface. However, for a crack in the membrane or a delamination at CL/membrane interface the orthotropic assumption can be applied in order to avoid the difficulty of the modelling [27,29,35,38,67].

It was assumed that the membrane (DuPont™ Nafion® 112) is an isotropic hardening material with elastic-perfectly plastic behaviour [28,68]. As shown in Figure 4.2 (a), the isotropic hardening is defined using the initial membrane yield stress where plastic strain \( \varepsilon_{\text{pl}} = 0 \), \( \sigma_0(T, RH, \varepsilon_{\text{pl}} = 0.0) \), and two additional stress points of \( \sigma_1(T, RH, \varepsilon_{\text{pl}} = 0.05) \) and \( \sigma_2(T, RH, \varepsilon_{\text{pl}} = 0.25) \) [28,29]. The isotropic hardening assumption has been performed for the considered range of humidity and temperature, as shown in Figure 4.2 (b). In this figure, the data corresponding to \( \varepsilon_{\text{pl}} = 0.05 \) are not shown for clarity. Therefore membrane viscoelasticity and loading rate dependent behaviours, such as creep and stress relaxation, were not considered in this model. The implication of these assumptions is that the fuel cell experiences relatively quick dry-out during shut-down cycles [34]. Furthermore, it was assumed that all components has linear thermo-elastic isotropic behaviour when they experience a thermal gradient [4,6,27–29].
As mentioned earlier, the material properties of membrane shows significant changes under the variation of humidity and temperature. Figure 4.3 shows the extreme changes of the Young's modulus of the membrane and the yield stress for humidity and temperature values. A subroutine was developed to account for the membrane fracture and material properties as a function of humidity and temperature variations. A time step of $\Delta t = 10^{-5}$ s was chosen to satisfy the convergence and stability of the solution.

Figure 4.3. Effect of temperature and humidity on Nafion: (a) Young’s modulus and (b) yield stress. The data presented in this figure was obtained from [28].
In order to model the damage zone, the values of the normal strength, \( \tau_{\text{normal}}^0 \), the shear strength, \( \tau_{\text{shear}}^0 \), and the normal and shear fracture toughness, \( G_{Ic} \) and \( G_{IIc} \), of the interface need to be defined. Nafion properties were conservatively chosen to define the strength and toughness of the membrane/CL interface [4,6,9], since Nafion is mechanically weaker than the C/Pt agglomerate. The interfacial normal strength, \( \tau_{\text{normal}}^0 \), was defined as the Nafion yield stress [39,52,54] using the data provided by Kusoglu et al. [28] over a range of temperatures and humidities. The same value (Nafion yield stress) was chosen for the \( \tau_{\text{shear}}^0 \) based on discussions with Turon et al. [52], as an acceptable alternative option\(^1\) in the absence of experimental data. Hence, the results under shear mode of damage propagation are conservatively predicted. The values of fracture toughness of Nafion are listed in Table 4.3 along with the related \( C \) and \( m \) (in Equation 3.33). The values for \( G_{Ic} \) were extracted from the crack growth graphs provided by Jia et al. [31]. In this table, the results from knife tests performed by Li et al. [32] were used as the second mode of the fracture.

### Table 4.1. Material properties of the PEM fuel cell components.

<table>
<thead>
<tr>
<th>Thickness (mm)</th>
<th>( E ) (MPa)</th>
<th>( v )</th>
<th>( \rho ) (Kg/m(^3))</th>
<th>( \alpha ) ((10^{-6} ) K(^{-1}))</th>
<th>( C_p ) (J Kg(^{-1})K(^{-1}))</th>
<th>( k ) (W m(^{-1})K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CL</td>
<td>0.010 [67]</td>
<td>450 [4]</td>
<td>0.18 [4]</td>
<td>2100 [67]</td>
<td>8.70 [67]</td>
<td>130</td>
</tr>
<tr>
<td>GDL</td>
<td>0.200 [67]</td>
<td>Table 4.2</td>
<td>Table 4.2</td>
<td>440 [67]</td>
<td>-0.80 [67]</td>
<td>500</td>
</tr>
<tr>
<td>Bipolar Plates [28]</td>
<td>11.0</td>
<td>10000</td>
<td>0.25</td>
<td>1800</td>
<td>5.0</td>
<td>750</td>
</tr>
</tbody>
</table>

\(^1\) Since the membrane fracture toughness remains constant during the simulation, the assumption of \( \tau_{\text{shear}}^0 = \text{yield stress} \) was applied. Furthermore, in this thesis the work hardening effects have been addressed to the membrane yield stress (the yield stress increases with increasing plastic strain, Figure 4.2), which means the ductility of the membrane has been considered to a reasonable extent.
Table 4.2. Material properties of the GDL.

<table>
<thead>
<tr>
<th>$E_{11}$ (GPa)</th>
<th>$E_{22}$ (GPa)</th>
<th>$E_{33}$ (MPa)</th>
<th>$G_{12}$ (GPa)</th>
<th>$G_{23}$ (MPa)</th>
<th>$\nu_{12}$</th>
<th>$k_{11}$ (W m$^{-1}$ K$^{-1}$)</th>
<th>$k_{22}$ (W m$^{-1}$ K$^{-1}$)</th>
<th>$k_{33}$ (W m$^{-1}$ K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.63</td>
<td>3.63</td>
<td>8.79</td>
<td>1.35</td>
<td>8.55</td>
<td>0.28</td>
<td>23</td>
<td>1.7</td>
<td>23</td>
</tr>
<tr>
<td>[68]</td>
<td>[68]</td>
<td>[68]</td>
<td>[68]</td>
<td>[68]</td>
<td>[68]</td>
<td>[67]</td>
<td>[67,73]</td>
<td>[67]</td>
</tr>
</tbody>
</table>

Table 4.3. Fatigue material properties of the membrane. The $C$ and $m$ values were extracted from the crack growth curves published by Reference[31].

<table>
<thead>
<tr>
<th>$G_{fc}$ (KJ/m$^2$)</th>
<th>$G_{f\ell c}$ (KJ/m$^2$)</th>
<th>$G_{th}$ (KJ/m$^2$)</th>
<th>$C$ (mm/cycle)</th>
<th>$M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RH = 30%</td>
<td>0.0275 [31]</td>
<td>0.869 [32]</td>
<td>0.0170 [31]</td>
<td>0.0054</td>
</tr>
<tr>
<td>RH = 60%</td>
<td>0.0226 [31]</td>
<td>0.454 [32]</td>
<td>0.0120 [31]</td>
<td>0.0092</td>
</tr>
<tr>
<td>RH = 90%</td>
<td>0.0177 [31]</td>
<td>0.382 [32]</td>
<td>0.0098 [31]</td>
<td>0.0705</td>
</tr>
</tbody>
</table>

4.3 Simulation Procedure

4.3.1 Applied Vibrations

The US Department of Energy (DOE) set the durability target of 5000 h for PEM fuel cells in automotive applications [1,74]. To simulate the MEA degradations due to applied vibrations, the fuel cell model was subjected to accelerated test conditions [3,75,76] for 300 h. As mentioned in chapter 2, the fuel cell experiences vibrations in range of 0.9-40 Hz in transportation applications. Furthermore, the maximum amplitude of vibrations in transportation applications generally does not exceed 0.95 g [3], where $g$ is the acceleration of gravity (9.81 m/s$^2$). However, in order to simulate the whole life of a car, higher magnitudes are generally applied in aggressive test conditions such as shocks and impact loads [3,19]. Applying the accelerated test conditions in the automobile industry provides the opportunity of simulating the whole life of a device (several years) in a short period test. Therefore, in this study, vibrations were applied in the negative $x$ direction and in the form of a sinusoidal acceleration $f(t) = A \sin \omega t$, where $A$ is
the amplitude and $\omega$ is the frequency of vibration, respectively. Vibration frequencies of 5, 10, 20, and 40 Hz with the amplitudes of 1, 2, 3, and 4 g were considered. Two cases for operating fuel cell under vibrating environment were considered:

a) A constant temperature and humidity corresponding to the maximum loading condition (RH= 90% and T= 80°C [3,28,38,75,76]).

b) Cyclic variations of humidity and temperature, which are introduced in the next section.

### 4.3.2 Humidity and Temperature Cycles

During the start-up/shutdown cycles of PEM fuel cells, the humidity varies between 30% to 95% during each cycle [3,28,38,75,76]. To investigate the effect of RH variation during fuel cell operation, five hydration-dehydration cases were designed, as shown in Figure 4.4. The cycles were characterized by a $RH_{\text{max}} = 95\%$ and a variable $RH_{\text{min}}$ which leads to an amplitude of $\Delta RH = RH_{\text{max}} - RH_{\text{min}}$. Values of 30%, 40%, 50%, 60%, and 70% were considered for $RH_{\text{min}}$ in order to simulate the variant working conditions of the fuel cell. Hence, the maximum $\Delta RH = RH_{\text{max}} - RH_{\text{min}} = 65\%$ will occur for the case with $RH_{\text{min}} = 30\%$. The corresponding temperature variations to these RH cycles are shown in Figure 4.4.

