



Short communication

The effects of excess phosphoric acid in a Polybenzimidazole-based high temperature proton exchange membrane fuel cell

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ABSTRACT

A series of experiments are conducted in order to investigate the performance of a proton exchange membrane (PEM) fuel cell using a commercially available polybenzimidazole (PBI)-based high temperature membrane. During the study a drastic degradation in performance is observed over time and a significant amount of solid material built-up is found in the flow field plate and the membrane-electrode assembly (MEA). The built-up material is examined by the use of a Scanning Electron Microscope (SEM). Further elemental analysis using Energy Dispersive X-ray Spectroscopy (EDS) finds that the built-up material contains large amount of phosphorus, thus relating it with the excess phosphoric acid found in the MEA. Additional experimental studies show that the built-up material is caused by the excess acid solution in the MEA, and when the excess phosphoric acid is removed from the MEA the fuel cell performance improves significantly and becomes very stable.

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1. Introduction

High temperature PEM (HTPEM) fuel cells based on phosphoric acid doped polybenzimidazole (PBI) membrane have received great attention from the research community due to their advantages of high CO tolerance and better reaction kinetics. Besides, water management is greatly simplified due to the lack of liquid water. Yet the durability of HTPEM fuel cells based on PBI membranes is still low.

Qi et al. [1] conducted a 350 h durability test and found that operating the fuel cell at open circuit voltage (OCV) for long period of time caused OCV to decline and performance loss. This decline in performance was attributed to the increase of the Pt crystallite size as X-ray diffraction showed. On the other hand, Seland [2] reported that fuel cross-over was the main reason for the low OCV. Tang et al. [3] found that the degradation rate increases as the temperature increases. AC impedance confirmed that the drop in performance was caused by the increase in membrane and kinetic-charge-transfer resistances. Schmidt [4] reported that the evaporation of phosphoric acid did not contribute significantly to HTPEM degradation and 55% of this degradation was a result of mass transport over-potentials, 30% caused by reduced oxygen reduction kinetics and 15% due to increase in cell ohmic resistance. In a 500 h life test, Hu et al. [5] concluded that HTPEM degradation was caused by catalyst sintering which results in decrease of electrochemical

surface area. The sintering rate was found to be faster in the cathode than in the anode due to the higher water vapor pressure, speeding up the agglomeration of Pt/C particles in the cathode [6].

In a preliminary experimental study performed by the authors [7], it was observed that when the MEA was removed from the manufacturer's package, there were a large amount of acid droplets in the GDL. If this excess acid was not removed, the performance of the cell decreased rapidly over time. When the cell was disassembled after 30 h of operation, a large amount of solid material build-up was observed in the flow channels.

The objective of this study is to determine the cause of this material build-up and to develop methodologies to eliminate this problem.

2. Experimental studies

In this study commercially available 5-layer, PBI-based, phosphoric acid doped high temperature MEAs were used. Pt based catalysts were used on both the anode and cathode, with a total catalyst loading of 1.7 mg cm^{-2} . The MEAs had an active area of 45 cm^2 and the fuel cell hardware used was designed and manufactured in house. The fuel cell compression was controlled by a series of eight tie-rods, however, gaskets were used to ensure uniform and proper MEA/GDL compression. These gaskets were supplied by the MEA manufacturer in order to prevent over-compression of the MEA/GDL and hence preventing damage to MEA. In this study experiments were conducted with hydrogen and air. The experiments were conducted on a test station supplied by Fuel Cell Technologies, Inc. This station allowed for the humidifiers to be

