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# Effects of temperature and backpressure on the performance degradation of MEA in PEMFC

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## ABSTRACT

The performance characteristics of proton exchange membrane fuel cells (PEMFCs) can be affected by a degradation of the membrane-electrode-assembly (MEA). In this paper, the performance degradation of MEA in a single cell PEMFC was examined at 80 °C and a backpressure of 10 psi after 100 h of operational time using open circuit voltage (OCV) conditions. A control experiment was conducted by testing the MEA at ambient temperature without backpressure. Both electrochemical impedance spectroscopy (EIS) and an OCV analysis showed that both the conductivity and the performance of the cell operating at 80 °C were less than the control values after 100 h of operation. In contrast, an application of 10 psi of backpressure improved the cell conductivity and can maintain OCV in compare with ambient and 80 °C conditions. Characterizations of the pre- and post-operation of the MEA (cathode, anode and membrane) by scanning electron microscope-energy-dispersive X-ray spectroscopy (SEM-EDX), transmission electron microscopy (TEM) and X-ray diffraction (XRD) showed that the MEA performance degradation at 80 °C after 100 h resulted mainly from carbon corrosion combined with Pt agglomeration and dissolution, producing a PtS compound with reduced activity at both the cathode and the anode and also drying and cracking of the membrane.

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## Introduction

As both the reliability and the durability of fuel cells (especially proton exchange membrane fuel cells, PEMFCs) are of considerable importance, the performance degradation of these fuel cells has recently generated increased attention in the literature. Degradation can be caused by many factors,

including the operating temperature and backpressure, the startup and shutdown conditions, the design and assembly of the materials, materials degradation, the operating conditions and the contaminants [1]. While performance degradation cannot be completely avoided, the rate of degradation can be minimized. Increasing the durability of PEMFCs is a major challenge with increased research attention focused on these types of improvements.

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To minimize the rate of degradation of the fuel cells, research has focused on understanding the degradation mechanisms of each component of the PEMFCs. Collective studies have shown that the performance degradation in the PEMFCs results mainly from degradations in performance from the gas diffusion layer (GDL), the membrane, the carbon substrate, the catalyst layer (CL) and the bipolar plate [1,2]. In addition, degradation can occur with an improper management of water (causing either flooding or dehydration) that can poison the fuel and the oxidant [3]. GDL degradation can occur with carbon oxidation, polytetrafluoroethylene (PTFE) decomposition and mechanical degradation [1,2,4]. CL degradation can result from catalyst maturation, catalyst loss (or removal), carbon corrosion, interfacial degradation [5] and active surface area reduction resulting from an agglomeration of the catalyst (especially in the cathode) [6].

Degradation of the CL during long-term operation can include either cracking or delamination of the layer, catalyst ripening, catalyst particle migration, catalyst washout, electrolyte dissolution and carbon coarsening [7]. Decreases in the concentration of platinum metal after a long-term operation may result from the dissolution of the Pt and the formation of PtO and PtO<sub>2</sub> in the anode and the cathode [8]. Under both constant current (CC) and OCV conditions, Chung [9] investigated the effects of fuel cell operating time on the degradation of the electro-catalyst, suggesting that the degradation of the catalyst resulted from Pt sintering and dissolution. With an oxidation of Pt to PtO, dissolution of Pt occurred preferentially in the cathode, compared with the anode. The effects of the carbon substrate on the stability of the catalyst have also been studied [10]. Mamat compared the stability of Pt/vulcan XC-72 with Pt/GNFs, indicating that the Pt/vulcan had improved stability with long-term use. A poisoning of the carbon was also observed with the oxidation of carbon to form C–O and C=O groups [8]. The analysis of catalyst failure in MEA due to the high temperatures and long operating time has also been done on DMFC [26].

Membrane degradation processes can be classified into three categories: mechanical degradation (perforations, cracks, tears, pinholes), thermal and chemical/electrochemical (peroxide and hydrogen peroxide production, hydrogen and air crossover) [1]. Wu studied PEMFC degradation processes to elucidate the multiple degradation mechanisms and generate improvement strategies. According to Wu, mechanical degradation can be the first observed element in the degradation of membrane performances, resulting from either congenital membrane defects or improper MEA fabrication processes. Thermal treatments can cause membrane degradation for PEMFCs operating at high temperatures. With glass transition temperatures at approximately 80 °C, conventional perfluorosulfonic acid (PFSA) membranes are subject to critical breakdown processes at high temperatures. As suggested by Ramaswamy [11], membrane degradation rates increase with increasing rates of oxygen reduction reaction (ORR) activity for temperatures up to 80 °C, as characterized by a decrease in conductivity and changes in the ion exchange capacity (IEC).