![Figure 4.4. Applied temperature and humidity cycles](image-url)
Two cases for the humidity distribution at the maximum loading condition were considered: 1) uniform loading where the whole membrane experiences same level of humidity, 2) a non-uniform (linear) loading where the humidity is 30% RH at the anode side and increases to the operating RH level at the cathode side. These profiles are shown in Figure 4.5. It was assumed that the material properties of the CL, GDL, and bipolar plates were unaffected by humidity (RH set to zero).

![Humidity Distribution Profiles](image)

Figure 4.5. Relative humidity distribution profiles employed for the MEA.

### 4.3.3 Simulation Steps

The simulation was performed in three stages using the following steps in ABAQUS:

**Stage 1:** The clamping force was applied in the form of a displacement, which fixed the upper boundary at the desired location as described in section 3.1. The gravity of $g = 9.81 \text{ m/s}^2$ was applied to the model in the $x$ direction (directions were defined in Figure 4.1). Initial humidity and temperature of 30% RH and 25 °C (ambient conditions) were also applied.

**Stage 2:** The humidity and temperature were increased linearly from the ambient conditions (30% RH and 25 °C) to reach the maximum working condition (95% RH and 85 °C). A body force with the magnitude of the vibration amplitude was also applied to the model simultaneously. This stage is necessary in order to avoid numerical instability. The working
temperature for bipolar plates was defined as 80 °C, while the working temperature for the membrane was defined as 85 °C with the assumption of no heat generation. It was also assumed that the temperature of the bipolar plates uniformly changes at all nodes, due to their high thermal conductivity.

**Stage 3:** Both cyclic hydration-dehydration loading and vibrations were applied simultaneously in order to combine the effects.

For hygrothermal-only simulations, the vibration body forces were neglected throughout the stages.

### 4.4 Summary

The details of the modelled geometry, boundary conditions, and material property assumptions were presented in this chapter. The fracture properties of the interface were defined using the membrane material properties from literature. A two-dimensional model was developed using the damage model introduced in chapter 2. A range of hygrothermal cycles and vibrations were introduced in order to simulate the range of working conditions for an automotive PEM fuel cell. The results of hygrothermal-only analysis, vibrations-only analysis, and combined vibrations and hygrothermal loading analysis will be presented in the following chapters.
Chapter 5

5 Humidity and Temperature Cycling Effects on Defects in PEM Fuel Cells

Temperature and relative humidity (hygrothermal) cycles during PEM fuel cell operation can lead to the introduction and exacerbation of micro-scale mechanical defects. The membrane swelling and shrinking in response to humidity and temperature variations result in cyclic in-plane compressive and tensile stresses in the membrane. Ex-situ cyclic studies have shown that these stresses are responsible for fatigue and mechanical degradations (initiation and propagation of defects) in the MEA, even in the absence of electro-chemical effects [26,27]. Although, stresses and fatigue of the MEA due to hydrothermal cycles have been widely investigated by several researchers [5,7,8,10,12,26–33], their impacts on PEM fuel cells mechanical damages have yet to be fully investigated.

In this chapter, the delamination/crack propagation in the MEA due to hygrothermal duty cycles is investigated. Specifically, the effects of the hygrothermal cycle amplitude, humidity distribution profile, defect location, and degree of anode/cathode channel offset on MEA defect propagation are studied. The developed model predicts the propagated delamination length as a function of RH cycling amplitude and the number of cycles required to cause delamination propagation. The findings of this chapter have been submitted as a manuscript to Wiley-Fuel Cells journal.
5.1 Effect of RH Cycle Amplitude

During an automobile operation, series of loading cycles (generated humidity and temperature) are applied to the fuel cell. The amplitude of these cycles depends on the power demands of a vehicle. To investigate the effect of amplitude variation during fuel cell operation, five hydration-dehydration cases were designed. The cycles were characterized by a $RH_{\text{max}} = 95\%$ and a variable $RH_{\text{min}}$ which leads to an amplitude of $\Delta RH = RH_{\text{max}} - RH_{\text{min}}$, as introduced earlier in Figure 4.3. Figure 5.1 illustrates the range of considered RH cycles and their effect on the delamination propagation. In this figure, the propagated delamination length for each $\Delta RH$ is shown versus the number of cycles required for the delamination propagation. Here, a $\Delta RH$ of 65% ($RH_{\text{min}} = 30\%$) coincides with start-up/shut-down cycles. As can be seen in Figure 5.1, for the start-up/shut-down cycles, the delamination grew rapidly to 0.1 mm within $3 \times 10^4$ cycles, which reaches the limit of the expected lifespan of a PEM fuel cell (40,000 start-up/shut-down cycles [10,77]).

The rapid growth of delaminations at larger $\Delta RH$ values (Figure 5.1) is attributed to the corresponding high in-plane stresses generated at the interface, as shown in Figure 5.2. Conversely, at smaller $\Delta RH$ amplitudes (higher $RH_{\text{min}}$ values), such as 35%, the delamination started to propagate after $2.7 \times 10^5$ cycles, where the significantly smaller delamination corresponds to the reduced in-plane stresses (Figure 5.2). It was also observed that when $\Delta RH = 65\%$ ($RH_{\text{min}} = 30\%$), the in-plane stress reached a maximum of 8.6 MPa, which approached the membrane yield stress, while when $\Delta RH = 25\%$ ($RH_{\text{min}} = 70\%$) the generated stresses were less than 1.6 MPa. For cycles with $\Delta RH = 25\%$, an absence of delamination propagation was observed.
Figure 5.1. Effect of the hygrothermal loading range on the delamination propagation for aligned gas flow channels. Not all data points have been shown for clarity.

Figure 5.2. Effect of the RH cycling on the in-plane stress for aligned gas flow channels.
5.2 Effect of RH Distribution Profile

The membrane swelling is directly related to the RH (water) distribution across the membrane thickness. The water distribution in the PEM fuel cell is a complicated phenomenon particularly when it is investigated in the GDLs as the porous layers. For the membrane, as a non-porous material, the water distribution modelling becomes less complicated in the absence of the porosity. Two assumptions for RH distribution have been considered before in the literature [28,38] to investigate the consequent effects on the generated stresses in the MEA (Figure 4.4). As described in section 4.3.2, these two distribution profiles are defined as uniform and linear. In this section, similar distribution profiles are employed to investigate their possible effects on the delamination propagation in the MEA.

A uniform hygrothermal loading resulted in more swelling and thermal expansion in the membrane compared to the linear distribution, since in the uniform distribution case the entire thickness of the membrane was fully engaged in these expansions. With the linear distribution, the elements near the anode maintained an RH = 30%, whereas the humidity for the elements near the cathode reached RH = 95%; however, this only resulted in a slightly higher stress concentration in the membrane near the delamination. The generated stresses associated with these humidity distributions are shown in Figure 5.3, where the stresses only differed by 4.4%. This is also in agreement with findings from Kusoglu et al. [28].

The delamination propagation of the two cases were compared in Figure 5.4 at $\Delta RH = 65\%$ ($RH_{\min} = 30\%$). The initiation of delamination (in terms of number of applied cycles) occurred 2.47% earlier for the linear distribution case, which shows the minor effect of the distribution profile on the damage state in the MEA, due to similar level of generated stresses.
Figure 5.3. Comparing the generated in-plane stress at the delamination tip under uniform and linear RH distributions.

Figure 5.4. Effect of RH distribution profile on the delamination propagation.
5.3 Effect of Location of the Defect

In this section, the influence of the defect location on the rate of defect propagation is discussed. As shown in Figure 5.6, three locations were considered: a delamination at the cathodic CL/membrane interface, and two cracks introduced at the centre and at a distance of \( L = 1/4 t_{membrane} \) from the centre of the membrane. The CL/membrane interface has been reported as one of the most vulnerable areas for the delamination initiation due to mechanical fatigue resulting from RH cycles [6,8,9,11,26,28,69].

Figure 5.5 compares the propagation of defects at these locations under a hygrothermal cycle with \( \Delta RH = 65\% \). A noticeable difference was observed between the starting time and the propagation rate of cracks and the delamination. While the cracks in the membrane started to propagate in less than 6,800 cycles, the delamination propagation took place after \( 1.2 \times 10^4 \) cycles. The applied in-plane stresses on the defects at these locations are shown in Figure 5.6. Because the swelling of the membrane is the cause for the stresses under hygrothermal loadings, the deformations occurring in the GDLs and CLs are the subsequent responses to the membrane deformation. Hence, the applied forces on the delamination are generated only from bottom, while a crack in the membrane experiences stresses from both top and bottom. Therefore, although the membrane/CL interface is vulnerable to damage due to the mismatch between the properties of the two neighbouring layers, a crack in the membrane can grow much faster. This result provides insight to the significant deteriorating effect that cracks within the bulk of the membrane can have on the life of the PEM fuel cell.
Figure 5.5. Propagation of defects at different locations in the MEA.