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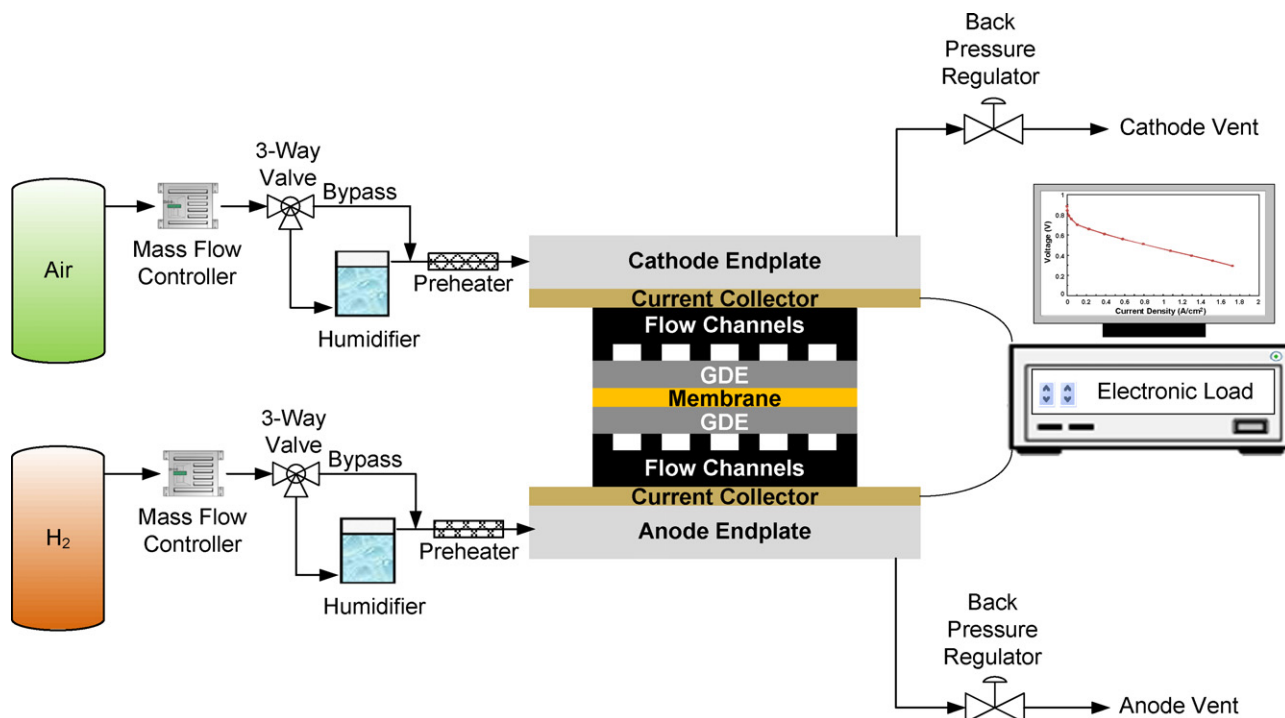


Fig. 1. Schematic of the experimental system.

bypassed such that the hydrogen and air were supplied completely dry. Fig. 1 shows a schematic of the experimental system.

A series of experimental studies were conducted in a temperature range from 120 °C to 175 °C with and without removing the excess phosphoric acid found in the fresh MEAs and polarization curves were obtained. Fuel cell performance degradations were also monitored for an extended period of time at constant current density of 200 mA cm⁻². The built-up material found in the flow fields and the MEA was examined by the use of a Scanning Electron Microscope (SEM). The elemental compositions of the material were also analyzed by Energy Dispersive X-ray Spectroscopy (EDS). The samples for the SEM and EDS are prepared in a vacuum chamber using a palladium coating.

3. Results and discussion

3.1. Performance degradation and material build-up

As mentioned above, when the MEA was removed from the manufacturer's package, there were a large amount of acid droplets in the GDL. In the first set of experiments, this excess acid was not removed and the cell performance decreased drastically, as shown in the polarization plots in Fig. 2. It can be seen from Fig. 2 that the performance of the cell decreases significantly over a short period of time. Due to the drastic and continued decrease in cell performance, the experiments were stopped and the cell was disassembled. Careful examination of the flow field plates revealed that a significant amount of built-up solid material was observed. A photograph of the flow field plate with the built-up material is shown in Fig. 3.

The material build-up that was observed in the plate was carefully scrapped and removed. Next, a sample of the material was prepared and examined using SEM and an SEM image of the material is shown in Fig. 4. In order to further investigate the causes of the performance degradation, the MEA was cut and a sample of the MEA placed in the SEM. The images showed a large amount of material build-up around the membrane and in the gas diffusion layer (GDL) as shown in Fig. 5. It can be seen that the material built-up

was found not only in the flow field but in the MEA as well. Further analysis is needed in order to determine the cause of the material build-up.

3.2. Analysis of the built-up material

In order to determine if the material in the flow field was the same material as that found in the MEA/GDL EDS analyses were performed. The result of EDS analyses of the built-up material in the flow field is shown in Fig. 6. The analyses of the material found in the flow field showed large peaks of carbon, oxygen and phosphorus. The palladium peak is due to the coating used to prepare the sample. Trace amounts of iron and nickel were also found.

