Failure Mode and Effect Analysis, and Fault Tree Analysis of Polymer Electrolyte Membrane Fuel Cells

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Abstract

Hydrogen fuel cells have the potential to dramatically reduce emissions from the energy sector, particularly when integrated into an automotive application. However there are three main hurdles to the commercialisation of this promising technology; one of which is reliability. Current standards require an automotive fuel cell to last around 5000 hours of operation (equivalent to around 150,000 miles), which has proven difficult to achieve to date. This hurdle can be overcome through in-depth reliability analysis including techniques such as Failure Mode and Effect Analysis (FMEA) and Fault Tree Analysis (FTA) amongst others. Research has found that the reliability field regarding hydrogen fuel cells is still in its infancy, and needs development, if the current standards are to be achieved. In this work, a detailed reliability study of a Polymer Electrolyte Membrane Fuel Cell (PEMFC) is undertaken. The results of which are a qualitative and quantitative analysis of a PEMFC. The FMEA and FTA are the most up to date assessments of failure in fuel cells made using a comprehensive literature review and expert opinion.

Keywords:
PEMFC, Reliability, Fuel Cell, Fault Tree

1. Introduction

With the increase in environmental awareness and climate change concerns in recent years, hydrogen fuel cells have been put forward as a tech-

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nology that could potentially reduce greenhouse gas emissions. Anthropogenic activities contribute to climate change mainly through Greenhouse Gas (GHG) emissions from fossil fuel based energy sources. These harmful GHGs are comprised of, among others, carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) that contribute to the greenhouse effect. Additionally, energy prices are set to continue to rise by alarming rates[1] which will disrupt the energy system of many countries due to a rise in oil prices. Therefore an alternative energy source would mitigate energy security and pricing concerns to a certain degree.

The United Kingdom (UK) emitted 549.3 Million tones of Carbon Dioxide equivelant ($MtCO_2e$) in 2011[2] and 122.2 $MtCO_2e$ was due to the transport industry, with 74% of this figure due to cars, taxis and buses[3]. Due to the aforementioned negative environmental impacts of emissions from fossil fuel energy sources, this figure needs to be dramatically reduced not only to meet government targets, but for the health of the biosphere. The UK government set out targets to reduce GHG emissions in the 'Climate Change Act' of 2008. The act presents the targets of an 80% reduction of greenhouse gas levels by 2050, with a closer target of a 34% reduction by 2020. These two targets are based upon the level of GHG emissions in 1990[4]. The targets are legally bound and therefore must be met, thus many initiatives and research has emerged to aid the UK in reaching these targets. Other countries have also pledged to tackle climate change, with the US president stating that the US will reduce CO_2 emissions 17% from 2005 levels by 2020, 42% by 2030 and finally 83% by 2050.

Hydrogen fuel cells have the potential to mitigate the aforementioned climate change concerns, as they are a zero-emission energy conversion device. They use H_2 and O_2 to form water, releasing heat and electrical energy. Their only emissions are water, meaning that at the point of use, the fuel cell has no carbon emissions associated with it. If the H_2 fuel is sourced from renewable means, the whole process is zero emissions and therefore has the potential to dramatically cut CO_2 emissions in a number of industries.

Fuel cells currently suffer from reliability concerns, and are more likely to contribute to the above issues if the current reliability issues are overcome.

Hence, this paper analyses the reliability of a PEMFC using in-depth techniques in order to understand how their performance can be improved. The layout of the paper is as follows:

In section 2, the reasons for studying PEMFCs is given, followed by a brief description of the techniques used in reliability analysis. Section 3 describes the reliability techniques adopted here and previous related studies on the reliability of PEMFCs. Section 4 describes the FMEA performed and the main conclusions drawn from it. Section 5 outlines the Fault Tree (FT) developed and section 6 concludes the findings of the study.

2. Reliability Analysis

The US Department of Energy (DoE), Japanese New Energy and Industrial Technology Development Organisation (NEDO) and European Hydrogen and Fuel Cell Technology Platform (HFP) Implementation Panel (IP) have all set reliability targets for PEMFCs in automotive application of a lifetime of more than 5000 hours of operation (equivalent to around 150,000 miles operation)[5]. The current state of fuel cell development struggles to meet these targets, and as such, an in-depth reliability analysis of PEMFCs is invaluable to help manufacturers and developers. Such an analysis requires obtaining a detailed understanding of the failure modes of all the different parts of the cell, and the effects the failures have on the cell as a whole.

Currently, the understanding of the reliability of PEMFCs is still in its infancy, and requires further development to help with the commercialisation of this promising technology.

The work presented in this paper uses the techniques of FMEA and FTA to comprehensively ascertain key failure phenomena and analyse their role and effects within in an automotive PEMFC system. Boundaries are set to only consider the PEMFC itself, the balance of plant and supporting ancillaries are omitted as shown in Figure 1, where the functional block diagram of a simple fuel cell automotive system is shown. The dotted rectangle shows the boundaries of the system considered here.

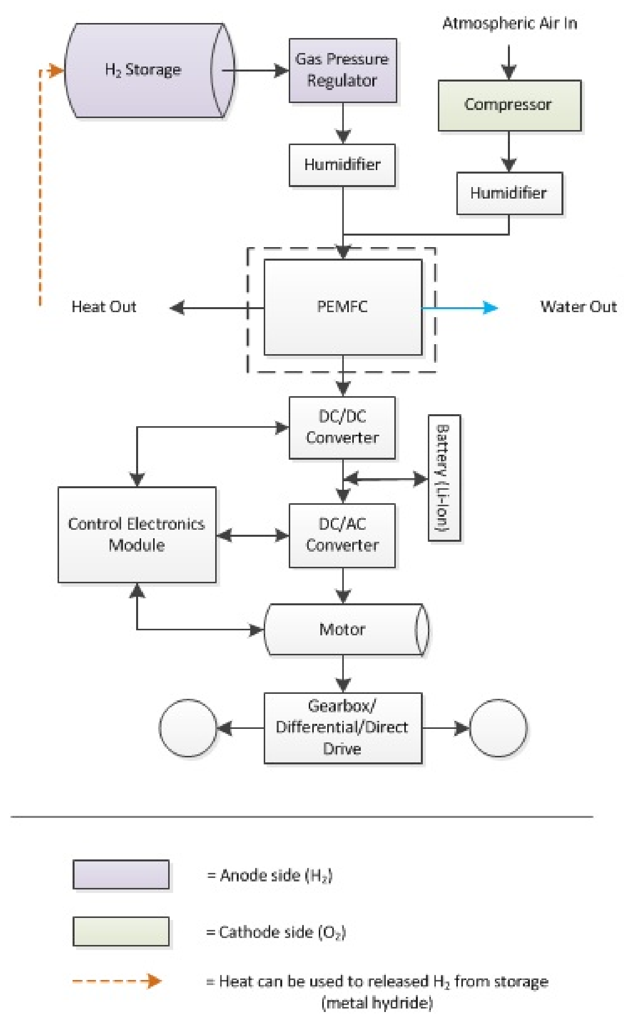

Figure 1: Boundaries of presented reliability analysis

2.1. PEM FMEA

FMEA is a bottom-up approach to analysing equipment, or a system, with relation to its failure events. That is to say that the analysis of the system starts with the individual components that make up the system, rather than looking at the overall system and working top-down. The technique is a systematic scrutiny of all of the individual ways in which a component or piece of equipment can fail, and the effect of that failure on the overall system's operation. Any additional features can be added to a basic FMEA such as mitigation strategies and poignant remarks for the reader. It is ideally used early on in the development cycle in order to ascertain key failure modes that can be designed out as early as possible. It should not, however, be limited to the design stage of system development, but should be used throughout the development stages as an ongoing process.

FMEA techniques were first used by the US military, and the standard MIL-STD-1629A [6] was developed to help standardise the FMEA process. The process of performing an FMEA includes: [7]

- Breaking down the equipment/system into components or sub-assembly blocks.
- Examining each component or block for its modes of failure.
- Listing each mode of failure according to the effect it has locally and on the system.
- Applying failure rates for each failure mode where quantification is required.

2.2. Advantages of FMEA

FMEA is a comprehensive way to analyse all of the potential component failure modes in a system. It is widely used in industry as a means to identify, rank and mitigate against the component failure modes.