Figure 5.6. The generated in-plane stresses in the MEA for the considered initial defect locations.
5.4 Effect of Gas Flow Channel Alignment

In this section, the effect of the anode/cathode channel offset on the delamination propagation is investigated. As shown in Figure 5.7 (a), channel offsets of $\lambda = 0.05$ mm and $\lambda = 0.1$ mm were applied to the lower bipolar plate. Figure 5.7 (b) provides a comparison between the resultant delamination propagation for the offset case and the original case ($\lambda = 0$ mm) when the maximum hygrothermal loading ($\Delta RH = 65\%$) was applied. It can be observed that the interface experienced a higher rate of delamination propagation due to anode/cathode channel offset compared to the aligned case. The delamination grew in length to 0.10 mm after $1.41 \times 10^4$ cycles for the $\lambda = 0.1$ mm case, while $3.27 \times 10^4$ cycles occurred before the delamination reached the same length for the aligned case.

The von Mises stress distributions at the tip of the delamination are shown in Figure 5.8. It can be observed that the anode/cathode channel offset affected the symmetry of the generated stresses in the MEA. As a result, the in-plane stresses at the delamination tip (9.34 MPa) were 8.6% higher compared to the original aligned case (8.6 MPa), which led to larger delaminations. It can be also observed that having a larger channel offset has a non-linear effect on the delamination propagation. A delamination length of 0.1 mm was achieved after $1.47 \times 10^4$, $2.63 \times 10^4$, and $3.27 \times 10^4$ cycles for $\lambda = 0$ mm, $\lambda = 0.05$ mm, and $\lambda = 0.1$ mm, respectively. The developed model can be used to investigate the damage behaviour of current materials employed in fuel cells, as well as to evaluate the alternative materials for the next generation of fuel cell development.
Figure 5.7. (a) Anode/cathode channel offset of $\lambda$. (b) Effect of the channels offset on the delamination propagation.

Figure 5.8. MEA deformed shape: Left) Aligned gas channels - Right) Gas channels with a misalignment of $\lambda$. Deformations are not to scale.
5.5 Concluding Remarks

In this section, the effects of humidity and thermal cycles were investigated on defect propagation in the MEA. It was found that the micro-defects can propagate to critical states under start-up and shut-down cycles even before the fuel cell reaches its expected lifespan. Also, the amplitude of RH cycles has a dominant impact on the delamination propagation rate due to higher generated swelling-induced in-plane stresses. Results showed that doubling the hygrothermal cycle amplitude resulted in a 6-fold increase in fatigue stresses at the interface, which also led to considerably faster rates of delamination.

It was also found that the cracks near the centre of the membrane began to propagate at an earlier point in time and had a faster rate of propagation compared to a delamination at the membrane/CL interface. The linear distribution of humidity resulted in 2.47% higher in-plane stresses and larger delamination propagation compared to the uniform humidity loading case. However, this difference is not significant compared to the effect of the RH amplitude on delamination propagation. In addition, it was found that having larger anode/cathode channel offsets led to non-linear increases in delamination propagation rates. Results showed that a channel offset of 0.1 mm led to over a 2-fold increase in delamination rates compared to the aligned case. The developed model can be used to investigate the damage behaviour of current materials employed in fuel cells, as well as to evaluate the alternative materials for the next generation of fuel cell development.
Chapter 6

6 Vibration Effects on Delaminations in PEM Fuel Cells

PEM fuel cells are widely exposed to high magnitude road-induced vibrations, shocks, and cyclic loads when employed in transportation and stationary applications. The shear stresses generated between PEM fuel cell layers due to vibrations can initiate or exacerbate defects such as pinholes, cracks, and delaminations and may result in operational failure. While fatigue and mechanical damage induced by cyclic loads is a common problem in industrial applications, their impacts on PEM fuel cells have yet to be fully investigated. The focus of this chapter is to investigate the damage propagation in the MEA under vibration conditions with a focus placed on the interface between the membrane and catalyst layer at the cathode. This chapter begins with a discussion of free vibration simulations (as a preliminary phase of this study), which are used to determine the range of frequency in which vibration resonance occurs. Next, the effects of vibration on delamination propagation in PEM fuel cells are investigated.

6.1 Free Vibration Analysis of a PEM Fuel Cell

As mentioned previously, the fuel cell experiences vibrations in the range of 0.9-40 Hz in stationary and transportation applications such as those received in passenger vehicles, power auxiliary devices in semi-trailers, or buildings near busy roads [3,15–17]. When placed in applications such as these, the PEM fuel cell may vibrate at an excitation frequency within the
band of its natural frequencies which results in high amplitude resonance vibrations. Vibrating at resonance frequency can lead to the initiation and acceleration of defect formation, which may ultimately result in operational failure [11,12]. Therefore, it is essential to identify the natural frequencies that a PEM fuel cell may experience in the context of the excitation frequencies expected in these applications. Vibration characteristics are also required to understand the vibration behaviour of PEM fuel cell components such as the membrane, catalyst layer, gas diffusion layers, and bi-polar plates.

In this section, free vibrations were simulated for a 20 cm×20 cm PEM fuel cell unit consisting of a membrane, gas diffusion electrodes (GDEs), and bi-polar plates. An in-house finite element program was developed in MATLAB to generate and assemble the elements and calculate the natural frequency of a fuel cell unit. The detailed formulation of this code is presented in Appendix I. This code does not include any damage modelling, and only was employed for this section for calculating the natural frequencies of a fuel cell unit. A parametric study is conducted to investigate how the natural frequency varies as a function of thickness, Young’s modulus, and density for each component layer. This section (6.1) covers the preliminary phase of this project. The presented work in this section was done collaboratively with Mr. Hasnet Eftakher Ahmed, a former student in the Thermofluids for Energy and Advanced Materials Laboratory (Prof. Bazylak) and the Vibration, Design, & Mechatronics Laboratory (Prof. Zu). These results have been published in the Journal of Power Sources [13].

### 6.1.1 Free Vibration Analysis Equations

The PEM fuel cell was modeled as a symmetrically laminated composite plate, composed of a membrane, gas diffusion electrodes (GDEs) and bi-polar plates. The applied material properties and thickness of the fuel cell components are listed in Table 6.1. The bi-polar plate was modeled as a solid graphite layer, without flow fields. Clamped boundary conditions were applied to all edges. A schematic of the discretized PEM fuel cell is shown in Figure 6.1. Reissner-Mindlin plate theory [78] and Hamilton’s principle [79] were used to derive the equations for the composite plate.
The equation of motion of a plate based on Hamilton’s principle is expressed as follows when damping effects are disregarded:

$$[M]\{\ddot{\Gamma}(t)\} + [K_m]\{\Gamma(t)\} = \{F(t)\}$$

(6.1)

where $[M]$ and $[K]$ are the mass and stiffness matrices, respectively, $\{\Gamma(t)\}$ and $\{F(t)\}$ are the displacement and external force vectors, respectively. Equation (6.1) can be used for the free vibration analysis if the force vector term was omitted. Therefore, the equation of motion is reduced to the following.

$$[M]\{\ddot{\Gamma}\} + [K_m]\{\Gamma\} = \{0\}$$

(6.2)

The solution of the above equation yields the natural frequencies (eigenvalues) and mode shapes (eigenvectors) of the system. To find the natural mode shapes of the structure, a solution form is assumed as

$$\{\Gamma(t)\} = \{\phi\}e^{i\omega t}$$

(6.3)

where $\{\phi\}$ is the mode shape (eigenvector), and $\omega$ is the natural frequency. Substituting equation (6.3) into equation (6.2) yields:

$$([K] - \omega^2[M])\{\phi\}e^{i\omega t} = \{0\}$$

(6.4)
Equation (6.4) has a nontrivial solution if the determinant of coefficients, 
\[ |[K] - \omega^2[M]|, \]
becomes zero. In other words, there exists \( n \) number of solutions, \( (\omega_1^2, \omega_2^2, \ldots, \omega_n^2) \), which satisfy the following equation:

\[ |[K] - \sigma[M]|\{\phi\} = \{0\} \]  \hspace{1cm} (6.5)

where \( \sigma = \omega_i^2 \) is an eigenvalue of the system with \( i = 1, 2, \ldots, n \). The Newmark integration method [80] was used to solve Equation (6.5).