The chemical/electrochemical membrane degradation can result from the exothermal reaction of H<sub>2</sub> and O<sub>2</sub>, which may damage the membrane and lead to pinholes. The integrity of

the membrane can be monitored from the rate of change of the gas crossover, the fluoride-ion emission rate (FER) and the ion exchange capacity. Membrane degradation processes caused by the operating conditions have also been discussed [7]. Operating the membranes under low humidity conditions can cause water shortages, initiating membrane damage. In addition, the rate of degradation can be accelerated using high temperature and low humidity operating conditions. One method to prevent these types of membrane damage involves increasing the humidity. Caution is needed, as increased humidity can also cause flooding [12]. Improvements in the durability of the membrane were explored by using a PTFE/Nafion composite membrane [13] with mixed results, as the performance of the PTFE/Nafion membrane was inferior to Nafion 211 at long operating times with the generation of creep deformation. Included to prevent crossover in the event of a membrane rupture, a PTFE layer can also increase the internal resistances of the membrane, especially after a separation from the nafion.

Operations under OCV conditions have been used to determine the durability of PEMFCs. With OCV operations (no electric loading applied), MEA can experience degradation, resulting from a chemical reaction between the reactant gases and the membrane materials to generate a peroxide radical at the cathode that can poison the membrane surface. Peroxide formation can occur with an imperfect reduction of oxygen or crossover events. The operation of the fuel cell using OCV conditions can also affect the performance of the CL. The OCV conditions can cause Pt agglomeration, carbon weight loss and ionomer deterioration [14]. In addition, the OCV can decrease with decreasing durability of the PEMFC. As characterized by reduced electrochemical surface area (ECSA), two of the factors that were determined to cause a decline in the OCV included a high potential that can result in the dissolution/migration of Pt particles and a carbon substrate oxidation [15]. Using OCV conditions, the consumption of reactants was also reduced to the point of either low levels or even a complete absence. As noted by Zhang, increased membrane degradation is observed at the electrode with OCV conditions. Baik [16] examined the effects of the GDL structure on both OCV and hydrogen crossover, suggesting that GDL structures with fine pore sizes had improved durability.

The effects of backpressure on the performance of the PEMFC have been reported by Zhang [17]. Increasing levels of backpressure resulted in increases in the exchange current densities of the reactions with the increase in the reactant partial pressures. Backpressure can help to increase the fuel cell performance by increasing the gas diffusion to the active sites of the catalyst in the CL. Applying backpressure to the system can also have negative effects by increasing the possibility of both crossover and leaking, as well as increasing the cost, size and weight of the PEMFC.

Operating the fuel cells at high temperatures can be advantageous by increasing the electrochemical kinetics, reducing the susceptibility of contamination and providing conditions that facilitate good water management. High temperature operations may also be limited with an increase in the rates of degradation of the fuel cell [3], a decrease in the proton conductivity (especially at low relative humidity) and increased difficulty in the water uptake of the membrane.

Maintaining the durability of the PEMFC equipment (especially for high current densities) should be accompanied by a strategy to maintain the performance. In a report on the mechanisms of PEMFC performance degradation and mitigation strategies, Wu [1] discussed several problematic factors, including the membrane, the CL, the GDL and the bipolar plates.

Characterization methods used for determining the extent of MEA degradation have been developed using multiple techniques, including electrochemical impedance spectroscopy (EIS) methods [13,18,19], cyclic voltammetry (CV) [11,20–22], XRD [10,11,22], TEM [9,10,22], XPS [10] and FESEM [22]. Among these methods, EIS is one of more important diagnostic tools that has been used in characterizing the PEMFCs and is used for CL investigations, a determination of the catalyst surface areas, catalyst loading and catalyst utilization [5]. CV is commonly used to determine the ECSA of the Pt by hydrogen adsorption. Both XRD and XPS are commonly used techniques to characterize the average Pt particle size and the change in the surface electronic structure during the degradation process. TEM is used for both characterizations of the topography and analysis of the particle size distribution.

