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Diagnosis of MEA Degradation for health management of Polymer Electrolyte Fuel Cells

Derek Low, Lisa Jackson, Sarah Dunnett
Department of Aeronautical and Automotive Engineering,
Loughborough University
Loughborough, United Kingdom
Tel.: +44 (0)1509 227309
D.Low@lboro.ac.uk

Abstract

Diagnostics and health management are fundamental components in a strategy to improve durability and lifetime of polymer electrolyte fuel cells. Fuel cells require a range of operating conditions to be well managed for achieving performance or durability objectives. So far, water management issues and single parameter diagnostics for individual degradation modes have been the focus of research in the literature. However, there has been minimal research on the application of fuzzy inference systems for online, multiple parameter diagnosis of fuel cells. This research presents an advanced fuzzy inference system for diagnostics and health management of a membrane electrode assembly (MEA) for polymer electrolyte fuel cells. The fuzzy inference system facilitates simplified connections of the complex relationships between numerous operating conditions and subsequent degradation modes. The approach utilises the most important operating parameters for diagnosis of high priority degradation modes using multiple health sensors. The developed fuzzy inference system classifies the fuel cell input data into simple linguistic categories for example ‘cell voltage is very high’ or ‘stack temperature is low’ through a fuzzification process. Based on a set of antecedent-consequent (if-then) rules, an inference calculation is performed without necessity for complex mathematical models. This enables a fast diagnosis with fuel cell parameters classified on a scale of inclusion to the linguistic categories. The linguistic classification of a degradation mode is converted back into a numerical value through a defuzzification process. The output data can be used to inform the user on the fuel cell state of health. The investigation has focused on the diagnosis of MEA degradation as it has been identified as having critical impact on fuel cell performance and lifetime. A single cell with a 25cm2 active area was used for testing under numerous moderate to extreme operating conditions known to cause membrane and electro-catalyst degradation. A database of if-then rules was initially developed based on knowledge in the literature and refined with experimental testing. Results so far have supported validation of the fuzzy inference system membership functions and the rule base for diagnosing the consequential degradation modes based on fuel cell operating conditions. This diagnostic and health management approach facilitates proactive decision making for mitigation strategies to be employed according to performance or lifetime targets and can increase fuel cell availability and lifetime therefore improving the overall value of the system.

Introduction

Polymer electrolyte fuel cells (PEFC's) are a promising technology that can produce electricity efficiently with zero carbon emissions. Therefore, the development of fuel cell technology plays an important part in the decarbonisation of industry and progression towards a low carbon sustainable society. The reliability and durability of PEFC's is still a remaining technological challenge as industry lifetime targets for automotive and stationary applications of 5,000hrs and 40,000hrs respectively are yet to be achieved [1][2]. Achieving these targets are crucial in order to compete with conventional technologies and increase widespread commercialisation. The wide range of fuel cell applications from small portable devices up to stationary power generation means they are required to perform under a range of operating and environmental conditions over their lifetime with a threshold for acceptable performance losses. Lifetime system efficiency losses below 10% and a degradation rate of 2-10μV/h are considered to be acceptable for the majority of applications [2]. Diagnostics and health management are fundamental approaches to improve the reliability and durability of PEFC's. Within data-driven diagnostics, much of the literature has focused on water management issues or diagnosis of single degradation modes [3][4]. There is a lack of emphasis on monitoring multiple parameters for proactive health management. A gap in the literature was identified on the application of fuzzy inference systems for diagnosis of multiple degradation modes in fuel cells based on the management of several key parameters. This paper presents the diagnosis of MEA degradation utilising several high priority parameters to aid proactive health management of PEFC's. MEA degradation is categorised into two critical degradation modes; chemical degradation of the membrane and electrocatalyst degradation. Development of a fuzzy inference system enabled these two degradation modes to be diagnosed based on the operating parameters without complex models. Furthermore, this approach enables classification of input and output parameters based on a scale of degrees of truth to a diagnostic classification. The output of the diagnostic fuzzy inference system helps to simplify interpretation of results and allows more effective management of operating conditions thereby increasing fuel cell reliability and durability.