<table>
<thead>
<tr>
<th>Table 6.1. Mechanical and physical properties of the PEM fuel cell [5].</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness</td>
</tr>
<tr>
<td>Bi-polar plate</td>
</tr>
<tr>
<td>GDE</td>
</tr>
<tr>
<td>Membrane</td>
</tr>
</tbody>
</table>

6.1.2 Natural Frequencies of the Fuel Cell Unit

The lowest three natural frequencies are calculated and presented in Table 6.2. From a convergence study, as shown in this table, higher order interpolating polynomials \( N_{i}(\xi, \eta) \) (higher number of nodes in the element) with coarser meshes were employed, which lead to less degrees of freedom and hence more efficient results. Therefore, a one-element solution with an \( 8^{th} \) order polynomial (81 nodes) is utilized for all simulations presented in this work. The corresponding first three mode shapes are shown in Figure 6.2, which provides insight into the trends of maximum displacement exhibited as well as the stresses experienced by the material.
Table 6.2. Comparison of natural frequencies (Hz) of a PEM fuel cell for different polynomial orders and meshes

<table>
<thead>
<tr>
<th>Number of Nodes in the Element</th>
<th>Mesh</th>
<th>Total DOFs</th>
<th>Mode 1</th>
<th>Mode 2</th>
<th>Mode 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>14×14</td>
<td>4205</td>
<td>2307.40</td>
<td>4342.90</td>
<td>5956.20</td>
</tr>
<tr>
<td>25</td>
<td>4×4</td>
<td>1445</td>
<td>2307.00</td>
<td>4341.60</td>
<td>5953.90</td>
</tr>
<tr>
<td>49</td>
<td>2×2</td>
<td>845</td>
<td>2307.00</td>
<td>4341.50</td>
<td>5953.80</td>
</tr>
<tr>
<td>81</td>
<td>1×1</td>
<td>405</td>
<td>2307.00</td>
<td>4341.80</td>
<td>5954.00</td>
</tr>
</tbody>
</table>

Figure 6.2. Mode shapes for a PEM fuel cell: (a) first mode, (b) second mode, and (c) third mode.
6.1.3 Parametric Study

A parametric study was performed to investigate the mechanical and geometrical property effects on the vibration characteristics of a PEM fuel cell. The thickness, Young’s Modulus, and density for each component layer are increased independently from the base case value, and the impact on the natural frequency of the first mode is determined. The effects of this parametric study have also been performed on the 2\textsuperscript{nd} and 3\textsuperscript{rd} modes, which resulted in similar trends.

6.1.3.1 Influence of Layers Thickness

Figure 6.3 illustrates the impact of independently increasing the thickness of the PEM fuel cell components on the first natural frequency. Increments of 5% of the thickness of the bi-polar plate, GDE, and membrane result in increases of thickness on the order of $10^{-1}$, $10^{-2}$, and $10^{-3}$ mm, respectively. The dominating effect of the bipolar plate thickness was exacerbated by the $t_k^3$ term in the material property matrices (Equations (3 a–e) and (11-12) in Appendix I). Therefore, increasing the thickness of the GDEs and membrane resulted in negligible changes to the stiffness and mass matrices of these layers, and hence negligible increases to the lowest natural frequency (less than 0.2%). However, increases to the thickness of the bi-polar plates resulted in a significant linear increase in the lowest natural frequency, with an increase of approximately 17% when the thickness of the plates increased by 25%.

![Graph showing the effect of independently varying component thickness on the first natural frequency.](image-url)
6.1.3.2 Influence of Young’s Modulus

The effect of independently increasing the Young’s modulus of different layers on the lowest natural frequency is shown in Figure 6.4. Variation in the Young’s modulus of the bi-polar plates resulted in a linear increase in the natural frequency. With a 25% increase in the Young’s modulus, the natural frequency increases by approximately 12%. On the other hand, the natural frequency was not affected by increasing the Young’s modulus of the membrane and the GDEs, since their thicknesses were too small with respect to the bi-polar plate to make significant impacts.

![Figure 6.4. Effect of independently varying Young’s modulus on the first natural frequency.](image)

6.1.3.3 Influence of Material Density

Figure 6.5 illustrates the effect of independently increasing the density of the components on the lowest natural frequency. The combination of the order of magnitude of density and thickness is the determinant factor in this behavior. Since the densities of the bi-polar plate and membrane are almost 4.5 times greater than the GDE and the thickness of the GDE and membrane are much less than the thickness of the bipolar plate, increasing the density for the GDEs and membrane did not result in any significant changes to the lowest natural frequency; whereas, increasing the density of the bi-polar plate resulted in a strong linear dependence of the lowest natural frequency.
6.1.4 Discussions and Concluding Remarks

A three-dimensional finite element model for the PEM fuel cell using Mindlin’s plate theory was presented. The fuel cell was modelled as a laminated composite structure with the membrane, GDEs, and bi-polar plates considered as composite material plies. The model was employed to characterize the vibration behaviour of the PEM fuel cell. A base case simulation was performed, and the first three natural frequencies and mode shapes were presented. A parametric study was performed to investigate the effect of independently increasing the thickness, Young’s modulus, and density of the bi-polar plates, GDEs and membrane on the lowest natural frequency.

It was found that increases in the GDE and membrane thickness had little effect, while increases in the bi-polar plate thickness had the most dominant effect on the natural frequency of the entire study. To a lesser degree, increasing the Young’s modulus of the bi-polar plates and GDEs and increasing the density of the bi-polar plate also had a significant effect on the lowest natural frequency. Increasing the Young’s modulus of the bi-polar plates and GDEs resulted in a linear increase in the natural frequency, while increasing the density of the bi-polar plates led to a linear decrease in the natural frequency. The magnitudes of the natural frequencies for this single PEM fuel cell have been found to be out of the range of frequencies (1–25 Hz) encountered in
common transportation and stationary applications [1–3]. These results provide insight into how the natural frequencies of the PEM fuel cell may be tuned to avoid high amplitude vibrations by modifying the material and geometric properties of individual components.

In this investigation, one single cell is investigated to provide insight into the dominance of the component layers. However, practical applications require fuel cell stacks to provide realistic power levels. Therefore, further investigations are required for the vibrations of a stack of fuel cells, where the natural frequencies may coincide with the range of industrial applications. In order to increase the accuracy of the model, the flow fields can be considered in the analysis as well. Furthermore, in the practical applications, fuel cells will be assembled under compression, hence future investigations need to include multiple PEM fuel cells assembled together to form a fuel cell stack, which will provide the proper context in which to investigate vibration-resistant material properties and stack geometry.
6.2 Effect of Vibrations on Delamination Propagation in PEM Fuel Cells

The numerical model introduced in Chapter 3 was employed to investigate the effect of external vibrations on delamination propagation in PEM fuel cells. In this section, the effects of temperature and humidity variations on the membrane behaviour, such as swelling, were not considered, since simulations were performed with constant maximum operating conditions ($80^\circ C$ and 90% RH) where variations in material properties and membrane swelling are not expected. The findings of this section have been published in the International Journal of Hydrogen Energy [14].

A schematic of the single PEM fuel cell unit employed in the FE model is shown in Fig. 6.6. The figure presents the MEA including two GDLs, two CLs, a Nafion membrane, as well as a simplified illustration of a delamination. The length ($x$ direction) of the modelled fuel cell is 10 mm. An initial delamination at the cathodic membrane/CL interface was considered with an initial length of $a = 25 \mu m$ (0.025 mm), which is consistent with experimental findings from literature [5]. The delamination length after each step of loading was considered as the summation of the initial length and the propagated damage.

Figure 6.6. The schematic illustration of the computational domain and the applied acceleration.
Using the equation introduced in section 4.1, the maximum allowable cohesive element length was calculated as 0.03026 mm, yielding 330 elements in the length direction. However, a mesh with 800 elements ($l_{cz} = 0.0125$ mm) was used in order to capture micro delaminations. An adaptive time convergence approach with an initial time step of $\Delta t = 0.002$ s was used. The vibration and accelerated test conditions introduced in section 5.3.1 were employed for the vibration analysis. The applied vibration is in the form of acceleration $f(t) = A \sin \omega t$ in the $x$ direction, which is aligned with the interface between the layers, where $A$ is the amplitude and $\omega$ is the frequency of vibration. The vibration simulations were performed for vibration frequencies ($\omega$) of 5, 10, 20, and 40 Hz with amplitudes ($A$) of 1g, 2g, 3g, and 4g for 300 hours of accelerated tests.

6.2.1 Effect of Vibrations Amplitude and Frequency

Figure 6.7 (a) illustrates the effect of the vibration frequency on the delamination propagation for a constant amplitude of 4 g. At time $t = 0$, the initial delamination length was $a = 0.025$ mm (prior to damage propagation). The frequency range of 5-40 Hz was applied which was corresponded to approximately $5 \times 10^4 - 40 \times 10^4$ loading cycles during the test. As shown in Figure 6.7 (a), the rate of delamination propagation rapidly increased in response to the application of higher frequencies. This was attributed to the increased number of cycles that occurred during the same time period, which rapidly exacerbated fatigue damage. Also, the delamination propagation started earlier for higher frequencies. It should be noted that delamination lengths on the order of 1 mm are expected to lead to PEM fuel cell failure; however, aggressive test times were simulated here to thoroughly investigate the trends of damage propagation.