## Methods

### MEA preparation

To prepare the MEA, P75T CPS carbon paper (Ballard Power Systems, Inc, Burnaby, Canada) was used as a backing layer (macro porous) GDL and combined with carbon black Vulcan-XC72R (Cabot Corporation, Boston, USA), Polytetrafluoroethylene (PTFE) solution (60 wt%, DuPont Inc., USA), Nafion Solution (5 wt%, DuPont Inc., USA), Pt/C (20 wt%, PMC, USA), isopropyl alcohol (IPA) (Sigma-Aldrich, USA) and ammonium bicarbonate (Sigma-Aldrich, USA). The procedure for fabricating the MEA was described in our previous work [23], with a total platinum content of  $0.5 \text{ mg cm}^{-2}$  at the anode and  $0.7 \text{ mg cm}^{-2}$  at cathode, using a Nafion membrane NR 212 (DuPont Inc., USA) as the electrolyte membrane.

### Characterization of the MEA degradation after 100 h of operation

The performances of the MEAs were tested in a single cell with a multi serpentine channel bipolar plate using a GasHub Fuel Cell station at a defined temperature ( $80^\circ\text{C}$ ) and backpressure (10 psi) for 100 h using OCV conditions and under load to determine polarization. A control experiment was performed by testing the MEAs at room temperature without backpressure (ambient conditions). Pure hydrogen gas was supplied to the anode at a flow rate of  $0.9 \text{ L min}^{-1}$ , and purified air was supplied to the cathode at  $1.8 \text{ L min}^{-1}$  at 100% RH.

Electrochemical characterizations of the MEAs were performed using EIS with a Metrohm Autolab PGSTAT128N (Netherlands). At time points both before and after 100 h of operation, the structures of both electrodes and membranes were analyzed and characterized using SEM-EDX (Zeiss Supra-55 VP). The structures of the platinum particles were analyzed by XRD (Bruker D8-Advance) and TEM (Philips CM12).

## Results and discussion

### EIS analysis

The EIS method has become a common technique used to analyze the electrochemical performance of fuel cells. EIS can distinguish the effects of the various processes. In this study, the effects of cell temperature and backpressure were analyzed using EIS, with the results shown in Fig. 1.

The EIS results at high frequency showed that the charge transfer resistance ( $R_{CT}$ ) in the MEA operating at  $80^\circ\text{C}$  was increased, compared with the measurements at ambient condition. The measurements obtained at elevated temperature may have resulted from several factors, including a drying of the membrane (as shown in Fig. 7) and Pt dissolution and agglomeration that can decrease both the number of active sites and the surface area of electrodes (Figs. 4 and 5). The effects of backpressure (to 10 psi) had a positive impact on the improvement of the conductivity and the reaction effectiveness, as determined from the decrease in  $R_{CT}$  relative to the measurements obtained using normal conditions with no backpressure.

### OCV performance and polarization curve

The operation of the fuel cell using OCV conditions can be used as an effective stressor for accelerated testing in PEMFC durability studies [15]. The effects of OCV on the performance degradation of the MEA may result from the membrane damage caused by the formation of peroxide radicals with high fluoride emission rates (FER) and hydrogen crossover with the resulting oxygen reduction reaction (ORR) over potential at the cathode. In these studies, the effects of time, temperature and backpressure on the OCV were determined, with the results shown in Fig. 2.

In general, the OCV decreased with increasing fuel cell operating time. Abundant electrons at the anode and the  $\text{H}^+$  ions that were retained at the interface of the cathode and membrane layers for an extended period of time facilitated the damage to the membrane. On the cathode side, abundant oxygen can oxidize platinum to generate the  $\text{PtO}_x$  products, forming catalyst materials with reduced activity. Over time, these processes can cause a decrease in the OCV.