1. Scientific Approach

Fuzzy logic forms the foundation of fuzzy inference systems. As opposed to traditional systems based on Boolean logic which only permit inclusive or exclusive membership to a category, this approach allows for input parameters and outputs to be expressed in linguistic terms and represent system behaviour on a spectrum with partial membership to categories [5]. This makes fuzzy logic well suited for implementation in knowledge based and control systems such as diagnostic applications for fuel cells. There are several key features of a fuzzy inference system: fuzzification, a control strategy based on a database of rules and defuzzification. The fuzzification process enables input data to be classified into broad categories described in linguistic terms. For example, the linguistic terms used to describe the categories can be low, normal or high for classifying input data. The input data for from the fuel cell to the fuzzy inference system includes cell voltage, cathode humidity and cell temperature. The database of diagnostic rules forms the central feature of the FIS, with development of the rules based on literature and refined through experimental testing. This stage of the FIS enables connection between fuel cell operating conditions and the occurrence of degradation. The defuzzification stage enables the broad linguistic classification to be output as a crisp numerical value. This output data can be used to inform the operator on the health of the fuel cell and make any adjustments towards durability targets. The key features of the fuzzy inference system are shown in Figure 1.

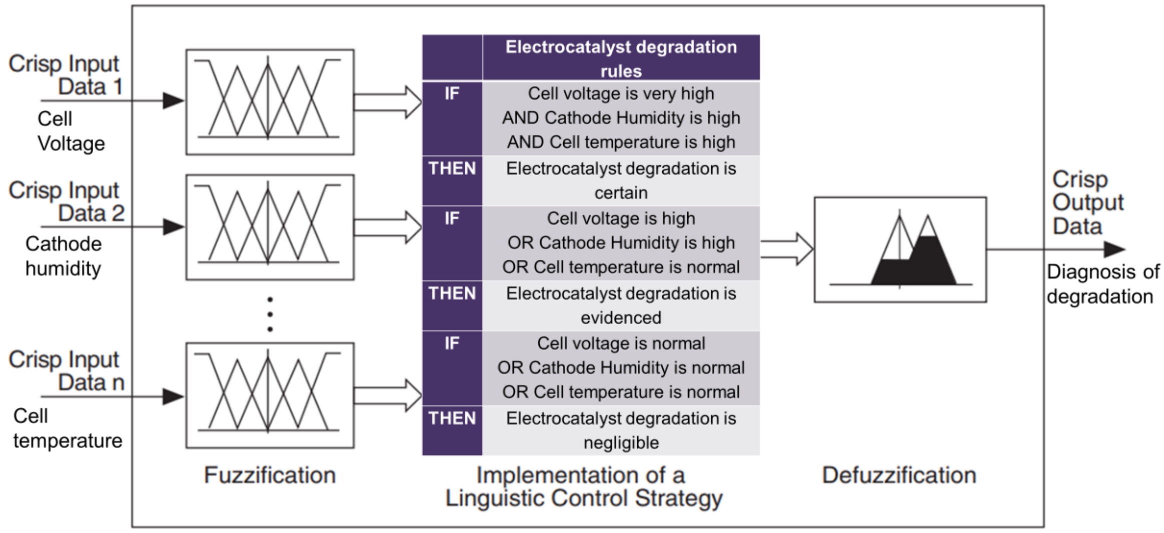

Figure 1 Fuzzy Inference System

As illustrated in Figure 1, the fuzzification process uses the selected fuel cell parameters as input data. The cell voltage, operating temperature and cathode humidity were identified in the literature as the most important parameters for diagnosis of MEA degradation and fuel cell health management [6][7]. Fuzzification of the input parameters requires development of membership functions which set boundaries for each linguistic classification. Membership to a category is on a scale between 0 and 1 (0% to 100%). The membership functions for the fuzzification of each parameter were developed from the literature review and are referenced in table 1. Figure 2 shows the membership functions for fuzzification of the cell voltage.