2.3. Disadvantages of FMEA

The main drawback when using only FMEA for reliability analysis, is that the technique is geared towards analysing individual component failure mode occurrences. Because these failure modes are considered one by one, the interaction of multiple failure mode occurrences are often not listed using this method. Additionally, this type of reliability process is not fully quantitative. Severity and risk rankings can be made, however overall reliability levels cannot be deduced using FMEA.

2.4. PEM FTA

FTA is a deductive technique that can be used to classify the instrumental relationships leading to a specific failure mode. Whereas FMEA is a bottom-up approach, FTA is a top-down approach and is a graphical representation of the relationships between the failure modes previously identified in the

FMEA. In order to describe this approach, Figure 2 shows an example branch of a FT from a larger FT for a fuel cell system.

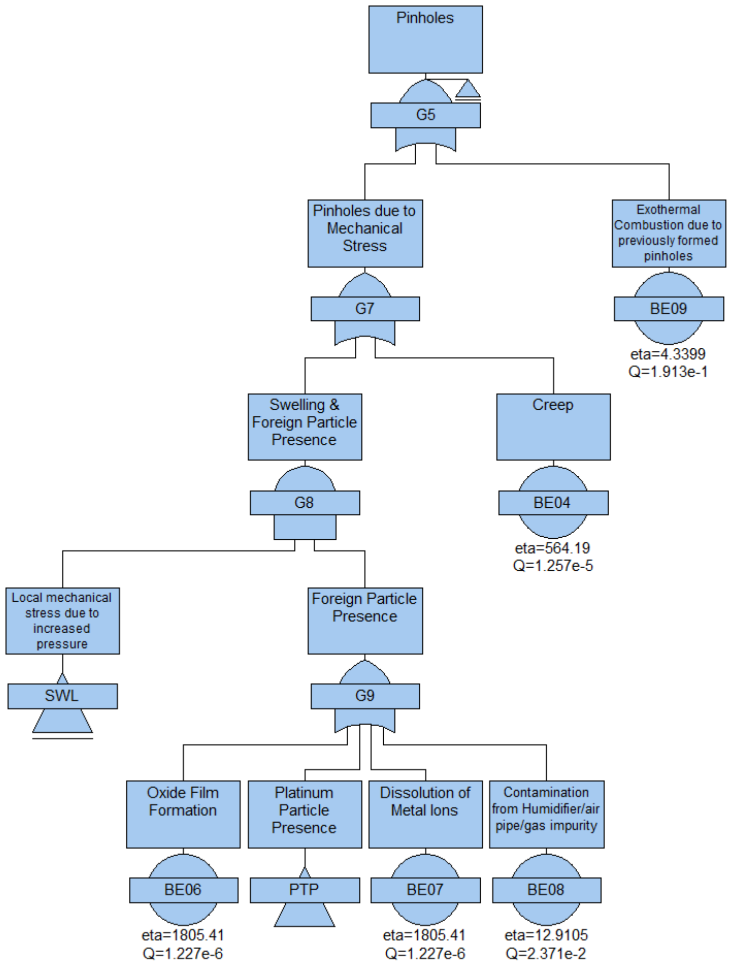

Figure 2: Example branch of a Fault Tree

'Pinholes' is the top event of the branch of the FT and indicates the overall undesirable event that the FT is modelling. This top event is split by an 'OR' gate into the intermediate event: 'Pinholes due to Mechanical Stress' and the basic event 'Exothermal combustion due to previously formed pinholes'. The 'OR' gate means that either of the two intermediate events could trigger the top event. The intermediate event is then broken down further. 'Pinholes due to Mechanical Stress' is fed by another 'OR' gate. 'Pinholes due to mechanical stress' is fed by an intermediate event 'Swelling & Foreign Particle Presence' and the basic event 'Creep'. 'Swelling & Foreign Particle Presence' is fed by an'AND' gate that is in-turn fed by an intermediate event ('Local mechanical stress due to increased pressure') and a transfer gate ('Foreign Particle Presence'). A transfer gate takes logic from another part of the overall FT and transfers this logic in without repeating large section of the graph. 'Foreign Particle Presence' itself is fed by an 'OR' gate resulting from the combinational occurrence of 'Oxide Film Formation', 'Platinum Particle Presence' transfered from another section of the overall tree, 'Dissolution of Metal Ions' and 'Contamination from Humidifier/air pipe/gas impurity'.

The values for 'eta' (η) listed underneath the basic events is the scale parameter for the quantification analysis using Weibull analysis which is discussed in section 4.2. The values for 'Q' are the unrealiability of the basic event, expressed as anmumber between zero and one. If Q = 0, the basic event is 100& live, and if Q = 1, the basic event is considered to be 0% live.

Basic events, such as 'Creep' in the above example, are events which cannot be broken down any further and for which basic information, such as failure rate, repair rate etc. is available. All intermediate events can be broken down further until reaching the basic events.

Once a full FT has been created, the Minimal Cut Sets (MCSs) can be obtained from the tree, where a MCS is a minimal combination of basic events that cause the top event. These can then be used to determine the probability or frequency of the top event[7].

2.4.1. Advantages of FTA

Due to being a graphical representation, FTA is structured in such a way that is easy for the reader to comprehend. The interactions between failure modes can be easily determined from the simple representation style. FTA can also be quantitatively analysed to ascertain overall system reliability.

2.4.2. Disadvantages of FTA

The main drawbacks of using FTA is that it cannot take into account dependencies between failure modes. They also don't tend to consider the cause of failure modes, rather just tackling the knock-on effect of the failure's occurrence. Also, a FT must be undertaken individually for each failure mode of interest. The entire range of operating conditions that the system can operate in are not considered in one tree. A tree must be made for each operating condition to be fully accurate.

2.5. Existing Reliability Analysis of PEMFC Systems

2.5.1. Fuel Cell Reliability

The application of reliability techniques to PEMFC systems in the literature is limited. Rama, et al. [8] adapted an FMEA approach and presented a tabular format list of failure modes in a PEMFC which was limited to only the area of the failure mode, and a brief description of the failure mode itself. It did not describe the effect of the failure mode on the system. It is a good start to ascertaining the different failure modes attributable to a PEMFC, however it can be further developed to provide additional information and comprehension of failure relationships in a PEMFC.

Other work in the area includes that of Placca & Kouta [9], who present an initial FTA of a PEMFC in no specific application. The work considered failure modes and their effects for a total of 37 individual basic events in a single cell PEMFC. Component failure modes including; 'Creep', 'Fatigue from relative humidity and temperature cycling' and 'Oxide film formation' were considered. The overall FTA top event of 'Degradation of the cell' was split into three of the four physical components of the cell; membrane, Catalyst Layer (CL) and Gas Diffusion Layer (GDL). The Bipolar Plate (BIP) was omitted for undisclosed reasons.

FTs have been used in other works regarding water management in PEMFCs [10], however this work was not targeted at PEMFC degradation, and rather singled out the contributing factors towards water management concerns.

FTA was used by [11] to explain failures in a solid oxide fuel cell. It used fuzzy logic terms for the basic events for failures, such as: 'Decrease in stack power' and 'Increase in stack power'. The authors discuss how FTA is used to "clear out" complex relationships between failure modes, however one of the main stumbling blocks of FTA is that it cannot take into account dependencies and intricate relationships.

Other reliability techniques such as Markov Modelling (MM)[12] and Petri-Net simulation[13] have been used to study fuel cell systems. In the study by [12] the reliability of PEMFCs in power plant environments was considered. The authors used the common fuel cell Nernst equation to model fuel cell performance, then used a simple Markov Model to plot reliability using a Weibull distribution for degradation rates, based upon an assumed overall lifetime of 5000 hours. Using MM for fuel cell reliability would require very large models that could show degradation in stages for each component.

Petri-Net simulation has been used by [13] to model the reliability of

PEMFCs using a relatively simple Petri-Net as shown in Figure 3.