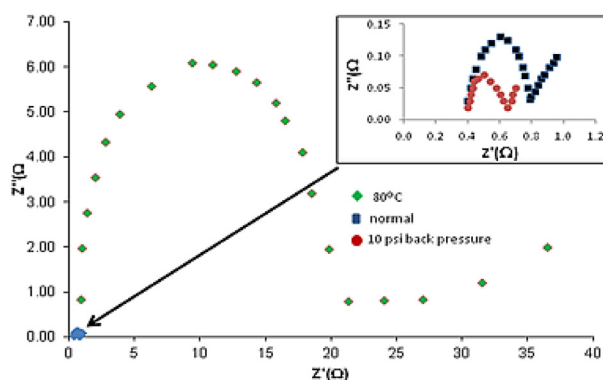
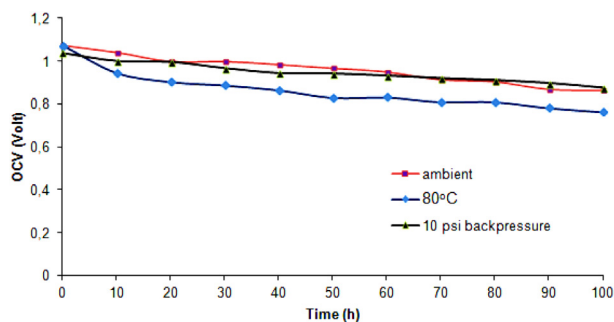
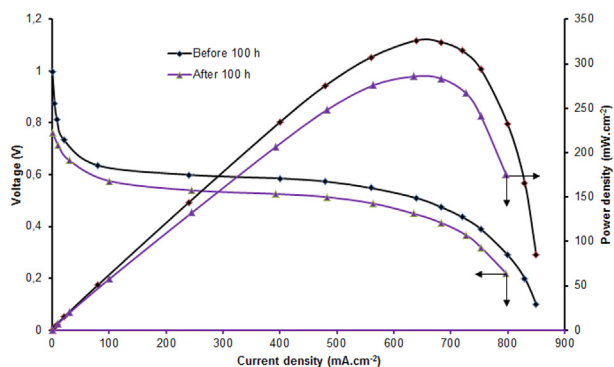


Fig. 1 – EIS performance of the MEAs at various conditions.



**Fig. 2 – OCV performance of the MEAs at various conditions.**



**Fig. 3 – Polarization curve of MEA before and after 100 h at 80 °C.**

The high temperature of the cell facilitated the decrease in the OCV during the first 3 h of operation, with possible continuations in the OCV decline at later time points. The measured OCV decline caused by the elevated temperatures was approximately 15%. Increasing temperatures can increase the reaction kinetics and the activity of the Pt, inducing an oxidation of the cathode Pt to form PtO or PtO<sub>2</sub> [24]. Platinum oxide formation can reduce the function of the Pt catalyst and decreasing the OCV. At OCV, the oxidation of the platinum is accelerated for stagnant oxygen at high

concentrations at the cathode [9]. In addition, a rise in temperature can cause membrane drying and cracking, opening the membrane pores and causing the hydrogen crossover and then will decrease the OCV. The relationship between temperature increase and decrease in OCV has been described by Zhang [25] through equation:

$$E_{theor}^{OCV} = 1.229 - 0.000846(T - 298.15) + \frac{RT}{4F} \ln [P_{O_2}(H_2)^2] \quad (1)$$

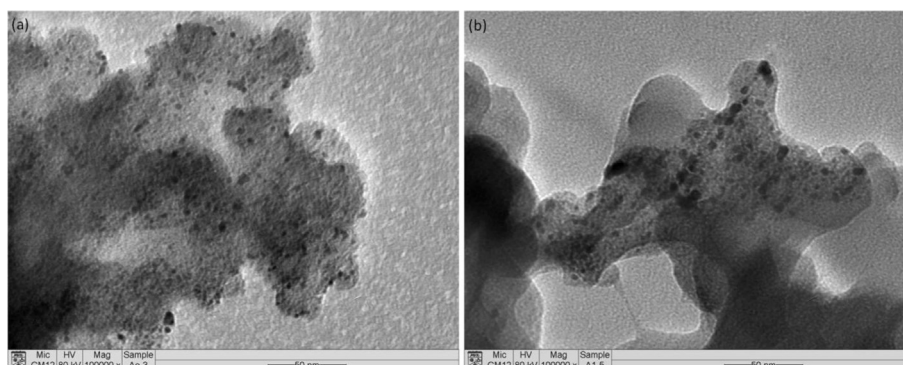
To maintain well-hydrated PFSA membranes, optimal working temperatures for a PEMFC usually range from 60 to 80 °C. Conventional PFSA membranes are subject to a critical breakdown at high temperatures resulting from glass transition temperatures of PFSA polymers at approximately 80 °C. To cope with drought membrane and maintain OCV at high operating temperatures, the addition of ultrapure water periodically into the humidifier has been done by Wang [22].

Backpressure can maintain OCV due to the influence of operation time, as compared with the decrease of the OCV operating at ambient conditions (without increasing the temperature and backpressure) and at 80°. Generally, backpressure can increase the PEMFC performance by increasing the partial pressures of the reactants, improving the gas permeability, enhancing the membrane conductivity, and maintaining the OCV with improvements in the theoretical voltage as shown also by Zhang [17]. Backpressure can also have negative effects (especially for high pressure), including high crossover, sealing problems, parasitic power losses and increased costs for compression [17].