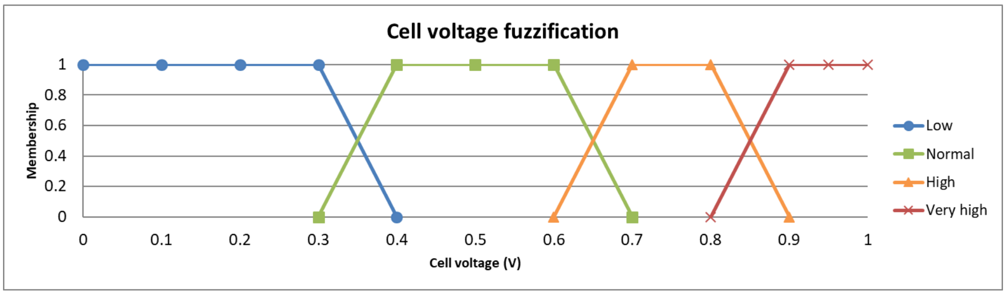

Figure 2 Cell voltage fuzzification

As shown in figure 2, the categories for 'very high' and 'high' voltage are based on the knowledge that voltages in this range are known to cause degradation. Typically, this would be at open circuit voltage (OCV) or low current loadings. The normal operating voltage range was based on the region where the fuel cell can typically provide useful power production [1][2].

The membership functions for the fuzzification of cathode humidity and cell temperature were developed in the same method. The next stage in the FIS process includes the database of diagnostic rules. The database of rules uses the information from the fuzzification process and identifies the parameters that are above the normal operating range that could lead to degradation. This was developed based on the three selected parameters which are known to significantly impact MEA degradation [8][9].

The rule database for the diagnosis of MEA degradation was separated into two degradation modes; membrane chemical degradation and electrocatalyst degradation. The development of the rules for membrane chemical degradation is discussed first. It has been identified in the literature that high operating voltages, low cathode humidity and high operating temperature all contribute to the acceleration of membrane chemical degradation [2][10]. The accelerated degradation test conditions involved an operating temperature of 95°C, 50% relative humidity of reactant gases and operation at open circuit voltage (OCV). Tests were conducted up to 200hrs. The data collected showed that membrane chemical degradation increased and open circuit voltage decreased by 75mV (450 μV/h) and 170mV (850 μV/h) [2][10]. Although, the fuel cell was operated under accelerated degradation test conditions, these results indicate the severity of the conditions and the consequential impact on component degradation and fuel cell durability. Further to this, [11] investigated the impact of operating temperature on membrane durability. Reactant humidity was kept constant at 36%RH, while the operating temperatures were set to 50, 70 and 90°C. Results demonstrated that membrane chemical degradation increased with temperature confirming that high temperature and low humidity have a significant impact on membrane durability. Several studies in the literature have found that lower humidities cause an increase in membrane chemical degradation and voltage degradation, ultimately resulting in reduced durability [12][13][14][15]. Low humidity leads to membrane dehydration which in turn leads to reduced water flux and protonic conductivity, in addition to increasing brittleness and rigidity. Furthermore, the production and accumulation of the destructive hydrogen peroxide accelerates the degradation process [2][8][16]. Table 1 outlines the database of rules developed for diagnosing membrane chemical degradation.

Rule	If	Then	References
1	Cell voltage is high AND Cathode humidity is low AND Cell temperature is high	Membrane chemical degradation is certain AND voltage degradation is high AND performance decrease is high	[2][10][11][12] [13][14] [15][17]
2	Cell voltage is high OR Cathode humidity is low OR Cell temperature is high	Membrane chemical degradation is evidenced AND voltage degradation is high AND performance decrease is high	[2][12][13][14][15]
3	Cell voltage is normal OR Cathode humidity is normal OR Cell temperature is normal	Membrane chemical degradation is negligible AND voltage degradation is low AND performance decrease is low	[2][17][8]

Table 1 Membrane chemical degradation rule database

The literature review also revealed that the most significant parameters contributing to the acceleration of electrocatalyst degradation included high operating voltage, high cathode humidity and high operating temperature. These severe conditions all result in electrocatalyst degradation but can cause this in a number of different mechanisms including platinum catalyst dissolution, agglomeration, loss or distribution and migration [2][16][18][19][20]. Table 2 outlines the database of rules for diagnosing electrocatalyst degradation.