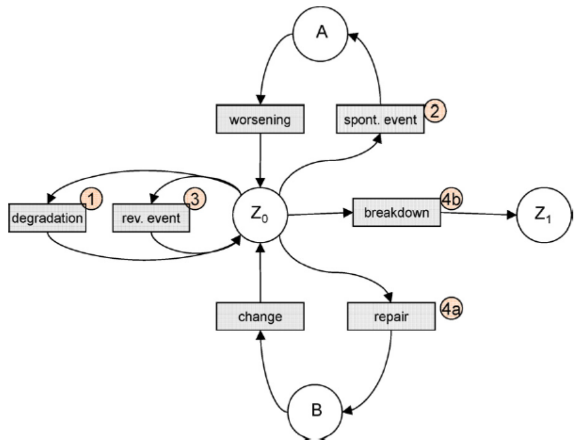

Figure 3: Petri-Net Model of fuel cell/stack/fleet of cars

The work uses the Petri-Net in Figure 3 to calculate a simulated reliability of a single cell, stack or even fleet of fuel cell cars. It uses a set of parameters for six of the conditions that a fuel cell can operate in, and an associated degradation rate when in those operating conditions. The degradation rates are taken from literature and applied throughout the running of the model. The authors acknowledge that the model is simplified as regards steady state degradation instead of changing rates determined by stack age or operational conditions.

2.5.2. Fuel Cell Degradation, Prognosis & Simulation

Although the area of fuel cell reliability modelling is not well covered in the literature, fuel cell degradation studies are prominent. Countless component level experimentation and analyses are presented in the literature body, with [5], [14] and [15] proving to be very good review papers discussing the range of failure modes analysed in the literature.

The vast majority of works in the literature related to degradation are individual component experiments, or studies of the operating condition's affect on PEMFC performance. An example of which is presented by [16], and looks at the lifetime prediction of a PEMFC under 'accelerated startup-shutdown' cycling.

Some prognosis work using neural network modeling to determine flooding and drying out of membranes is presented by [17]. This work uses FTA techniques to qualitatively understand what happens when a membrane drys or floods, then uses said information to inform the neural network model to simulate flooding and drying out.

Additional work by [18] used polarisation curve and Electrochemical Impedance Spectroscopy (EIS) techniques to characterise real world fuel cell degradation, then predicting ageing time in the future through analysis of key features in the polarisation and EIS data sets..

As the work described in this paper uses FMEA and develops a FT for a PEMFC, the previous studies of [8] & [9] are directly relevant and hence have been described in more detail below.

2.5.3. Rama, et al. [8] 'Failure mode identification'

The previous work in [8] identified 22 failure modes attributable to reduction in performance or catastrophic cell failure. Overall degradation was divided into the electrochemical overpotential pathways; activation, mass transport, ohmic and fuel efficiency losses, with catastrophic cell failure also noted as a division of overall degradation. A list of faults is presented that shows a cause, however no system effect for each failure mode is given. The comprehensive list of failure modes relating to the loss mechanisms includes all types of PEMFC construction at the time of writing, some of which are no longer used.

2.5.4. Placca & Kouta [9] FTA

FTA was recently presented by Placca & Kouta [9] in an attempt to model the reliability of a single cell PEMFC. From various literary sources, they came to the conclusion that there are 37 individual basic events to be considered when analysing the degradation of a PEMFC. The FT presented is a physical analysis of a single cell PEMFC, splitting the top-event of the 'Degradation of the Cell' down through an OR gate into three physical components of a PEMFC; Membrane (G2), Gas Diffusion Layer (G4) and Catalyst Layer (G3) as shown in Figure 4. These are three of the four main physical components of a PEMFC with only the bipolar plate being omitted.

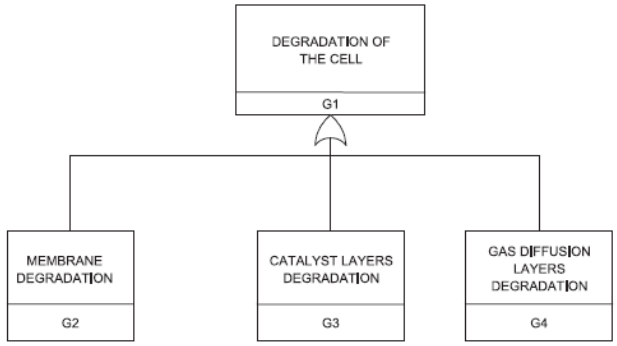

Figure 4: 'Global' Fault Tree presented in [9]

G2, G3 and G4 each had 12, 12 and 6 intermediate events respectively, which further branched down through OR gates to the basic events. As all of the gates in the presented FT were of the OR variety, the minimum cut sets are simply single events, representing the basic events of the tree.

2.6. Contribution of this Research

The qualitative failure identification table presented by Rama, et al. [8] has proved to be a good start in identifying the multitude of failure modes in a PEMFC system.

The aforementioned presented quantitative FTA by Placca & Kouta [9] has proven to be a good first step in degradation analysis and failure forecasting. Some areas that need to be addressed have been identified in [19] & [20], in particular critical component omission, basic event logic & structure, ambiguity of events and lack of standardised data sets. It is envisaged that if these issues can be addressed, the overall degradation analysis of PEMFCs will become increasingly more accurate.

The research contained within this paper contributes to the reliability area by providing the *first, fully comprehensive FMEA* which details the *most up-to-date failure modes* in a tabular format. The FTA contains the *most current and advanced logic* of failure in a PEMFC.

3. Proposed FMEA

3.1. PEMFC Construction

Due to the range of materials and components that can be used to create a PEMFC, the following analysis is based upon the key assumptions of material and construction (Figure 5);

- Standard PEMFC construction
  - Polytetrafluoroethylene (PTFE) based membrane
  - Carbon GDL
  - Pt/C catalyst layer
  - Stainless-Steel BIP
- Using H_2 fuel feed with a purity of 99.97% as required by the ISO standard 14687-2:2012 [21]

In the FMEA & FT the PEMFC has been considered to be composed of the following components: membrane, GDL, catalyst and BIP as described in the following sections.

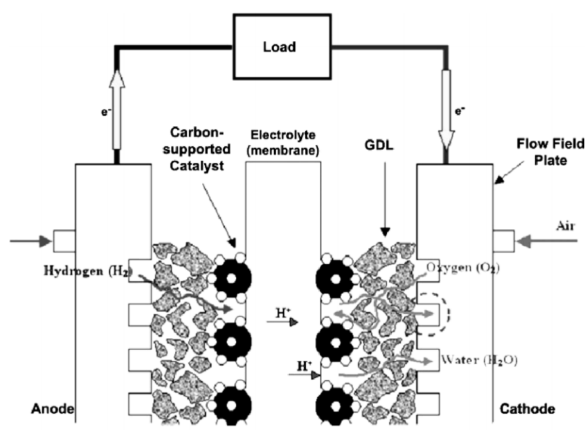

Figure 5: Components of a PEMFC [22]

3.1.1. PTFE Membrane

PTFE membranes are perfluorinated polymers, with the most commonly available being Nafion. Perfluorinated polymer membranes are also available from Tokuyama (Neosepta-F®), W. L. Gore and Associates, Inc. (Gore-Select®), Asahi Glass Company (Flemion®), Asahi Chemical Industry (Asiplex®) and Dow. Nafion has a backbone chemical structure very similar to PTFE (Teflon®) however, where it differs is that Nafion includes sulfonic acid ($SO_3{-}H^+$) functional groups. The PTFE backbone forms the strength of the membrane, and the $SO_3{-}H^+$ terminal groups provide charge sites for protonic transport.

3.1.2. Carbon GDL

The GDL is made from a carbon-fibre based material that is either formed into a paper or woven cloth type. Carbon-fibre is used due to its high electrical conductivity and high porosity values. Due to the materials for each method of constructing the GDL being identical, the failure mechanisms that can be experienced by either construction method are the same, therefore in any reliability analysis of the PEMFC it is not necessary to consider the construction methods separately.

3.1.3. Pt/C Catalyst

Pt and C are mixed in an ionomer and usually ball milled to mix into an ink. This is then either screen printed or directly painted onto the membrane or GDL surfaces.

3.1.4. Stainless-Steel BIP

The endplates, or BIPs are usually made from steel, and are routed to form serpentine channels for the gas to be delivered to the GDL component.