The influence of the vibration amplitudes is shown in Figure 6.7 (b). Increasing the vibration amplitude resulted in a higher rate of delamination propagation under a constant vibration frequency of 40 Hz. However, compared to the cases with amplitudes of 1g and 2g, the difference between the delamination propagation for 3g and 4g was significantly less. Although not presented here, it was observed that crack propagation was absent for amplitudes less than 0.5g, which was attributed to an insufficient applied force for the delamination propagation.
Figure 6.7. Investigating the effect of vibration conditions on delamination length: (a) with a constant amplitude of 4g and (b) with a constant vibration frequency of 40 Hz. Not all data points have been shown for clarity.
Figure 6.8 illustrates the upper and lower bounds of frequency and amplitudes studied in this work. The worst case scenario (upper bound) is represented with $A = 4g$ and $\omega = 40$ Hz, while the best case scenario (lower bound) is represented with $A = 1g$ and $\omega = 5$ Hz. At the final simulation time of 300 hours, a three-fold increase in delamination length was found when the frequency increased from 5 Hz to 40 Hz at $A = 4g$, whereas at $A = 1g$, the delamination increased by two-fold. Also, for $\omega = 40$ Hz the increase in the final delamination length due to the increase of amplitude from 1g to 4g (shown by $L$ in Fig. 7) was approximately 3 times larger than the case with $\omega = 5$ Hz ($L'$). Furthermore, the rate of delamination propagation tended to decrease after 200h for cases with $A = 1g$, while for $A = 4g$ the delamination propagation continued to increase significantly. This behavior can be explained by the aggressive vibration conditions present for cases with an amplitude of $A = 4g$.

Figure 6. 8. Illustrating the upper bound (worst case) and lower bound (best case) of the vibration conditions of this study. Not all data points have been shown for clarity.
The final delamination length after 300 hours was compared for amplitudes of 1g to 4g, and frequencies of 5 Hz to 40 Hz, in Figure 6.9. As shown in this figure, the delamination propagation was highly affected by both amplitude and frequency. Furthermore, the effect of the vibration frequency became more significant in the presence of larger amplitudes. As can be observed in Figure 6.9, the effect of increasing the frequency dominated over the effect of increasing the amplitude on the final delamination length for $A = 3g$ and $4g$, due to the shift of the fatigue state to higher level stresses and low cycle fatigue. At 10 Hz, increasing the amplitude from 2g to 3g led to an increase in the final delamination length from 0.51 mm to 0.74 mm, while the final delamination length only increased from 0.74 mm to 0.81 mm when the amplitude increased from 3g to 4g. Furthermore, the effect of increasing the amplitude on the delamination length was not linear, with decreasing effects at larger amplitudes.

![Graph showing final delamination lengths for different amplitudes and frequencies.](image)

Figure 6.9. The final delamination lengths for a range of amplitudes and frequencies after 300h.
6.2.2 Effect of Initial Delamination Length

The effect of the initial delamination length on the rate of propagation is illustrated in Figure 6.10. In this figure, the best and worst case scenarios are compared for initial lengths of \( a = 0.025 \text{ mm} \) and \( a = 0.250 \text{ mm} \). As can be seen from this figure, increasing the initial delamination length significantly increased the rate of propagation. For the case where \( A = 1g \) and \( \omega = 5 \text{ Hz} \), increasing the initial delamination length from 0.025 mm to 0.250 mm increased the final delamination length from 0.13 mm to 1.05 mm. However, this behaviour was more significant for the case where \( A = 4g \) and \( \omega = 40 \text{ Hz} \) (with an increase in delamination length from 1.46 mm to 2.86 mm). Also, it was observed that the final delamination length for the worst case \( (A = 4g \text{ and } \omega = 40 \text{ Hz}) \) for the smaller initial delamination length \( (a = 0.025 \text{ mm}) \) was higher than that for the best case \( (A = 1g \text{ and } \omega = 5 \text{ Hz}) \) with the larger initial delamination length \( (a = 0.250 \text{ mm}) \). These results show that aggressive vibration conditions can dominate the effect of initial delamination length on the final delamination length.

![Figure 6.10](image.png)

Figure 6.10. Effect of the initial delamination length on damage propagation. Not all data points have been shown for clarity.
6.2.3 Concluding Remarks

In this section, the effect of mechanical vibrations on delamination propagation at the membrane/CL interface was investigated for the first time. To accelerate the MEA degradation due to applied vibrations, the fuel cell was subjected to accelerated test conditions for 300 hours. The crack propagation was studied for a range of vibration frequencies of 5, 10, 20, and 40 Hz with amplitudes of 1g, 2g, 3g, and 4g. The effects of temperature and humidity variations on the membrane behaviour were not considered, since the simulation was performed during constant maximum operating conditions (80°C and 90% RH) where these effects are not expected.

It was found that the delamination propagation was significantly impacted by both amplitude and frequency. Increasing the vibration frequency and amplitude led to noticeable increases in the rate of crack propagation. It was also observed that the effect of increasing the amplitude on the delamination length was non-linear. This effect became less significant at larger amplitudes, where increasing the frequency dominated the impact on final delamination length. Also, while a simulation case with \( A = 4g \) and \( \omega = 40 \) Hz had the most severe damage, no damage was observed for cases with amplitudes less than 0.5g, as the applied force by vibration was insufficient to propagate the crack within the 300 hour simulation. The effect of the initial delamination length was also investigated, and while it has a major impact on the final delamination length, it was found that aggressive vibration conditions (4g at 40 Hz) can dominate this impact.
7 Combined Effects of Environmental Vibrations and Hygrothermal Fatigue on PEM Fuel Cell Damage

Automotive PEM fuel cells are widely exposed to high magnitude road-induced impact loads and vibrations as well as high-level cyclic stresses due to humidity and temperature variations during operation. The resulting plastic strain can be significant enough to initiate or exacerbate defects such as delaminations and cracks in the fuel cell, with operational failure as a possible outcome. In Chapters 5 and 6 the degrading effects of hygrothermal cycles and external vibrations were studied independently. However, having a combination of both loadings is a common situation in automotive fuel cells, which may result in more severe degradation. These loadings are applied in various directions: the hygrothermal cycles generate membrane expansion in the through-plane direction, while vibrations are applied along the in-plane direction.

In this chapter, the combined effects of hygrothermal cycles and external vibrations on defect propagation in automotive PEM fuel cells are studied for the first time. The geometry and loading condition introduced in Chapter 4 were employed in the simulations. A parametric study is performed to gain insight into the degradation effects of combining hygrothermal loading cycles and ambient vibrations in an automotive PEM fuel cell. In the following sections, first the effects of the hygrothermal cycle amplitude on PEM fuel cell delaminations are investigated in the presence of vibrations. Next, the effects of vibration characteristics are studied under a
hygrothermal cycle with the maximum $\Delta RH$ ($\Delta RH = 65\%$). The influence of channel offset and the initial defect location were also taken into consideration. The findings of this chapter have been submitted as a manuscript to the international Journal of Hydrogen Energy.

7.1 Effect of RH Cycles Amplitude

The hydration-dehydration cases introduced in Chapter 4 were considered for simulating the applied hygrothermal cycles to the fuel cell. To simulate the road-induced vibrations, sinusoidal accelerations of the form $f(t) = A \sin \omega t$ were applied to the fuel cell, where $A$ is the amplitude and $\omega$ is the frequency of vibration. Vibration frequencies of 5, 10, 20, and 40 Hz with the amplitudes of 1, 2, 3, and 4 g were considered, according to accelerated test routines [2,18,75,76].

In this section, the effects of hygrothermal cycle amplitude were investigated for the maximum ($A = 4$ g and $\omega = 40$ Hz) and the minimum ($A = 1$ g and $\omega = 5$ Hz) vibration conditions considered in this study. Hygrothermal amplitudes of $\Delta RH = 65$, 55, and 45% were applied under these vibration conditions. Figures 7.1 (a) and 7.1 (b) show the delamination propagation under the minimum and maximum vibration conditions, respectively. In these figures, the propagated delamination length is presented versus the number of applied hygrothermal cycles. Delamination propagation in the absence of vibrations is illustrated by dotted lines.