The result of EDS analyses of the built-up material in the GDL near the catalyst layer is shown in Fig. 7. It can be seen from

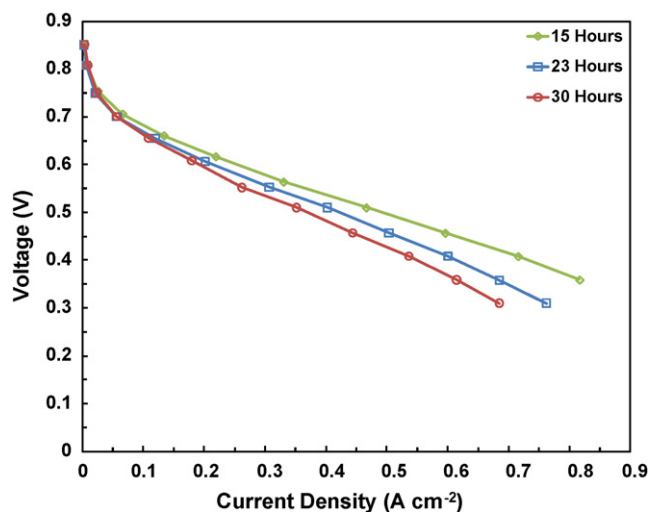


Fig. 2. Polarization curves show drastic performance degradation over 30 h. Cell temperature is 160 °C. Reactant stoichiometries: H₂ 1.2 and air 2.

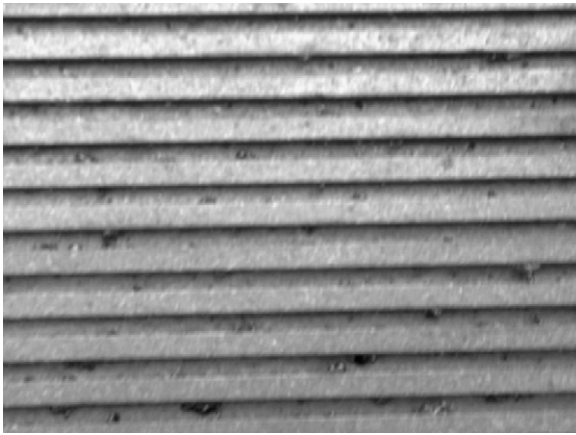


Fig. 3. A photograph of the flow field plate with the built-up material after 30 h of operation.

Figs. 6 and 7 that the material found in the flow field has almost the same elemental compositions as the material found near the catalyst layer. The main peaks are carbon and phosphorus with trace amounts of other elements. Furthermore, the material near the catalyst layer shows a platinum peak which is to be expected. The solid material found in both contains large amount of phosphorus.

Since large amount of excess acid solution was found in fresh MEAs and the built-up material contains large amount of phosphorus, it was believed that there was a connection between this excess acid solution and the material build-up in the flow field and near the catalyst.

3.3. Pre-treatment of the MEA

Based on the hypothesis that the excess acid solution found in the MEAs is the cause for the material build-up and that the material build-up was, in turn, causing the performance to degrade, a technique was developed to remove all of the excess acid solution before use. It was necessary to not only remove the excess acid from the surface of the GDL but also from underneath the GDL near the membrane. The process of pre-treatment of the MEA can be summarized as follows. (a) Remove the excess liquid acid by dabbing the GDL with paper (a delicate task wiper); (b) blow pressurized nitrogen gas on the GDL for about 30 s to drive the acid in the GDL pores to its surface; (c) place a piece of the delicate task wiper on

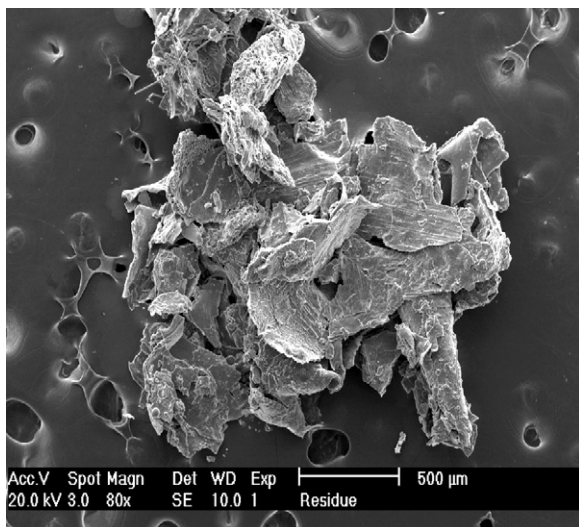


Fig. 4. An SEM image of the built-up material in flow field after 30 h of operation.