3.2. Operating Conditions

The operating conditions for the system are considered to be reflective of the power requirements of the New European Drive Cycle (NEDC), used to assess the emissions of car engines and fuel economy in passenger cars. The NEDC is representative of the typical usage of a car in Europe, consisting of an Economic Comission for Europe (ECE)-15 urban drive cycle repeated four times, followed by an extra-urban driving cycle. The product of which is shown in Figure 6. It is assumed that due to the power demand from the vehicle during this cycle, a range of failure modes can occur.

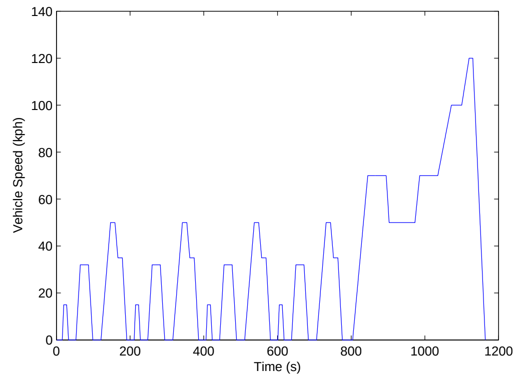

Figure 6: New European Drive Cycle

The fuel cell is assumed to be of an open anode configuration, and therefore purging strategies need not be considered in the failure analysis. During operation in the above context, the fuel cell can experience a range of operating conditions that can trigger a number of failure modes. The FMEA developed in this work details the entirety of these based upon the current knowledge of PEMFC degradation.

3.3. New, comprehensive FMEA

The full FMEA developed contains 15 individual failure modes (Table 1) pertaining to the four main components of a PEMFC; Membrane, CL, GDL and BIP. The failure modes listed in bold font are carried over from the work presented by Placca & Kouta [9]. The other failure modes have been obtained from previously published experimental results from numerous sources, however built upon to more accurately represent up-to-date PEMFC reliability analysis. Certain failure modes identified in [8] were omitted from this work. Namely:

- 'Gas leak from seals' - This is not considered as part of this work as seal degradation has been singled out as a negligible failure mode when PEMFC construction is quality controlled, See [14]. Gasket seals that do suffer from degradation are the liquid applied sealant types used in the past. Modern systems use a solid type gasket that doesn't suffer the same degradation.

- 'BIP warping of polymer matrix' - As the boundaries for this work state a steel BIP, a polymer BIP failure is not necessary.

- ‘BIP cracking’ - This has been omitted as the steel plates do not suffer from cracking, only the polymer and graphite BIPs suffer from this.
- ‘Injection-moulded BIP low electrical conductivity’ - Polymer material BIPs are not considered in this work
- ‘Coated stainless-steel BIP loss of surface electrical conductivity’ - As above, only plain stainless steel BIPs are considered in this work.

Basic Events - Membrane
Flooding
Ice Formation
Incorrect BIP torque
Creep
Fatigue from Relative Humidity and Temperature cycling
Oxide Film Formation
Dissolution of Metal Ions
Contamination form Humidifier/air pipe/gas impurity
OH or OOH Radical Attack
Previously Formed Pinholes
Excess Heat
Exothermal Combustion due to previously formed pinholes
Basic Events - Catalyst
Pt Loss and Distribution
Pt Migration
Dissolution of Metal Ions
Contamination form Humidifier/air pipe/gas impurity
Pt Agglomeration/Dissolution
Ice Formation
Flooding
Creep
Exothermal Combustion due to previously formed pinholes
Basic Events - Gas Diffusion Layer
OH or OOH Radical Attack
Flooding
Ice Formation
Basic Events - Bipolar plate
Oxide Film Formation
Corrosion leading to release of multivalent cations

Table 1: List of Events

The four failure modes related to the BIP are all omitted due to the material considerations. The work in [8] considered multiple construction materials for the BIP, however for the sake of an accurate end result pertaining to a single construction type PEMFC that would be manufactured with only one type of BIP, this work only considers one construction type BIP (stainless-steel).

Aside from the above omissions from previous studies, this work shares some similarities with previous examples, however developments to logic and basic event definitions have been made.

The full FMEA was constructed by considering each of the component failure modes listed in Table 1 in detail. The effects that the failure mode has local to the component and to the cell as a whole were identified. Any methods available to detect the failure were listed. The FMEA also included information on mitigation strategies and relationships between the failure modes resulting in 14 pages. The full FMEA has not been included here for brevity.

Although the majority of the failure modes in Table 1 are re-designated and present the latest understanding of failure logic, the failure modes listed in bold are new for this work.

One of the most important component failure mode identified by the authors is presented in Table 2 and explained below. The importance is derived from the effect that the failure mode has on the system, and it's relationship with other failure modes and operating conditions of the fuel cell.

Identification	Function	Failure Mode	Local Effect	System Effect	Failure detection method	Mitigation Strategy	Remarks	Relationship	Source
1.0 Polymer Electrolyte Membrane	The 'heart' of the PEMFC. Forms the electrolyte at the centre of the cell. Blocks passage of gasses and electrons, but facilitates passage of hydrogen protons from anode to cathode side	1.0/2.1 OH and OOH radicals & H_2O_2 contamination to PTFE	End group unzipping. The Polytetrafluoroethylene (PTFE) core material is modified with side chains of Perfluorosulfonic acid Ionomers. These can be lost through OH and OOH radical attack. (PFSI) membrane	Weaker membrane, and therefore increase in risk of mechanical damage. Reduction in voltage output	Electron Spin Resonance (ESR) spectroscopy, Polarisation Curve, Linear Sweep Voltammetry	Modifying polytetrafluoroethylene with in situ sol-gel polymerization of titanium isopropoxide to generate titania quasinetworks in the polar domains of a polymer electrolyte membrane fuel cell, can mitigate against the risk of H2 and O2 gas crossover.	Low humidity and OCV can exacerbate the attack and degradation	Protonic resistance of membrane, H2O2 formation, Mechanical Damage	Wang, H, et al. (2012) PEM fuel cell failure mode analysis. New York, CRC Press. (pp87)

Table 2: Failure Mode and Effect Analysis - Radical and Hydrogen Peroxide Attack

Radical and Hydrogen Peroxide attack in the membrane has a complicated relationship with other components and failure modes within a PEMFC system. The ways in which this failure mode was analysed is through results from chemical degradation studies [5] [23] [24]. It has been discovered that radicals can be formed from oxygen molecules permeating through from the cathode side of the fuel cell, to the anode side of the fuel cell. This O_2 can reduce at the anode Pt catalyst, forming $\cdot OOH$ radicals, and then lead on to H_2O_2 formation, and more radical formation. [5] showed that Hydrogen and Platinum can interact, forming radicals and ultimately, hydrogen peroxide.

If there are foreign ions present such as Fe_2^+ and Cu_2^+ released from BIP degradation, the H_2O_2 formed can further develop into $\cdot OH$ and $\cdot OOH$ radicals, and at a higher rate. Therefore the metal ions from the BIP catalyse, and severely increased the rate of radical and peroxide degradation to the membrane, as presented in [5].

Another mechanism for radical and peroxide attack is presented in [25]. The authors proposed a method of production of radicals, which occurs due to the diffusion of gasses through the membrane, and formation of H_2O_2.

It is also suggested in [26] that peroxide can form by a 2 electron reduction of O_2 pathway.

Due to the above, OH and OOH radical attack, and H_2O_2 attack were grouped into one basic events; 'OH and OOH radicals & H_2O_2 contamination to PTFE', which represents the formation under normal conditions, and H_2O_2 created from 2 electron reduction of O_2 on Pt.

The way in which radicals and peroxide degrade the membrane, is through end-group unzipping, as stated in the local effect column of the FMEA entry (Table 2). The PTFE backbone of the membrane is modified with end-groups or side chains of perfluorosulfonic acid ionomers which help facilitate the fuel cell reaction. These are attacked and 'unzip' from the PTFE core, releasing fluorine into the exhaust water. All the entries in Table 2 are explained below.

Column:

1. Identifies the component of the PEMFC where the given failure mode is experienced. In this instance, 'OH and OOH radicals & H_2O_2 contamination to PTFE' affects the membrane, and as such the Polymer Electrolyte Membrane component is listed.
2. Gives a brief description of the component and its function within the PEMFC. The Polymer Electrolyte Membrane component of a PEMFC

is the central part of the cell which forms the electrolyte, and serves to block the passage of reactant gasses and electrons released during the reaction, however allows the passage of hydrogen protons from the anode side, to cathode.