MEA polarization curves before and after 100 h of operation is shown in Fig. 3. MEA performance decrease an average of 10% during the 100-h operation. The decreasing of MEA performance can be caused by the factor of agglomeration and oxidation of catalyst, drying of membrane and corrosion of carbon as described at Sections 3.3–3.5.

### TEM analysis

A TEM analysis can provide an indication of the MEA durability by examining the changes in the structure of the catalyst layer. Specific changes to be considered include the redistribution and relocation of the Pt resulting from migration, changes in the platinum particle size from agglomeration and changes in the structure of the membrane surface. The



**Fig. 4 – TEM images of the anode both (a) before and (b) after 100 h at 80 °C.**

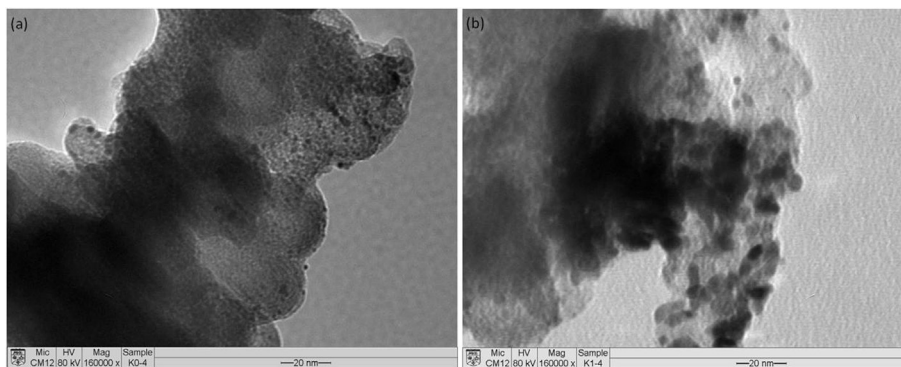


Fig. 5 – TEM images of the cathode both (a) before and (b) after 100 h at 80 °C.

influences of the operational time and temperature on the PEMFC stack are shown in Figs. 4 and 5.

As shown in Figs. 4(a) and 5(a), the Pt particles were evenly distributed in both the anode (3.77 nm average particle sizes) and the cathode (3.61 nm). With the Pt content in the cathode exceeding the amount in the anode ( $0.7 \text{ mg cm}^{-2}$ ), the distribution of the Pt appears in almost all parts of the cathode. After 100 h (Figs. 4(b) and 5(b)), both accumulation and agglomeration of the Pt particles were observed in several parts of the anode (4.40 nm average particle sizes) and the cathode (5.75 nm). The Pt agglomeration was caused by both dissolution and migration of the small Pt particles in the ionomer phase to redeposit on the large particles that were separated by a few nanometers, forming a well-dispersed catalyst. As an inherent

characteristic, Pt nano-particles have a tendency to minimize the high specific surface energy through agglomeration processes [5]. The Pt migration into the membrane considerably decreases both stability and conductivity [2]. Reactions of Pt with both oxygen and sulfur groups can enhance the particle growth in Pt/C catalysts by forming  $\text{PtO}_x$  and PtS. Caused by a reaction of the Pt catalyst with sulfur groups from the ionomer, the formation of PtS was studied, as shown in Fig. 9. The coarsening of the catalyst particle sizes after long-term PEMFC operation have been explained using several mechanisms, including dissolving the Pt particle in the ionomer phase with a redeposit on the surface of large particles, as well as an agglomeration of the Pt particles on the carbon support resulting from a minimization of the clusters Gibbs free energy [1].

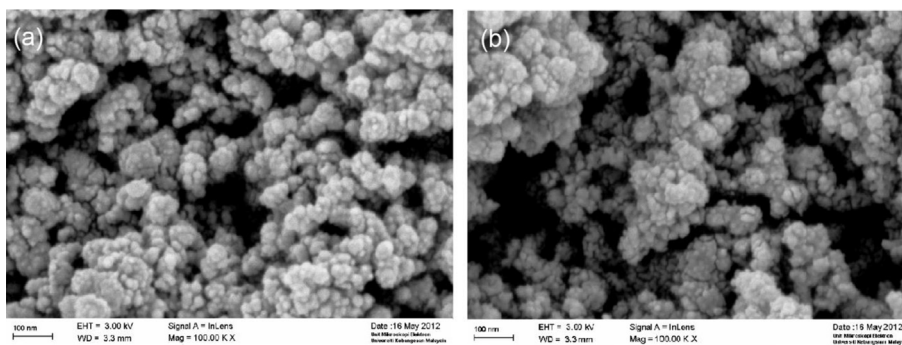


Fig. 6 – FESEM images of the cathode both (a) before and (b) after 100 h at 80 °C.