By combining vibration and hygrothermal cycles, delamination propagation was intensified as expected, for both minimum and maximum vibration conditions. As shown in Figures 7.1 (a) and (b), higher rates of delamination propagations occurred under larger hygrothermal cycle amplitudes, due to the larger in-plane stresses generated at the interface. It can be also observed that hygrothermal cycles with smaller amplitudes, in which the cell was operating at higher temperatures and humidities (Figure 4.4), were more significantly affected by vibration. Under maximum vibrations and at a hygrothermal cycle amplitude of $\Delta RH = 65\%$ (Figure 7.1 (b)), the delamination expanded to 0.06 mm, with a 5-fold increase in growth rate ($\Delta a / \Delta N$, where $a$ is the defect length and $N$ is the number of cycles) compared to the case with $\Delta RH = 45\%$. 
In the considered ranges of vibrations and hygrothermal cycles, it can be seen from both figures (7.1 (a) and (b)) that the hygrothermal cycle had a more dominant impact on the damage propagation compared to vibrations. Although applying vibrations resulted in a noticeable increase in the delamination length, the shift in the order of propagated delamination length is more significant with increasing hygrothermal cycle amplitude. This was attributed to the activation of the first mode of damage propagation (opening mode) by deformations and stresses under hygrothermal cycles, while the second mode of damage propagation is mainly activated during applied vibrations. The needed energy release rate for delamination extension in the membrane is smaller for mode I compared to that of mode II ($G_{IIc} > G_{Ic}$). Therefore, for the same energy release rate, delamination extension under mode I loading is more likely to occur compared to mode II loading. Furthermore, the assembly pressure limits the defect propagation in the in-plane (shear) direction.
Figure 7.1. The effect of hygrothermal cycle amplitude on delamination propagation under: (a) minimum applied vibrations, and (b) maximum applied vibrations. Not all data points have been shown for clarity.
7.2 Effect of Vibration Magnitude and Frequency

In this section, the degrading influences of the frequency and amplitude of the applied vibrations under a specified hygrothermal cycle are investigated. The hygrothermal cyclic loading with the amplitude of $\Delta RH = 65\%$ ($RH_{\text{max}} = 95\%$ and $RH_{\text{min}} = 30\%$) was applied, which corresponds to start-up/shut down cycles in PEM fuel cells. Vibrations with a frequency range of $\omega = 5-40$ Hz and an amplitude range of $A = 1-4$ g were applied simultaneously with these hygrothermal cycles.

Figure 7.2 (a) shows the effect of frequency variation under a constant amplitude of 4g. For the applied range of frequency, it was observed that the curves became close (2 % difference) after $2.5\times10^4$ cycles, particularly for $\omega = 5$ Hz and 10 Hz. The effect of the amplitude variation is shown in Figure 7.2 (b) under a constant frequency of 40 Hz. A more noticeable difference was observed between the propagated delamination length, which indicates that the amplitude of vibrations had a dominating impact on damage initiation and propagation (compared to vibration frequency). Under a vibration condition of $A = 4$ g and $\omega = 40$ Hz, the delamination length reached 0.1 mm after $2.94\times10^4$ hygrothermal cycles, which was 13% faster than the case without vibrations (0.1 mm after $3.27\times10^4$ hygrothermal cycles). Assuming an expected lifespan of 40,000 start-up/shut-down cycles for a PEM fuel cell [10,77], it was observed that this damage length was reached within 75% of the fuel cell life under these combined loading conditions.
Figure 7.2. Investigating the effect of vibration conditions on delamination length under: (a) a constant amplitude of 4 g, and (b) a constant vibration frequency of 40 Hz. Not all data points have been shown for clarity.
7.3 Location of the Defect

The effect of defect location was investigated under the worst case (upper bound) scenario conditions of hygrothermal cycles ($\Delta RH = 65\%$) and vibrations ($A = 4g$ and $\omega = 40$ Hz). Three locations were considered: a delamination at the cathodic CL/membrane interface and two cracks, one at the membrane centre and the other at a distance of $L$ from the interface (Figure 7.3). The damage propagation is shown for each case in Figure 7.4, where the simulated cases without vibrations are also presented with dotted lines.

It can be observed that cracks in the membrane grew considerably faster compared to the delamination case, under the same hygrothermal cycles and in the absence of vibrations. On the other hand, vibration effects are more significant on delamination propagation. Under the applied vibrations, delamination propagation is 80.4% faster compared to the case without vibrations, while the crack propagation rate at the membrane centre increased only by 6.7%. This difference can be attributed to the applied stresses on the defects at these locations, as shown in Figure 7.3. Because membrane swelling causes stresses under hygrothermal loadings, the deformations occurring in the GDLs and CLs are the subsequent responses to this membrane deformation. Hence, the applied forces on the delamination are generated only from below, while a crack in the membrane experiences stresses from both above and below. In the case with applied vibrations, all fuel cell components were affected simultaneously by volumetric forces. The mismatched properties of the two neighbouring layers affected the delaminations to a higher degree compared to the cracks situated within the same material (membrane).
Figure 7.3. The generated in-plane stresses in the MEA for the considered initial defect locations (under hygrothermal loading).

Figure 7.4. Propagation of defects at various locations in the MEA.
7.4 Gas Flow Channel Offset

The effect of combined loadings on the delamination propagation is shown in Figure 7.5, where a channel offset of $\lambda = 0.1$ mm (Figure 7.6) was applied to the lower bipolar plate. In this figure, the damage propagation is presented under the worst case scenario introduced in section 7.3 ($\Delta RH = 65\%$, $A = 4g$, and $\omega = 40$ Hz). Although the existence of a channel offset is unfavourable, small channel offsets may be unavoidable in practice. While these small offsets may be tolerable for cell operation, Figure 7.5 shows that they have a significant impact on the propagation of the delamination studied herein. It can be observed that in the absence of applied vibrations within $3 \times 10^4$ cycles, the damage length increased by 94% from 0.085 mm (for no channel offset) to 0.165 mm (for a channel offset of $\lambda = 0.1$ mm).

As shown in Figure 7.6, significant changes to the stress distributions in the fuel cell will occur due to large channel offset relative to the width of the channel (1 mm). Therefore, the resultant delamination length (for a channel offset in the absence of vibrations) was longer than for the scenario without a channel offset under the applied vibrations (where the delamination grew to 0.115 mm after $3 \times 10^4$ cycles). However, the combination of vibrations and channel offset severely intensified the degradation, where a 2.5-fold increase in delamination length was observed compared to the original case within $3 \times 10^3$ cycles (Figure 11). Furthermore, damage propagation began considerably earlier (51% earlier) in this situation compared to the original case without channel offset and vibrations.
Figure 7.5. Effect of the channels offset on the delamination propagation.

Figure 7.6. Anode/cathode channel offset of $\lambda$ and the resultant von Mises stress in the MEA. Deformations are not to scale.
7.5 Concluding Remarks

Vibrations and hygrothermal cycles were applied simultaneously to a PEM fuel cell unit to investigate their degrading effects on MEA defects, for the first time. Both hygrothermal cycles and vibrations contribute to damage propagation when applied separately. As expected, combining these sources of mechanical stress severely intensified the damage propagation under the considered loading ranges. The maximum damage propagation occurred at the maximum hygrothermal and vibration conditions, where a considerably large delamination length (0.1 mm) occurred within 75% of the fuel cell expectancy.

It was also observed that the effect of the applied vibrations was more significant for fuel cells operating at a higher temperature and humidity conditions (smaller ΔRH in Figure 4.4). Furthermore, the vibration amplitude had a dominating impact compared to the frequency of vibration on delamination propagation due to the larger generated stresses in the MEA. Under hygrothermal cycles, cracks at the membrane were found to be more prone to severe propagation compared to delaminations. However, the influence of vibrations was more significant on the delamination, and the applied vibrations led to only a slight impact on the crack propagation rate. Moreover, introducing an anode/cathode channel offset under the combined loadings (vibrations and hygrothermal cycles) led to a 2.5-fold increase in the delamination length compared to the case with no channel offset.
8 Conclusions

In this thesis, a finite element damage model based on cohesive zone theory was proposed to simulate the propagation of micro-scale defects (cracks and delaminations) in the MEA under fuel cell operating conditions. The presented 2-D model included two bipolar plates, two GDLs, two CLs, and a Nafion membrane. The modelling framework included the swelling behaviour of the membrane as well as its elasto-plastic behaviour. The variation of membrane material properties under humidity and temperature cycles were also taken into consideration. The effects of loading conditions (operational hygrothermal cycles and external vibrations), defect location, and presence of channel offset on damage propagation in the MEA were also investigated.

8.1 Conclusions and Contributions

The aim of this study was to address the aspects of MEA mechanical damage and particularly the degradation due to external vibrations which are currently absent from the PEM fuel cell literature. Presented in this thesis were three main contributions that provided insight into damage propagation in the MEA under i) hygrothermal cycles, ii) external applied vibrations, and iii) the realistic conditions where a combination of both these loadings was applied.

In Chapter 5, the effect of hygrothermal cycles on delamination propagation was investigated for a fuel cell unit. It was found that:
• Micro-defects can propagate to critical states under start-up and shut-down cycles, prior to reaching the expected lifespan of the fuel cell.