3. Contains the identification number and description of the failure mode to affect the PEMFC. The number 1.0 is in relation to the Polymer Electrolyte Membrane, listed in column one. The number /2.1 identifies the second failure mode listed of that section, in it's own sub-section. Therefore failure modes 1.0/2.1 and 1.0/2.2 are both primarily related to mechanical degradation.
4. Contains information pertaining to the local effect of the failure mode, as explained earlier.
5. Lists how this local effect affects the system overall. For this example if the membrane is weakened, there is an increased risk of mechanical damage to the membrane and an overall reduction in the performance of the stack/cell. This can be observed in a polarisation curve from a linear drop in the centre section of the curve.
6. Lists the potential methods to detect this failure mode's affect on the system. For this example, a polarisation curve would show a drop, as the failure mode is affecting the system. Linear sweep voltammetry could potentially identify this failure mode as it is most commonly used to identify gas crossover. The rate of gas crossover would change with mechanical damage of the membrane through radical attack.
7. Lists any potential mitigation strategies to reduce the likelihood of occurrence, or the severity of the effect. For this example, preconditioning the membrane with a modified PTFE compositing to include in-situ sol-gel polymerization of titanium isopropoxide to generate titania quasinetworks in the polar domains of the membrane. [27]
8. Contains any pertinent remarks that would either help the reader to understand the entire row, or any factors to consider regarding the failure mode.
9. Lists any relationships that this failure mode may have with other aspects of the FMEA. For this example, The resistance of the membrane relating to proton exchange is affected through membrane thinning. Additionally, H_2O_2 formation is increased through an increase in gas crossover, and of course, mechanical degradation is facilitated.
10. Finally, the source of the data is noted for ease of referencing the experimentation that tested the failure mode. The references for this

example are from a review book [27].

The FMEA showed that there are many failure modes in a PEMFC that are not completely understood. The work now provides the first fully comprehensive FMEA using the latest information to understand more failure modes than ever before. Relationships are considered which prove to be invaluable in linking failure modes which is of paramount importance in PEMFC science.

4. Proposed FT

Following investigation into the operation of the PEMFC and the FMEA analysis carried out to understand the effect of the component failure modes described above, a FT was constructed to consider the event '<5000h cell lifetime with >5% drop of output voltage'. 15 basic events were found relating to this top event, and for which data is available for a quantitative analysis.

The structure of the FT presented by [9] was modified to more accurately represent an up-to-date analysis of PEMFC degradation. The top event in Figure 4 was modified to be less ambiguous, BIP degradation was added to the 'global tree' (see Figure 7), and the interactions between basic event failure logic were vastly modified. The level 2 intermediate events are also presented in Figure 7, Catalyst Layer Degradation, Membrane Degradation, Gas Diffusion Layer Degradation and Bipolar Plate Degradation. All intermediate events lead to a 5% drop in voltage corresponding with the top event. The Bipolar plate omission by [9], has been addressed with the addition of a fourth level 2 intermediate event; 'Bipolar Plate Degradation'. The basic events feeding this intermediate event are; 'Oxide film Formation' and 'Dissolution of metal ions', both of which cause the plate to degrade. Cho, et al. [28] showed that the corrosion of the metal bipolar plates for stainless steel releases metallic elements such as Fe, Ni, Cr and Ti. The dissolution of these metals into the Membrane Electrode Assembly (MEA) can increase the ohmic resistance and the charge transfer resistance by taking up space on the active sites of the catalyst. Wu, et al. [15] discuss the degradation mechanisms of bipolar plate materials in a PEMFC, paying attention to the formation of an oxide film on the plate. A large concern with bipolar plates, is the contact resistance between the BIP and the GDL, attributed to the resistance caused by the formation of the oxide film. Due to the aforemen-

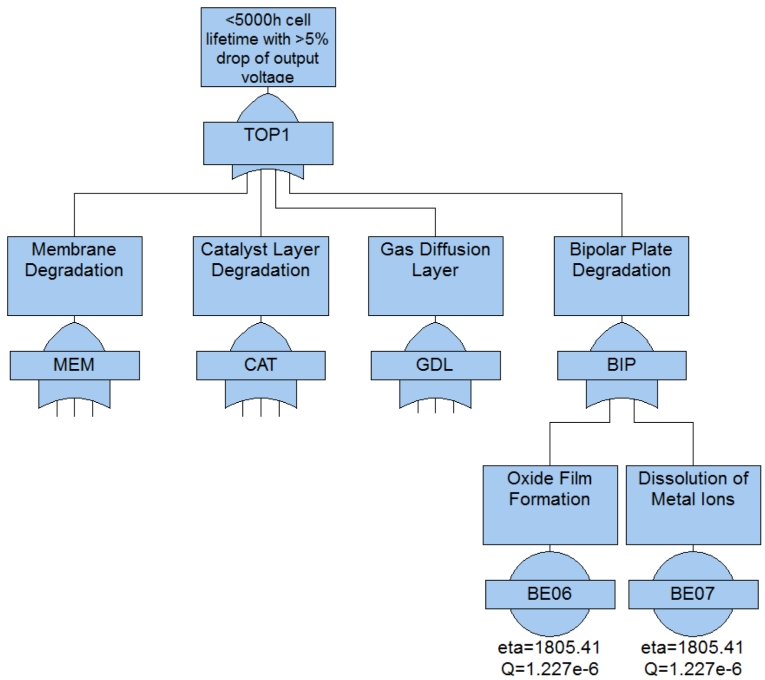

Figure 7: Proposed Change to 'Global' Tree

tioned factors observed in [28] and [15], these two factors are included in the presented FT as shown in Figure 7.

All of the intermediate events shown in Figure 7 are expanded out until they only contain basic events. For example; The membrane degradation branch of the global FT is further split down into the three main pathways of degradation in the membrane; 'Mechanical Degradation', 'Chemical Degradation' and 'Thermal Degradation', with the mechanical section being presented in Figure 8 for brevity.