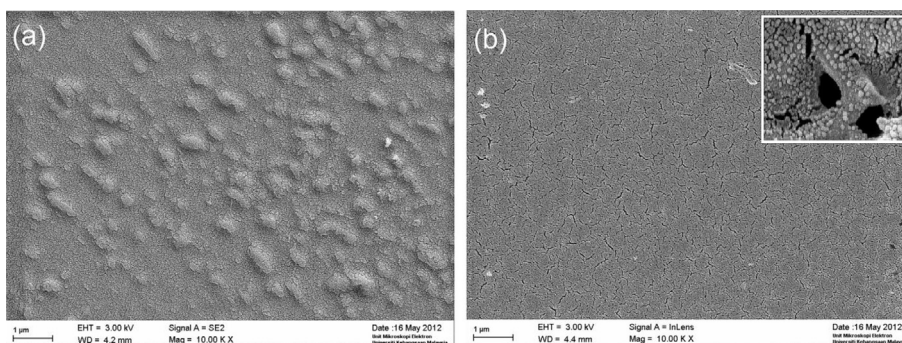


Fig. 7 – FESEM images of the membrane both (a) before and (b) after 100 h at 80 °C.

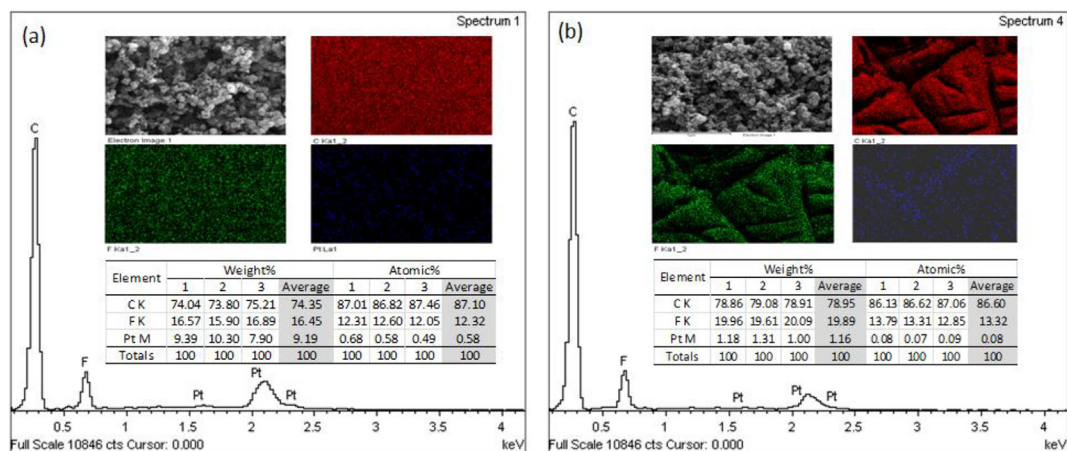


Fig. 8 – Images of the EDX–SEM and the mapping electrode both (a) before and (b) after 100 h at 80 °C.

### SEM analysis

As a characterization tool, SEM can be used to view the structures of surface or cross sectional morphology of either the MEA or the electrode. As shown in Fig. 6(b), the carbon corrosion at the cathode changed the structure of the electrode and the Pt distribution on the carbon support (Pt/C), as indicated by the reduction of the carbon substrate content and the bright color reduction from the Pt/C. The bright color in Fig. 6(a) is dominated by Pt/C, consistent with the work by Hwang [27] and our previous research [23]. Large amounts of Pt had moved or detached from the carbon support during the carbon corrosion process, becoming less active

electrochemically. Carbon corrosion can be caused by an oxidation of the carbon in aqueous acid electrolyte, as described by the equation [28–30]:



Carbon corrosion is one of the primary MEA degradation mechanisms that can influence the PEMFC performance during long term [31] or abnormal [32] operating conditions.