Rule	If	Then	References
4	Cell voltage is very high AND Cathode Humidity is high AND stack temp is high	Electrocatalyst degradation is certain AND voltage degradation is high AND performance decrease is high	[2][16][18] [19][20]
5	Cell voltage is high OR Cathode Humidity is high OR stack temp is normal	Electrocatalyst degradation is evidenced AND voltage degradation is high AND performance decrease is high	[2][16][18] [19][20]
6	Cell voltage is normal OR Cathode Humidity is normal OR Stack Temperature is normal	Electrocatalyst degradation is negligible AND voltage degradation is low AND performance decrease is low	[2][16][18] [19][20]

Table 2 Electrocatalyst degradation rule database

After the database of rules, the next stage of the FIS process is the defuzzification stage which outputs a numerical value of certainty from the broad linguistic classification. The output data informs the operator on the state of health of the fuel cell and enables adjustments of operational parameters for improved health management. The FIS output data includes the certainty of the degradation diagnosis, voltage degradation severity and performance decrease. The severity of voltage degradation was included to inform the operator on the severity of the irreversible degradation. Conversely, the performance decrease was included to inform on the immediate impact on performance but with recoverable degradation. Both these aspects were identified to be important for health management. The membership functions developed for the defuzzification of the degradation modes are illustrated in Fig. 3.

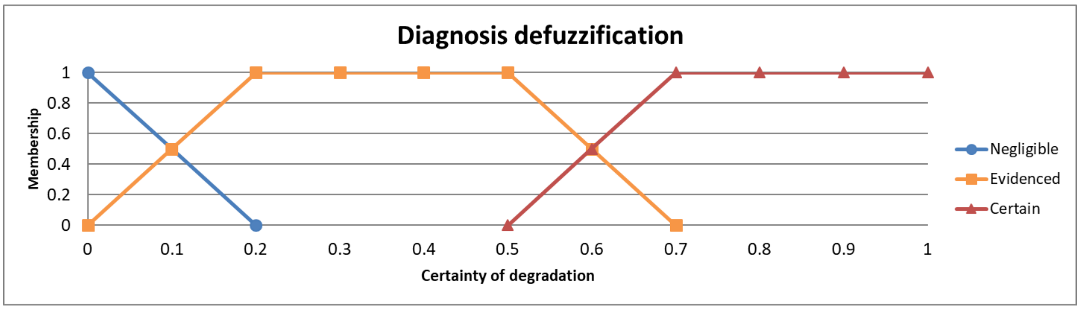

Figure 3 Diagnosis defuzzification

For a simple interpretation of results, the diagnosis defuzzification enables classification of the outputs from the database of rules into basic categories. This allows the operator to make an informed decision on how to manage fuel cell operating conditions for health management. The category for a degradation mode to be classified as ‘fully certain’ was based on results showing a high degree of support (above 70%), with this shifting to the evidenced category as the support drops towards 50%. The evidenced category was classified as between 20% and 50% support. Below 20% support, the certainty of degradation occurring is negligible. The membership functions for the defuzzification of voltage degradation and performance decrease were developed using the same method.

2. Experiments/Calculations/Simulations

The first stage of testing was conducted on a Pragma Industries fuel cell. Fuel cell components included a 100cm^2 Nafion XL membrane (27.5µm thickness), catalyst loading of 0.2 mg Pt/cm^2, carbon paper GDE and graphite bipolar plates. Other subsystems included a 150A electronic load bank controller, mass flow rate controllers, humidifiers and pressure sensors for reactant gas supplies. Fuel cell temperature was controlled via heated water circulation. The second stage of testing focussed on operation at high temperatures and was conducted on a 25cm^2 Scribner fuel cell due to temperature limitations on the Pragma fuel cell. All other component specifications and subsystems were the same expect for the temperature control unit which used electrically heated end plates. Table 3 shows the operating conditions for the steady state experimental testing.