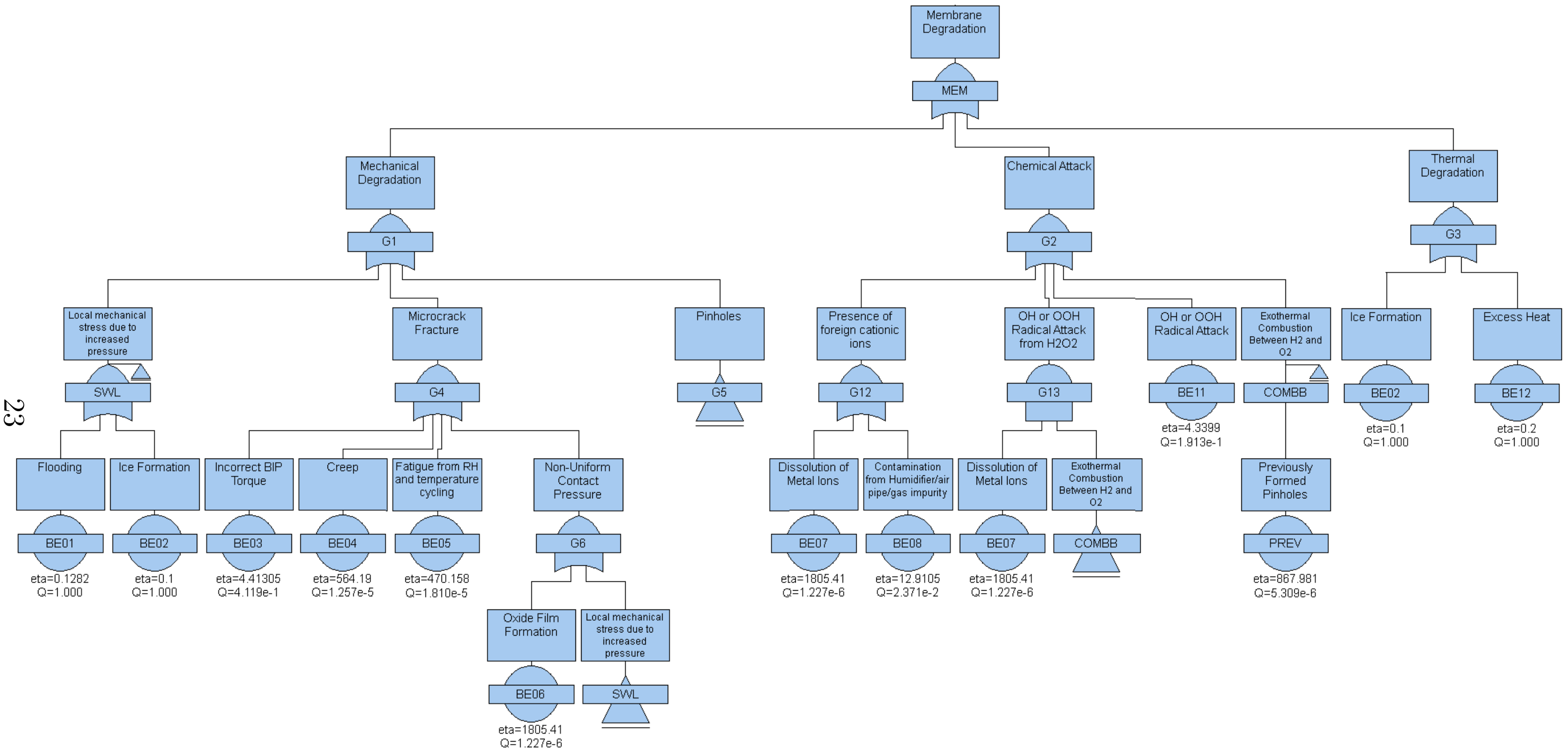

Figure 8: Proposed 'Membrane' FT Mechanical

The intermediate events of the sub-branch shown in Figure 8 include; 'Local mechanical stress due to increased pressure', 'Microcrack Fracture' and 'Pinholes'. Any localised mechanical stress is caused by swelling inside the cell, and as such the swelling relationships detailed under the event 'Local mechanical stress due to increased pressure' are repeated in the 'Microcrack Fracture' branch as shown by the transfer symbol. Microcrack fractures can be considered to be anything that results in a physical breach of the membrane, and is segregated from pinholes due to geometry. Microcracks can be considered to be tears, whereas pinholes are circular holes. These are not grouped under one mechanical breach intermediate event due to the varying conditions and events leading to each phenomena. The Pinholes section describes the basic events and combinations of events leading to the formation of pinholes on the membrane material. The two main pathways described are from either mechanical stress (such as punctures from foreign bodies) and a branch transferred in via the transfer gate (denoted by a triangle) labelled 'COMB' in Figure 8 from the chemical degradation segment of the membrane FT. The branches 'Chemical Degradation' and 'Thermal Degradation' of the membrane were developed in a similar way.

4.1. Fault Tree Summary

The FT was split into branches representing the physical components of a PEMFC; membrane, CL, GDL and BIP. These were further broken down depending upon the categorisation of the failure phenomena. The FT was drawn based upon information from the FMEA completely previously.

The membrane is a single component which can experience failures from mechanical, thermal or chemical degradation mechanisms. Therefore this section was split into the three degradation mechanisms.

The GDL has a single component construction, however there are two GDL layers in a PEMFC and as such, this segment was split into anode side and cathode side degradation mechanisms. Mechanical compression was also included which would affect both sides of the GDL. The BIP is a very simple segment with only few failure mechanisms that do not need to be further split down into sub-categories. The CL is split into its constituent carbon support, ionomer and Platinum particle construction materials. These three intermediate events then branch down into the basic events and intermediate events leading to the degradation of the component materials for the CL.

In terms of the full tree, there are 37 indistinct intermediate events. The majority of basic events input into OR gates as each basic event can lead to the overall top event individually, leaving only two AND gates in the membrane section. Similarly to the work in [9], the MCS for the overall FT are just single basic events. Due to the complicated nature of the interactions of basic events, and the gradual degradation of components in a PEMFC, individual component failure modes can cause the top event in the presented FT.

4.2. Quantification

Quantification of the FT was undertaken to gain an understanding of the expected failure occurrence during operating life. Degradation rates were sought from the literature where available, with any gaps in the data filled by expert evaluation as in Table 3. For example, where available, previously published experimental studies were analysed and the degradation rate presented due to an adverse operating condition was used in this work as the rate associated with the same basic event occurring. For example [29] found that when flooding occurred, a degradation in voltage equal to 0.39 Vh^{-1} was observed. Therefore this rate was used to correspond to the failure mode of "flooding".

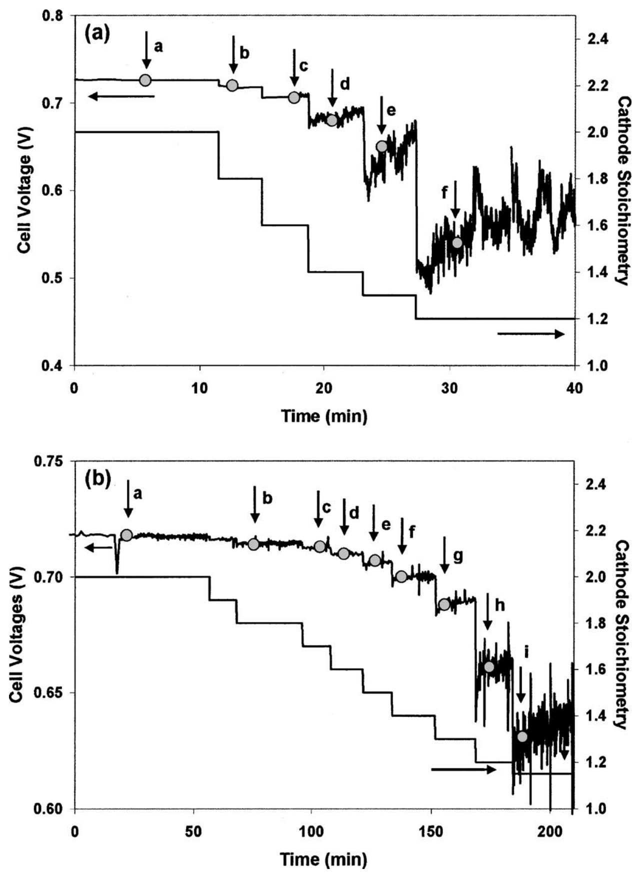

Figure 9: PEMFC Membrane flooding degradation test [29]

In their experimentation, the flow rate of cathode supply feed was decreased to induce flooding effects in the cell, and produced the results presented in Figure 9. Two testes were conducted, and for integrity of results, both test were considered and averaged for the overall voltage drop due to cell flooding of 0.39 Vh^{-1}.

Table 3 shows the basic event codes for each corresponding basic event description. This code will be used in later tables for brevity and formatting limitations.

As in [9], for each basic event listed in Table 3, $\mu(t)$ is assumed to follow a Weibull distribution, where $\mu(t) = 1/\lambda(t)$ and $\lambda(t)$ is the degradation rate. The probability density function $F(t)$ is given by Equation 1.

ID	Failure Mode Parameter	Value (Vh^{-1})	Ref
BE01	Flooding	0.39	[29]
BE02	Ice Formation	0.5	Proposed
BE03	Incorrect BIP torque	10^{-3}	Proposed
BE04	Creep	10^{-5}	Proposed
BE05	Fatigue from Relative Humidity Cycling	1.2 x 10^{-4}	[30]
BE06	Oxide film formation	3.125 x 10^{-5}	[31]
BE07	Dissolution of metal ions	3.125 x 10^{-5}	[31]
BE08	Contamination from Humidifier..	4.37 x 10^{-3}	[32]
BE09	Exothermal Combustion due to..	1.3 x 10^{-2}	[33]
BE10	Previously Formed Pinholes	1.3 x 10^{-3}	[33]
BE11	OH or OOH Radical Attack	1.3 x 10^{-3}	[33]
BE12	Excess Heat	0.25	[29]
BE13	Pt Agglomeration/Dissolution	2.5 x 10^{-2}	[34]
BE14	Pt Loss & Distribution	2.5 x 10^{-2}	[34]
BE15	Pt Migration	2.5 x 10^{-2}	[34]

Table 3: List of Degradation Parameters Used

$$F(t) = \frac{\beta}{\eta_d}\left(\frac{t-\gamma}{\eta_d}\right)^{\beta-1} e^{-\left(\frac{t-\gamma}{\eta_d}\right)^{\beta}} \tag{1}$$

Where β is the shape parameter or Weibull slope, η_d is the scale parameter or characteristic lifetime, and γ is the location parameter. The shape parameter is equal to the slope of the line in a probability plot.