Both the duration of time and high operating temperatures affected the membrane degradation. The high temperature operation caused the membrane to undergo drying, as shown in Fig. 7(b). Both drying and cracking of the membrane caused

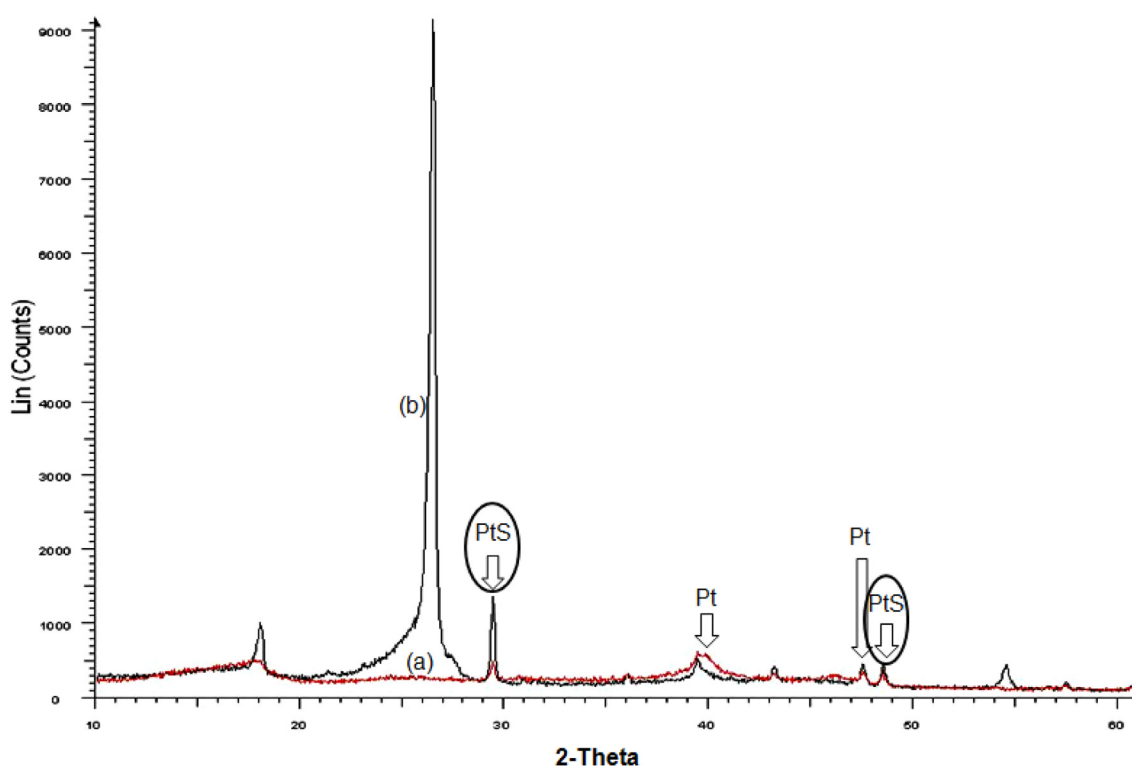


Fig. 9 – XRD patterns of anode almost same as cathode (a) before (b) after 100 h at 80 °C.

pore enlargement on almost all surfaces of the nafion membrane, as shown clearly in the picture inset. The formation of large pores can also increase the possibility of gas crossover.

The OCV treatment also allowed for the generation of peroxide radicals that can lead to the chemical decomposition of the membranes. The peroxide radicals originate from the hydrogen peroxide that can be generated from either an incomplete oxygen reduction or a reaction between hydrogen (through gas crossover) and oxygen [7].

The distribution of the electrode component content from the EDX–SEM measurements (As shown in Fig. 8), suggested that the content of carbon and F from both PTFE and nafion were dominant, with a relatively small amount of Pt. The Pt content decreased after 100 h at 80 °C (Fig. 8(b)).

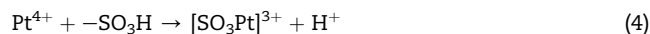
### XRD analysis

XRD analysis for the electrodes as a function of temperature and operating time are presented in Fig. 9.

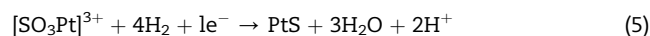
As shown in Fig. 9, the formation of PtS (as also indicated by Mamat [10]) after 100 h of fuel cell operational time was observed. The formation of PtS may have resulted from the dissolution of Pt particles during the testing process and generated by a reaction with  $-\text{SO}_3\text{H}$  groups from the ionomer nafion in the electrode [10]. The formation of PtS is obtained after several steps following the equation and initiated from the oxidation of Pt through the following reaction [8]:



The  $\text{H}^+$  ions may have originated from the oxidation reaction with the hydrogen gas that did not cross to the cathode. The  $\text{Pt}^{4+}$  ions may have dissolved, reacting with the  $-\text{SO}_3\text{H}$  of the nafion according to the following reactions:



$[\text{SO}_3\text{Pt}]^{3+}$  can be reduced by  $\text{H}_2$  to form PtS [10]:



The reactions of the  $-\text{SO}_3\text{H}$  groups with Pt may have decreased the ionic conductivity at the interface of the CL and the membrane, increasing the ohmic resistances (especially compared with the initial conditions). Increasing ohmic resistances were also evident from an analysis of the EIS (Fig. 1). In addition, the active sites of the catalysts decreased with the formation of PtS.