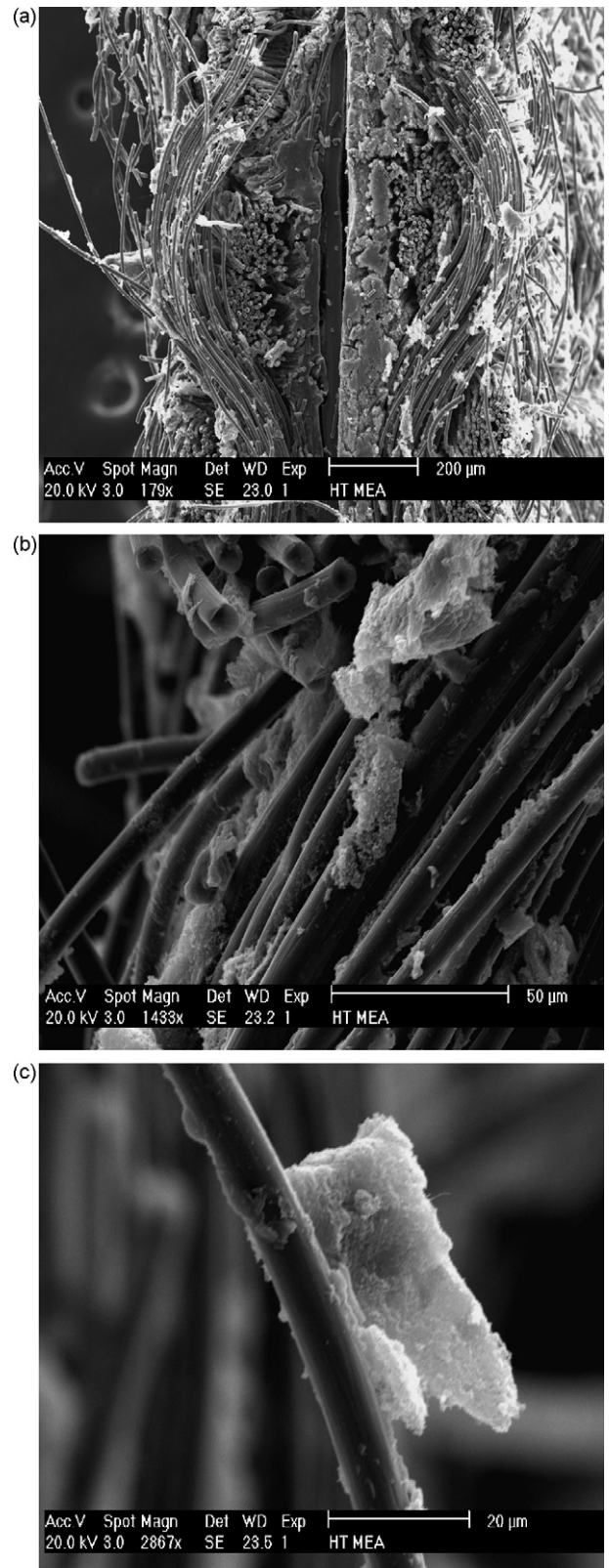


Fig. 5. SEM images of the solid material found in the MEA after 30 h of operation. (a) Cross-section of the MEA. (b) 1433 \times . (c) 2867 \times .

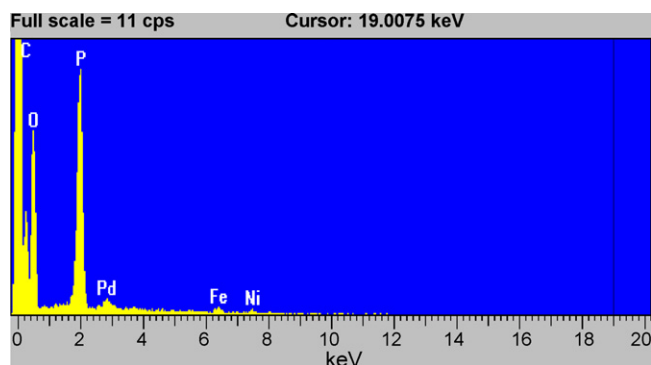


Fig. 6. EDS analysis of the material found in the flow field.