Test Condition	Specification
Hydrogen & Air flow rates	0.25 slpm (Hydrogen), 0.92 slpm (Air)
Nominal conditions	Stage 1: 55°C, 100% RH, 0.6V Stage 2: 70°C, 100% RH, 0.6V
Open circuit voltage	Operation at 0A under nominal conditions
Dehydration conditions	No gas humidification
High temperature conditions	80°C
Combined dehydration and OCV conditions	No gas humidification and OCV

Table 3 Fuel cell operating conditions

Ion chromatography analysis was performed on the fuel cell exhaust water to assess membrane chemical degradation by quantification of the Fluoride release rate (FRR) of the membrane. Ion chromatography enabled diagnosis without invasive or destructive methods. A relationship exists between fuel cell lifetime and Fluoride release rate which can be used to determine membrane health [21][22]. Due to laboratory time restrictions and test protocols, each test condition was conducted for six hours.

3. Results

The polarisation curves obtained from each of the test conditions is shown in Figure 4.

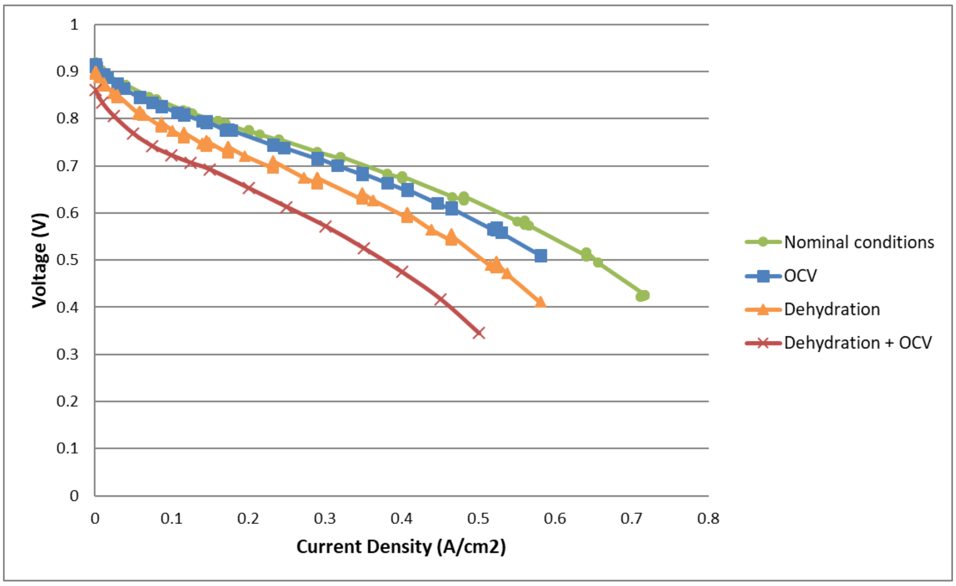

Figure 4 Polarisation curve results

The polarisation curve after OCV testing shows a minor performance drop in the ohmic region of the curve but not the activation region. This suggests that the impact of OCV conditions in isolation are not severe. However, a performance decrease is still evidenced, particularly in the medium current density range (0.5-0.6A/cm^2) where power output is highest. The polarisation curve after dehydration testing shows a more pronounced performance decrease over the whole curve. The performance drop was observed to increase with current density and confirms that low humidity in isolation can significantly impact performance. The smaller performance drop in the activation region along with the larger drop in the ohmic and mass transport regions indicate that the humidity conditions have a greater impact on the membrane properties than the catalyst. The polarisation curve after combined dehydration and OCV testing shows a much more significant decrease in performance in all regions of the curve. This means that these conditions in combination severely impact both membrane and electrocatalyst properties. These results support the database of rules outlined in table 1 by validating the performance decrease diagnosis. Furthermore, the ion chromatography analysis also supports these results by quantifying the irreversible membrane chemical degradation. Figure 5 shows the Fluoride release rates from each degradation test condition.