The scale parameter can be determined from:

$$\eta = \frac{\mu(t)}{\Gamma(1+\frac{1}{\beta})} \tag{2}$$

Where:

$$\Gamma(\eta) = \int_0^\infty x^{\eta-1}e^{-x}dx \tag{3}$$

The location parameter, γ, is left at 0 for this study, as it is assumed that all degradation starts at the beginning of life for the cell.

It was shown in [35] that if $\mu(t)$ follows a Weibull distribution with parameters β & η_d then times to failure (T) will also follow a Weibull distribution with parameters β and $\eta = D_f \eta_d$. Where D_f is the degradation level at which failure occurs. In the analysis performed here, failure is assumed to occur when there is a 5% drop in voltage. Therefore $D_f = 0.05V_{in}$ where V_{in} is the initial voltage of the cell. V_{in} is assumed to be 1 V for this work.

Using the parameters η and β for T in the fault tree, enables the probability of the top event to be determined.

Each parameter calculated for each basic event is listed in Table 4, and shows the degradation rate, multiplicative inverse, scale parameter for $\mu(t)$, scale parameter for T, gamma function, and the shape parameter.

ID	Deg. Rate	Mu (t)	Scale Parameter	Critical Deg. Scale	Gamma Function	Shape Characteristic
	$\lambda(t)$	$\mu(t)$	η_d	η	$\Gamma(\alpha)$	β
BE01	0.39	2.56	2.56	0.13	1	1
BE02	0.5	2	2	0.1	1	1
BE03	10^{-3}	100	88.26	4.41	1.13	0.8
BE04	10^{-5}	10000	11283.79	564.19	0.89	2
BE05	1.2 x 10^{-4}	8333.33	9403.16	470.16	0.89	2
BE06	3.125 x 10^{-5}	32000	36108.13	1805.41	0.89	2
BE07	3.125 x 10^{-5}	32000	36108.13	1805.41	0.89	2
BE08	4.37 x 10^{-3}	228.83	258.21	12.91	0.89	2
BE09	1.3 x 10^{-2}	76.92	86.80	4.34	0.89	2
BE10	1.3 x 10^{-2}	76.92	86.80	4.34	0.89	2
BE11	1.3 x 10^{-2}	76.92	86.80	4.34	0.89	2
BE12	0.25	4	4	0.2	1	1
BE13	2.5 x 10^{-2}	40	35.30	1.77	1.13	0.8
BE14	2.5 x 10^{-2}	40	35.30	1.77	1.13	0.8
BE15	2.5 x 10^{-2}	40	35.30	1.77	1.13	0.8

Table 4: Table of Weibull distribution data used

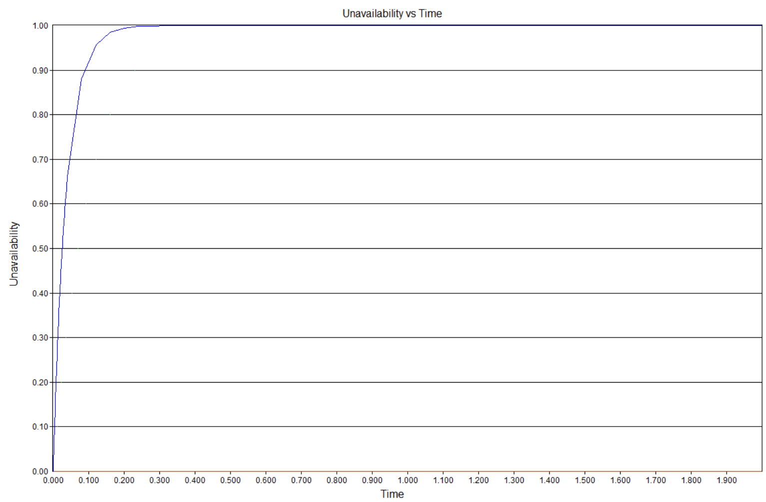

Figure 10: Unavailability of cell over Time

4.3. Results

The minimal cut sets for the FT developed are in fact the basic events themselves due to the fact that the vast majority of the logic gates are of 'OR' gates. This means that the basic event with the highest likelihood of failure will trigger the top event first under every iteration of the model. A plot of the unavailability of the cell over time is shown in Figure 10.

As can be seen, the unavailability of the fuel cell - when the cell is considered failed - is after around 30 minutes hours. This is a very low lifetime for a fuel cell, and is solely due to the highest degradation rate interacting with the logic of the FT. BE02 - Ice Formation, has a degradation rate of $0.5Vh^{-1}$ as operating a fuel cell in sub-zero temperatures has severe effects on the materials of the fuel cell and even the blockage of feed gasses to the reactant sites, however the probability of this occurring depends on operating conditions.

If high degradation failure modes such as BE12, BE02 and BE01 are removed, we see the unavailability increase to around 3 hours of operation (Figure 11), which is consistent with a failure due to the next highest degradation rate. This shows that the failure mode with the lowest η and corresponding β will be the failure mode to trigger the top event soonest.

BE01, BE02 and BE12 are failure modes that shouldn't occur under normal operating conditions, however they can be triggered by the occurrence of alternative failure modes. If pinholes occur during normal operation, they

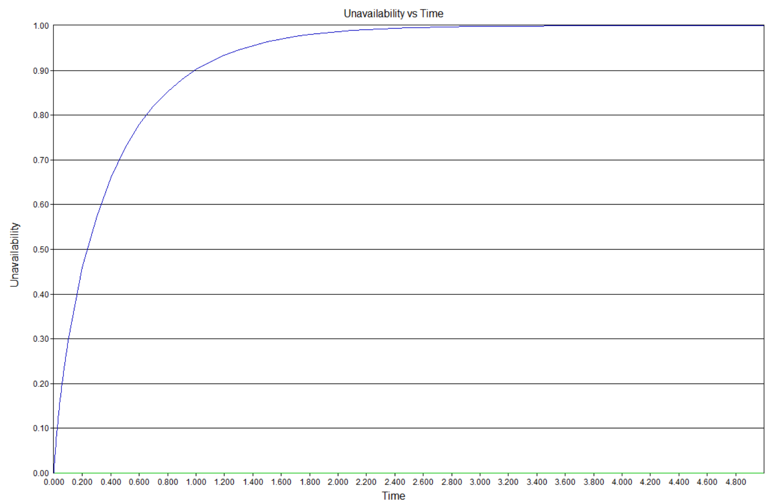

Figure 11: Unavailability

can trigger the exothermal combustion of the feed gasses, which leads to excess heat. The FTA approach does not consider these knock on failure occurrences, and is an additional pitfall to using this technique for a highly accurate degradation model.

Also, in order to understand the degradation experienced under all possible operating conditions, a FT would need to be analysed for each condition, which can be considered to be infeasible. Alternative methods to understand degradation in fuel cells is needed to overcome this shortfall.

5. Conclusions

This work has re-evaluated FT logic determined in the earlier work, including the addition of previously omitted failure modes. The new FT layout developed here is a more logical progression of the failure modes in a PEMFC than shown previously, and as such is a step forward in the reliability analysis of PEMFC. Up to date validity of the causes of degradation in a PEMFC have also been shown, enhancing the understanding of reliability issues in PEMFCs.

The presented FMEA and FTA work provides an understanding of failure logic in a PEMFC which can be used by developers and manufacturers of PEMFC systems, to identify key areas of improvement in the area. The FMEA provides a detailed, systematic breakdown of each failure mode that a PEMFC can experience, and the failure modes' effect on the system, and other components. To date, this FMEA is the only comprehensive, up-to-date listing of failure modes that a PEMFC can experience, to this level of detail.