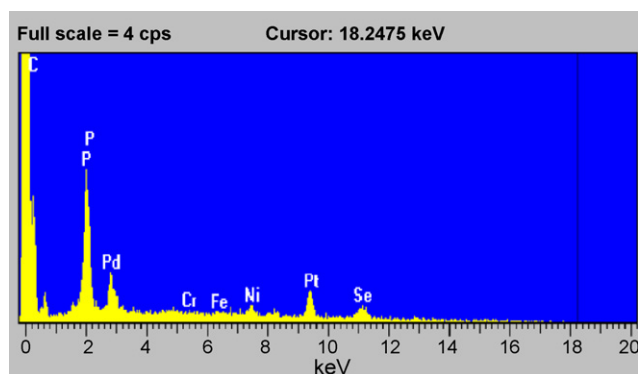


Fig. 7. EDS analysis of the material found in the GDL near the catalyst layer.

the surface of the GDL and apply a load (about 1.94 kg) to absorb all acid droplets. Repeat steps (b) and (c) until no further acid droplets are visible on the GDL surface.

Using a new MEA with all the excess acid removed, the experimental results show that the cell performance was very stable. A comparison of the cell voltage variations of the pre-treated MEA and the untreated MEA is shown in Fig. 8. The test was performed at a constant current density of 200 mA cm^{-2} . It is clear from Fig. 8 that when the excess acid solution is removed the performance is very stable and when the acid is not removed the performance degrades rapidly. Furthermore when the excess acid solution was completely removed no build-up material was observed in the flow field. The

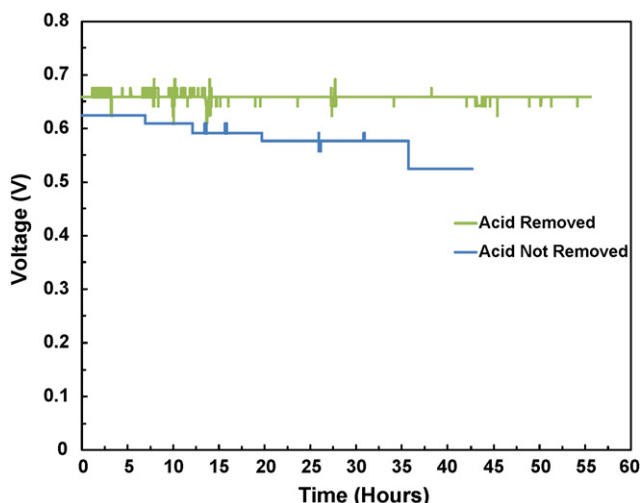


Fig. 8. Comparison of the cell voltages between the pre-treated and the untreated MEAs.

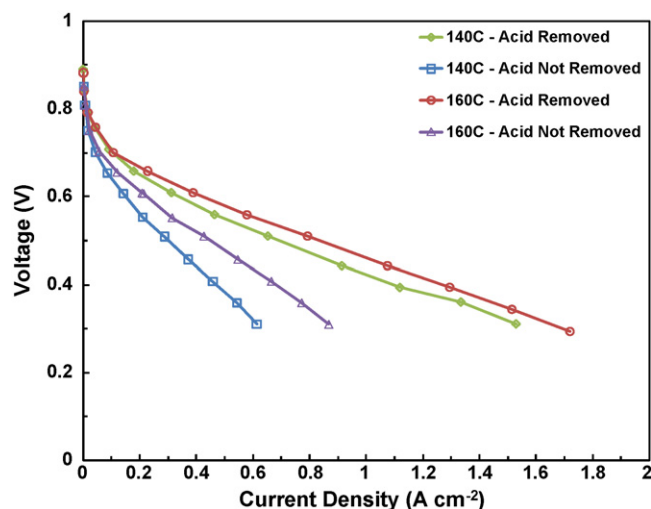


Fig. 9. Results displaying the effect of temperature and acid removal on the HTPEM MEA. Reactant stoichiometries: H_2 1.2 and air 2.

hypothesis that the excess acid was the cause of the material build-up and the performance degradation is proved correct.

Some additional experiments were conducted and Fig. 9 shows a comparison between performance at different cell temperatures when the acid solution was removed and when it was not removed. It is clear from Figs. 8 and 9 that when the acid solution is removed there is a considerable increase, not only in stability over time but overall performance as well.

4. Conclusion

In this experimental study, the cause for drastic degradation in cell performances of a high temperature PEM fuel cell with commercially available phosphoric acid doped PBI-based MEAs was studied and a technique to eliminate/mitigate the performance degradation was developed. Experimental results showed that the technique developed was very effective.

- Drastic performance degradations were observed in PEM fuel cells using a commercially available phosphoric acid doped PBI-based MEA.
- The degradations were found to be caused by a significant amount of solid material built-up in the flow field plate and the MEA.
- The built-up material was found to be caused by the excess acid in the MEA.
- A technique of pre-treatment of the MEA to remove the excess acid was developed and found to be very effective.

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