• Doubling the hygrothermal cycle amplitude resulted in a 6-fold increase in fatigue stresses at the cathodic membrane/CL interface, which also led to considerably faster rates of delamination.

• Cracks near the centre of the membrane began to propagate at an earlier point in time and had a faster rate of propagation compared to a delamination at the membrane/CL interface.

• The effects of humidity distribution profiles (across the membrane) were found to be negligible on the resultant damage compared to the RH amplitude effect.

• Having larger anode/cathode channel offsets led to a 2-fold non-linear increase in delamination propagation rates compared to the aligned-channel case.

In Chapter 6, the effect of mechanical vibrations on the delamination propagation at the membrane/CL interface was investigated for the first time. The accelerated test conditions for 300 hours were applied to the model in the absence of hygrothermal effects. It was found that:

• Increasing the vibration frequency and amplitude both led to noticeable increases in the rate of delamination propagation. Furthermore, at larger amplitudes, increasing the frequency dominated the impact of amplitude on the final delamination length.

• The initial delamination length had a major impact on the final delamination length; however, aggressive vibration conditions could dominate this impact.

• The first three natural frequencies and mode shapes of a fuel cell unit were presented.

• A parametric study was performed to investigate the effects of independently increasing the thickness, Young’s modulus, and density of the fuel cell components on the lowest natural frequency. Bipolar plate properties had a dominant impact on the natural frequency with the plate thickness as the most effective parameter.
• The magnitudes of the natural frequencies for a single PEM fuel cell were found to be out of the range of frequencies (1–25 Hz) encountered in common transportation and stationary applications [1–3]. However, further investigations are required for the vibrations of a stack of fuel cells, where the natural frequencies may coincide with the range of industrial applications.

In Chapter 7, the combined effects of hygrothermal cycles and external vibrations on defect propagation in PEM fuel cells were studied for the first time. It was found that:

• The simultaneous presence of hydrothermal cycles and vibrations severely intensified the damage propagation and can result in considerably large defects (0.1 mm) within 75% of the fuel cell life expectancy.

• In the considered ranges of vibrations and hygrothermal cycles, the degradation effects of hygrothermal cycles were found to be dominant compared to those caused by the applied vibrations.

• Under hygrothermal cycles, membrane cracks experienced more severe propagation compared to membrane/CL delaminations. However, the degrading influence of vibration was more significant on delamination propagation.

• The presence of an anode/cathode channel offset under the combined loadings lead to a 2.5-fold increase in the delamination length compared to a case with no channel offset.

It should be noted that the developed model in this thesis needs further development by including the viscoelastic behaviour to capture the time dependent behaviours of the membrane. In addition, the interaction of GDL fibres with the CL needs to be incorporated in order to use the model in investigating the defects at the GDL/CL interfaces.

In summary, this thesis presented an analysis of the micro-scale defect propagation in the MEA. The fracture characteristics of fuel cell components were introduced, including the fracture toughness of the components. These assumptions are particularly important and have not been explicitly reported in the literature prior to the work from this thesis. Furthermore, the effects of
loading conditions on the state of damage in automotive PEM fuel cells were investigated for the first time. The model presented provides a valuable tool for fuel cell designers for estimating the life of currently available MEA materials as well as for designing new materials for the next generation of PEM fuel cells with enhanced durability.

8.2 Future Work

The presented damage model can be extended to study the following as the future works:

- Although the effects of membrane viscoelasticity were considered in the modelling using a combination of elastic-perfectly plastic model isotropic hardening, incorporating the membrane viscoelasticity directly into material equations will provide more realistic estimations.

- In this study, the damage behaviour of the MEA delaminations and cracks in the in-plane direction (along the component interfaces) were studied. Investigating the damage behaviours of pinholes and cracks across the membrane can also provide insight into the most critical damage situations in PEM fuel cells.

- Modelling the interactions of GDL fibres with the CL and investigating the damages at the GDL/CL interfaces can add insight to mechanical damages at the GDL area.

- In this study, the fracture properties of the interface were defined using the membrane properties, due to its weaker mechanical properties compared to those of the C/Pt agglomerate. Furthermore, the available fracture toughness data for the membrane were reported for specific humidities. Further experiential studies are highly suggested to accurately define the exact fracture properties of the fuel cell components.

- The higher number of degrees of freedoms in a fuel cell stack will result in considerable lower natural frequencies for the system which may coincide with the range of industrial applications. Therefore, investigating the damage and vibration behaviours of a fuel cell stack instead of one fuel cell unit will be beneficial to define a more applicable safe range of applied vibrations.
References


Appendix I

An in-house finite element program code was developed in MATLAB [81] for free vibration analysis of a fuel cell unit presented in section 6.1. This code does not include any damage modelling, and has only been employed for this section for calculating the natural frequencies of a fuel cell unit. The PEM fuel cell was modelled as a symmetrically laminated composite plate, composed of a membrane, gas diffusion electrodes (GDEs) and bi-polar plates, which are considered as the plies of the composite plate.

A) Plate Equations

Reissner-Mindlin plate equations [78] were deduced in this section from the elasticity equations in the Cartesian coordinates $x$, $y$ and $z$. The thickness $h$ of the plate is considered to be uniform and small compared to the other dimensions in $x$-$y$ plane, which is taken as the reference plane in this formulation. The displacements at any arbitrary point in the plate are defined by $u' = u + z\beta_1$, $v' = v + z\beta_2$, and $w' = w$ where $u$, $v$, and $w$ are displacement components at the middle plane of the plate in the $x$, $y$, and $z$ axes respectively. Coordinate $z$ is measured along the perpendicular to the middle plane. Also, $\beta_1$ and $\beta_2$ denote respectively the rotational components of the normal to the reference plane.

The strain-displacement relations for the first order shear deformable plates are given as [82,83],

$$\{\varepsilon\} = [Z]\{\chi\} \text{ and } \{\chi\} = [d]\{\psi\} \quad (1)$$

where,

$$\{\varepsilon\}^T = \{u'_x \ v'_y \ \gamma'_{xy} \ \gamma'_{yz} \ \gamma'_{zx}\}$$

$$\{\chi\}^T = \{u_x \ v_y \ \gamma_{xy} \ \gamma_{yz} \ \gamma_{zx} \ \kappa_x \ \kappa_y \ \kappa_{xy}\}$$
\[
\{\psi\}^T = \{u \ v \ w \ \beta_1 \ \beta_2\}
\]

\[
u_x = u_{,x}, \ v_y = v_{,y}, \ w_x = w_{,x}, \ w_y = w_{,y}, \ \gamma_{xy} = u_{,y} + v_{,x}, \ \gamma_{yz} = w_{,y} + \beta_2,
\]

\[
\gamma_{xz} = w_{,x} + \beta_1, \ \kappa_x = \beta_{1,x}, \ \kappa_y = \beta_{2,y}, \ \kappa_{xy} = \beta_{1,y} + \beta_{2,x}.
\]

Matrices \([Z]\) and \([d]\) in Equation (1) are defined as follows:

\[
[Z] = \begin{bmatrix}
1 & 0 & 0 & 0 & z & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & z & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & z \\
0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 0
\end{bmatrix}
\]

(2)

In Equation (2) the subscripted commas represent the partial derivatives, i.e. \(\epsilon_{,x}\) stands for the partial derivative with respect to \(x\). The stress vector is defined as

\[
\{\sigma\} = [C]\{\varepsilon\}
\]

(3)

Here the stress vector \(\{\sigma\}^T = \{\sigma_x \ \sigma_y \ \sigma_{xy} \ \sigma_{yz} \ \sigma_{zx}\}\) with the strain vector \(\{\varepsilon\}\) defined in Equation (1). Matrix \([C]\) is a fifth order elasticity matrix and is composed of elastic and shear moduli, the Poisson’s ratios, and the shear correction factor \(\alpha = 5/6\):
\[
C = \begin{bmatrix}
C_{11} & C_{12} & 0 & 0 & 0 \\
C_{12} & C_{22} & 0 & 0 & 0 \\
0 & 0 & C_{44} & 0 & 0 \\
0 & 0 & 0 & C_{55} & 0 \\
0 & 0 & 0 & 0 & C_{66}
\end{bmatrix}
\]

where

\[
C_{11} = \sum_{k=1}^{n} \frac{E_k}{1-\nu_k^2} \left( t_k z_k^2 + \frac{t_k^3}{12} \right) \quad (3a)
\]

\[
C_{12} = \sum_{k=1}^{n} \frac{\nu_k E_k}{1-\nu_k^2} \left( t_k z_k^2 + \frac{t_k^3}{12} \right) \quad (3b)
\]

\[
C_{22} = C_{11} \quad (3c)
\]

\[
C_{44} = \sum_{k=1}^{n} \frac{\nu_k E_k}{2(1-\nu_k^2)} \left( t_k z_k^2 + \frac{t_k^3}{12} \right) \quad (3d)
\]

\[
C_{55} = C_{66} = \alpha \sum_{k=1}^{n} \frac{E_k}{1-\nu_k} \ t_k \quad (3e)
\]

In the above equations, Young’s modulus, Poisson’s ratio, and the thickness of layers are presented by \(E_k\), \(\nu_k\), and \(t_k\), respectively. Subscript \(k\) denotes the respective component layer.