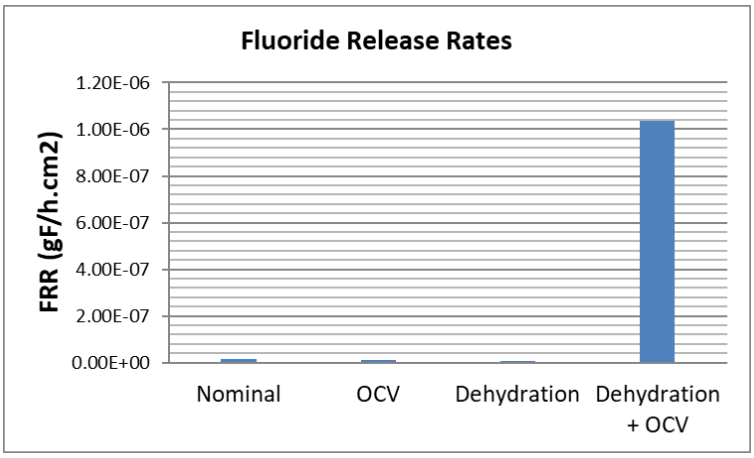

Figure 5 Fluoride release rate results

Figure 5 shows that, when the OCV and dehydration conditions were tested independently, the FRR levels were minimal and in the same range as the nominal conditions. Therefore, this implies that these conditions in isolation do not cause membrane chemical degradation for certain but do show some evidence of fluoride release. In contrast, combined dehydration and OCV conditions resulted in a significantly increased FRR which can be used as an indicator for severe membrane chemical degradation. These results support the proposed rules for diagnosing membrane chemical degradation outlined in table 1. The FRR results from this study are significantly lower in comparison to other published data [2][10]. However, the substantially longer test durations in the literature studies (up to 200hrs) are a contributing factor to the higher Fluoride release rates. This suggests that further tests should be conducted in order to quantify the change in FRR over time periods and implies that longer periods under such harsh conditions can increase the rate of degradation.

The diagnosis of electrocatalyst degradation required analysis of the voltage degradation at OCV. This is because at OCV, the only losses present are the activation losses from catalytic activity which can be used as an indicator for electrocatalyst degradation. The voltage degradation results from stage 1 of testing are shown in figure 6.

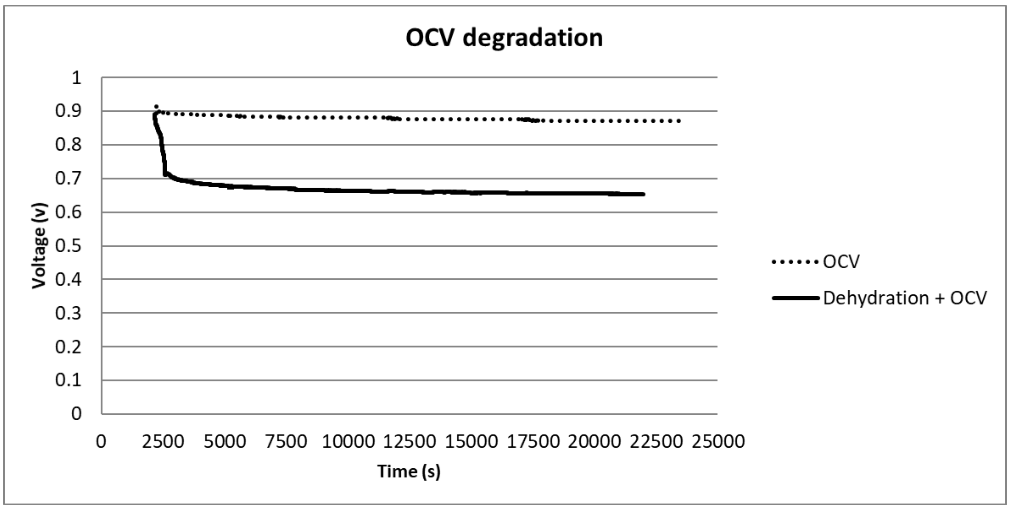

Figure 6 OCV degradation

The combined dehydration and OCV conditions initially cause a rapid drop in OCV. However, this is due to reversible losses so for a more accurate representation of the voltage degradation, a stabilisation period should be taken into consideration. A comparison of the voltage degradation rates is shown in table 4.