The presented FTA goes on from the FMEA to graphically show the logical interactions between failure mode areas. The FTA has highlighted where each failure mode stems from, with reference to each physical component of a PEMFC. Although the FTA presented is a step forward in the qualitative reliability understanding of PEMFCs, the work has uncovered the fact that relationships and dependencies between failure modes exist that make a quantifiable reliability analysis not totally accurate when using FTA methods. Dependencies have been found to exist between failure modes which would discount FTA for a quantitative analysis of a PEMFC. Specifically, any failure due to pinholes was highlighted as an area where loops occur, and basic events are intrinsically linked through dependent relationships. As pinholes can be caused by the crossover of gas, which increases the rate of gas crossover, which in turn increases pinhole production. Additionally, due to the minimal cut sets being each individual failure mode, the failure mode with the shortest η is the failure mode that will inevitably cause the occurrence of the top event first. The presented FTA considers all possible failure modes in a fuel cell, and as such contains failure modes that are not normally observed in ideal operating conditions. A FT would need to be developed for each operating condition for every time-step for it to be completely accurate, which is infeasible due to scale.

Hence, although FTA can be seen as a tool to gain a greater understanding of how failure occurs in a PEMFC, and what basic events lead on to in a cell, it has limited use in reliability assessment as no useful quantification can be made. If a true understanding of the probability or frequency of failure is required, a different approach must be adopted.

Markov modelling and Petri-Net simulation can take into account dependencies between failure modes and could therefore be exploited in a PEMFC study. However, as discussed in section 2, Markov Modelling is not suitable for detailed component failure modelling dues to the sheer amount of states that would be required for each of the many components in the system. As such, future work will entail development of a Petri-Net model that can take into account dependencies between failure modes and deal with the inherent issues with using FTA for quantitative analysis of PEMFCs.

Acknowledgements
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References

[1] BERR, DTI Energy Price Scenarios in the Oxford Models, Technical Report, BERR, 2006.

[2] DECC, 2012 UK Greenhouse Gas Emissions, Provisional Figures and 2011 UK Greenhouse Gas Emissions, Final Figures by Fuel Type and End-User, Technical Report, DECC, 2013.

[3] D. for Transport, Factsheets: UK transport greenhouse gas emissions, Technical Report, DfT, 2013.

[4] U. Gov, Climate change act 2008, 2008.

[5] R. Borup, J. Meyers, B. Pivovar, Y. S. Kim, R. Mukundan, N. Garland, D. Myers, M. Wilson, F. Garzon, D. Wood, P. Zelenay, K. More, K. Stroh, T. Zawodzinski, J. Boncella, J. E. McGrath, M. Inaba, K. Miyatake, M. Hori, K. Ota, Z. Ogumi, S. Miyata, A. Nishikata, Z. Siroma, Y. Uchimoto, K. Yasuda, K. I. Kimijima, N. Iwashita, Chemical reviews 107 (2007) 3904–3951. Cited By (since 1996):920.

[6] MIL-STD-1629A, Procedures for performing a failure mode, effects and criticality analysis, 1980.

[7] J. D. Andrews, T. R. Moss, Reliability and Risk Assessment, Professional Engineering Publishing Limited, London, England, 2nd edition, 2002.

[8] P. Rama, R. Chen, J. Andrews, Proceedings of the Institution of Mechanical Engineers, Part A: Journal of Power and Energy 222 (2008) 4214–441. Cited By (since 1996): 4.

[9] L. Placca, R. Kouta, International Journal of Hydrogen Energy 36 (2011) 12393–12405. Cited By (since 1996): 2.

[10] N. Yousfi-Steiner, P. Mootguy, D. Candusso, D. Hissel, A. Hernandez, A. Aslanides, Journal of Power Sources 183 (2008) 260–274. Cited By (since 1996): 60.

[11] N. Y. Steiner, D. Hissel, P. Mootguy, D. Candusso, D. Marra, C. Pianese, M. Sorrentino, Fuel Cells 12 (2012) 302–309.

[12] M. Tanrioven, M. S. Alam, Renewable Energy 31 (2006) 915–933. Cited By (since 1996): 12.

[13] C. Wieland, O. Schmid, M. Meiler, A. Wachtel, D. Linsler, Journal of Power Sources 190 (2009) 34–39. Cited By (since 1996): 2.

[14] F. A. D. Bruijn, V. A. T. Dam, G. J. M. Janssen, Fuel Cells 8 (2008) 3–22. Cited By (since 1996): 168.

[15] J. Wu, X. Z. Yuan, J. J. Martin, H. Wang, J. Zhang, J. Shen, S. Wu, W. Merida, Journal of Power Sources 184 (2008) 104–119. Cited By (since 1996): 127.

[16] S. J. Bae, S.-J. Kim, J. I. Park, C. W. Park, J.-H. Lee, I. Song, N. Lee, K.-B. Kim, J.-Y. Park, International Journal of Hydrogen Energy 37 (2012) 9775–9781.

[17] N. Y. Steiner, D. Hissel, P. Mootguy, D. Candusso, International Journal of Hydrogen Energy 36 (2011) 3067–3075.

[18] R. Onanena, L. Oukhellou, D. Candusso, F. Harel, D. Hissel, P. Aknin, International Journal of Hydrogen Energy 36 (2011) 1730–1739.

[19] M. Whiteley, L. Jackson, S. Dunnett, in: Proceedings of the European Safety and Reliability Conference, ESREL, CRC Press, 2013, p. 603.

[20] M. Whiteley, A. Fly, J. Leigh, S. Dunnett, L. Jackson, International Journal of Hydrogen Energy (2015). Article in Press.

[21] ISO, Hydrogen fuel – product specification – part 2: Proton exchange membrane (pem) fuel cell applications for road vehicles, 2012.

[22] S. G. Kandlikar, Z. Lu, Applied Thermal Engineering 29 (2009) 1276–1280. Cited By (since 1996):53.

[23] M. Inaba, T. Kinumoto, M. Kiriake, R. Umebayashi, A. Tasaka, Z. Ogumi, Electrochimica Acta 51 (2006) 5746–5753. Cited By (since 1996):205.

[24] T. Kinumoto, M. Inaba, Y. Nakayama, K. Ogata, R. Umebayashi, A. Tasaka, Y. Iriyama, T. Abe, Z. Ogumi, Journal of Power Sources 158 (2006) 1222–1228. Cited By (since 1996):142.

[25] A. LaConti, M. Hamdan, R. McDonald, W. Vielstich, A. Lamm, H. Gasteiger (Eds.), Handbook of Fuel Cells: Fundemental, Technology, and Applications., volume 3, 2003.

[26] A. Pozio, R. F. Silva, M. D. Francesco, L. Giorgi, Electrochimica Acta 48 (2003) 1543–1549.

[27] H. Wang, H. Li, X. Yuan (Eds.), PEM Fuel Cell Durability Handbook - Fuel Cell Failure Mode Analysis, volume 1, CRC Press, Boca Raton, 2012.

[28] E. A. Cho, U. S. Jeon, S. A. Hong, I. H. Oh, S. G. Kang, Journal of Power Sources 142 (2005) 177–183.

[29] J. M. L. Canut, R. M. Abouatallah, D. A. Harrington, Journal of the Electrochemical Society 153 (2006) A857–A864. Cited By (since 1996):85.

[30] M. Fowler, J. C. Amphlett, R. F. Mann, B. A. Peppley, P. R. Roberge, Journal of New Materials for Electrochemical Systems 5 (2002) 255–262. Cited By (since 1996): 20.

[31] N. Y. Steiner, D. Candusso, D. Hissel, P. Mooteguy, Mathematics and Computers in Simulation 81 (2010) 158–170. Cited By (since 1996): 1.

[32] S. Y. Ahn, S. J. Shin, H. Y. Ha, S. A. Hong, Y. C. Lee, T. W. Lim, I. H. Oh, Journal of Power Sources 106 (2002) 295–303. Cited By (since 1996): 54.

[33] K. Teranishi, K. Kawata, S. Tsushima, S. Hirai, Electrochemical and Solid-State Letters 9 (2006) A475–A477. Cited By (since 1996):89.

[34] C. G. Chung, L. Kim, Y. W. Sung, J. Lee, J. S. Chung, International Journal of Hydrogen Energy 34 (2009) 8974–8981.

[35] M. A. Freitas, M. L. G. de Toledo, E. A. Colosimo, M. C. Pires, Quality and Reliability Engineering International 25 (2009) 607–629.