The next task is to develop a numerical solution method for a plate represented by a quadrilateral region as shown in Figure 1 in the \(x\)-\(y\) plane. The reason to select the quadrilateral geometry with curved boundaries is that the equations for this shape can be used without much difficulty by simply manipulating the coordinates of the points on the region for the analysis of different shaped plates such as rectangular, trapezoidal, parallelogram, and even the circular ones.
Next, the quadrilateral area is mapped into a square using the standard natural coordinates \((\xi, \eta)\). Cartesian coordinates \((x, y)\) of a point on the middle plane of the quadrilateral plate under consideration can be interpolated as follows:

\[
x(\xi, \eta) = \sum_{i=1}^{n} N_i(\xi, \eta) x_i, \quad y(\xi, \eta) = \sum_{i=1}^{n} N_i(\xi, \eta) y_i
\] (4)

where \(N_i(\xi, \eta)\) with \(i = 1, 2, 3, \ldots, n\) are the element shape functions in terms of the dimensionless coordinates \(\xi\) and \(\eta\) bounded by \(-1 \leq (\xi, \eta) \leq 1\) with \(n = \) number of nodes in the element. A different set of nodes is introduced to represent the geometry, which each geometry node has five degrees of freedom of \(u, v, w, \beta_1, \) and \(\beta_2\). The values of these components are interpolated as follows:

\[
\begin{align*}
    u &= \sum_{j=1}^{p} S_j(\xi, \eta) u_j, \quad v = \sum_{j=1}^{p} S_j(\xi, \eta) v_j, \quad w = \sum_{j=1}^{p} S_j(\xi, \eta) w_j \\
    \beta_1 &= \sum_{j=1}^{p} S_j(\xi, \eta) \theta_j, \quad \beta_2 = \sum_{j=1}^{p} S_j(\xi, \eta) \Theta_j
\end{align*}
\] (5)

In the above, \(S_j(\xi, \eta)\) are the geometry shape functions and indices \(u_j, v_j, w_j, \theta_j\) and \(\Theta_j\) correspond to \(u, v, w, \beta_1\) and \(\beta_2\) respectively at the \(j\)th displacement node. In Equation (5), \(p\) is the number of geometry nodes of each element. Hence \(\{\psi\}\) in Equation (1) can be written as
\{\psi\} = [\bar{S}(\xi, \eta)]\{\Gamma\} \quad (6)

Here, \{\Gamma\}^T = \{u_1, v_1, w_1, \Theta_1, \ldots, u_p, v_p, w_p, \Theta_p\}, and

\[[\bar{S}(x, y)]_{5 \times 5p} = [[\hat{S}_1(x, y)] [\hat{S}_2(x, y)] \ldots [\hat{S}_p(x, y)]]. \text{ For } j = 1, 2, \ldots, p:\n

\[
\hat{S}_j(x, y) = \begin{bmatrix}
S_j(x, y) & 0 & 0 & 0 & 0 \\
0 & S_j(x, y) & 0 & 0 & 0 \\
0 & 0 & S_j(x, y) & 0 & 0 \\
0 & 0 & 0 & S_j(x, y) & 0 \\
0 & 0 & 0 & 0 & S_j(x, y)
\end{bmatrix}
\]

By substituting Equation (6) into Equation (1) the following equation is obtained,

\{\chi\} = [d]\{\psi\} = [d][\bar{S}]\{\Gamma\} = [B]\{\Gamma\} \quad (7)

So far the basic plate equations and the displacement fields for a quadrilateral domain have been presented. These will be used in the potential energy function to develop the equations of motion for the vibration of composite plates using Hamilton’s principle [79].

**B) Energy Functions and Equation of Motion**

Mindlin’s plate theory [78] was utilized for the energy formulation, which incorporates the transverse shear deformation. The maximum strain energy of the plate is written as

\[U = \frac{1}{2} \int_V [\varepsilon]^T [C][\varepsilon] dV \quad (8)\]

\[T = \frac{1}{2} \int_V [\dot{\psi}]^T [A][\dot{\psi}] dV \quad (9)\]
where $V$ is the volume of the plate, and $[A] = \sum_{n=1}^{N} \rho_{\text{thickness}} \int [\vec{Z}]^T \{ [Z] \} dz$. Vector $\{ \psi \}$ is the time derivative of the displacement vector $\{ \psi \}$ defined in Equation (1), and $\rho$ is the mass density of the $n$th layer. Matrix $[\vec{Z}]_{3x5}$ is defined as

$$[\vec{Z}] = \begin{bmatrix} 1 & 0 & 0 & z & 0 \\ 0 & 1 & 0 & 0 & z \\ 0 & 0 & 1 & 0 & 0 \end{bmatrix}$$

The maximum strain energy of the plate can be rearranged as

$$U = \frac{1}{2} \int_{\text{Area}} ((d) \{ \psi \})^T [\vec{Z}] ([d] \{ \psi \}) dx dy \quad \text{where} \quad [\vec{Z}] = \int_{\text{Thickness}} [Z]^T [C] [Z] \; dz$$

By substituting the local coordinates in the element area, the element stiffness matrix, $K^e$, and mass matrix, $M^e$, are computed as follows:

$$U = \frac{1}{2} \{ \Gamma \}^T \left( \int_{\text{Area}} [B]^T [\vec{Z}] [B] \; dx \; dy \right) \{ \Gamma \} = \frac{1}{2} \{ \Gamma \}^T [K^e] \{ \Gamma \} \quad (10)$$

$$T = \frac{1}{2} \int_{\text{Area}} \{ \tilde{\Gamma} \}^T \left[ S \right]^T [A] \left[ S \right] \{ \tilde{\Gamma} \} \; dx \; dy = \frac{1}{2} \{ \tilde{\Gamma} \}^T [M^e] \{ \tilde{\Gamma} \} \quad (11)$$

Where,

$$K^e = \int_{-1}^{+1} \int_{-1}^{+1} [B]^T [\vec{Z}] [B] \; J(\xi, \eta) \; \left| d\xi \; d\eta \right|$$

$$M^e = \int_{-1}^{+1} \int_{-1}^{+1} \left( \sum_{n=1}^{N} \rho \begin{bmatrix} t_k & 0 & 0 \\ 0 & t^3_k / 12 & 0 \\ 0 & 0 & t^3_k / 12 \end{bmatrix} \left[ S \right] \right) \; J(\xi, \eta) \; \left| d\xi \; d\eta \right|$$

These matrices are calculated by integration along the plate thickness, one sub-layer at a time. Evaluation of matrices involves double integration on the middle plane of the plate along $x$ and $y$
axes, or equivalently ξ and η axes. The infinitesimal area \( dx \, dy \) is replaced by \( |J(\xi, \eta)| d\xi \, d\eta \), where \( |J(\xi, \eta)| \) is the Jacobian matrix for the quadrilateral plate. After calculating element stiffness and mass matrices using a numerical program written in MATLAB [81], the matrices are assembled together to form the overall stiffness and mass matrices for a complete single PEM fuel cell. These assembled stiffness and mass matrices are used in the equation of motion, which is discussed below.

Based on Hamilton’s principle [79], the variation of the total potential energy in the presence of work from external forces, \( W \), is expressed as

\[
\int_{t_1}^{t_2} \delta \Pi \, dt = \int_{t_1}^{t_2} (\delta T - \delta U + \delta W) \, dt = 0
\]  

(12)

where \( t_1 \) and \( t_2 \) are the time limits. Substituting Equations (10) and (11) into the potential energy functional in Equation (12) and taking the variation of the integral equation with respect to time, we have,

\[
\int_{t_1}^{t_2} (\delta \{\Gamma\})^T (-[M]\{\ddot{\Gamma}\} - [K]\{\Gamma\} + \{F(t)\}) \, dt = 0
\]

(13)

\[
[M]\{\ddot{\Gamma}\} + [K]\{\Gamma\} = \{F(t)\}
\]

where \([M]\), \([K]\), \(\{\Gamma\}\) are the total mass matrix, stiffness matrix, and displacement matrices of the plate, respectively. \(\{F\}\) is the vector of external forces. Equation (13) can also be used for the free vibration analysis by omitting the forcing function. Therefore, the equation of motion will be reduced to the following.

\[
[M]\{\ddot{\Gamma}\} + [K_m]\{\Gamma\} = \{0\}
\]

(14)