The effects of operating time and temperature on the membranes were also determined, as shown in Fig. 10.

The characteristic broad peaks of nafion at  $2\theta \sim 16^\circ$  and  $2\theta \sim 17.5^\circ$  (Fig. 10) were attributed to the amorphous and crystallinity scattering of the nafion main chains, respectively [33–36]. Nafion has a semi-crystalline structure [36]. After 100 h at 80 °C, the peaks of the nafion decreased, as indicated by the disappearance of the sharp peak at  $2\theta \sim 17.5^\circ$ , suggesting a decrease in the crystallinity of the nafion. Both Pt and PtS were observed at the surface of the membrane. As the membrane for the XRD analysis was obtained from the MEA (before and after the treatment), both Pt and PtS peaks appeared in the XRD patterns.

### Conclusions

A PEMFC operating at 80 °C for 100 h exhibited considerable performance degradation with c.a. 20% decrease in the OCV, compared with the measurements obtained from operations at ambient temperature (<15% OCV drop). These reductions in

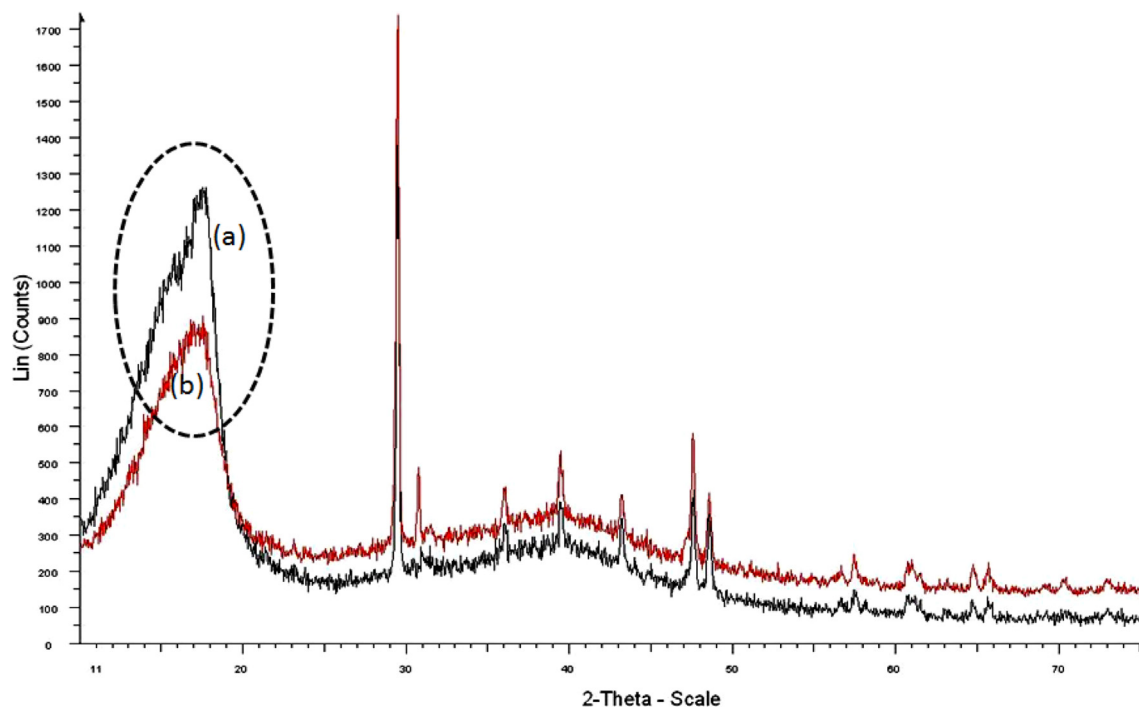


Fig. 10 – XRD patterns of membrane (a) before (b) after 100 h at 80 °C.

the OCV may have resulted from the dissolution and agglomeration of the catalyst particles, causing carbon corrosion, reduction in the active surface area and cracking of membrane. The PEMFC operating at 10 psi at ambient temperature had improved conductivity with decreased performance degradation.

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