Test conditions	Voltage degradation rate (mV/h)	Voltage degradation rate after stabilisation (mV/h)
Normal RH, OCV, 50°C	7.76	3.936
Dehydration, OCV, 55°C	43.57	8.118

Table 4 Voltage degradation rates

The inclusion of a 20-minute stabilisation period still resulted in the OCV degradation for both test conditions being very high, indicating that electrocatalyst degradation was occurring. This provides evidence that validates rule 5 for electrocatalyst degradation outlined in table 3. In order to further support the diagnosis of electrocatalyst degradation, polarisation curves were conducted before and after each test condition. Figure 7 shows the polarisation curve results from stage 2 of testing at high temperature.

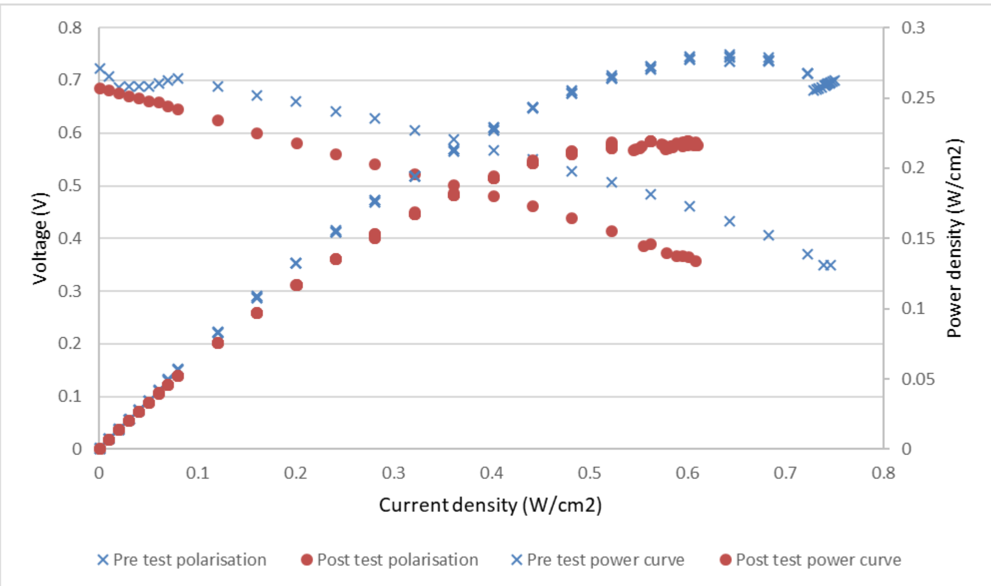

Figure 7 Polarisation and power curves

Figure 7 shows that at high temperatures and high humidity, the fuel cell performance overall is decreased. The drop in OCV was observed due to the occurrence of electrocatalyst degradation because with no current loading only catalytic activity or activation losses would be impacting the voltage. This decrease was under the 10% cell failure threshold [23]. However, the drop in peak power was more than 10% which is where useable load currents would be needed. These polarisation and power curves support the electrocatalyst degradation rules outlined in table 3.

In conclusion, diagnosis of each component of MEA degradation was supported by the results. The polarisation curves conducted under each of the test conditions and Fluoride release rates support the diagnostic rules for membrane chemical degradation. Testing each condition in isolation showed only slight drops in performance which implies that the impact is not severe if harsh conditions are not combined. Whereas the combined dehydration and OCV conditions showed a significant performance drop. The FRR results further validated this. From stage 2 testing, the polarisation curves and extended OCV testing support the diagnostic rules for electrocatalyst degradation. The results showed isolated degradation conditions can lead to moderate electrocatalyst degradation but is substantially increased by combined conditions in addition to increasing the rate of degradation. Overall the results have highlighted the importance of the three selected parameters for diagnosis of each component of MEA degradation and the importance of including voltage degradation and performance drops in the FIS outputs. Recommended further testing should seek to develop the diagnostic capability for fuel cells operating under dynamic conditions representative of automotive applications.

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