

Influence of micro-porous layer and operating conditions on the fluoride release rate and degradation of PEMFC membrane electrode assemblies

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Abstract

In this study, the influence of micro-porous layers (MPL) on polymer electrolyte membrane fuel cell (PEMFC) durability was investigated. Two fuel cells were built, one with a micro-porous layer on the anode side, and a second cell with MPL on both sides. Experiments were conducted by varying operational parameters such as current density, reactant stoichiometry, and inlet relative humidity. Fuel cell degradation was evaluated by measuring fluoride release rates. The largest factor determining fluoride release rate was found to be the presence of MPL; the cell with MPLs on both sides exhibited significantly reduced fluoride release rates compared to that of cell with one MPL. Increasing the current density also reduced the fluoride release rate for cells with only one MPL whereas there was only a moderate effect on cells with two MPLs. Microscopy analysis showed small but significant changes in ionomer layer thickness. Polarization measurements indicated that there was little change in the performance for both cells over the test period.

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1. Introduction

Enhancing the durability of fuel cells is one of the key research and development goals currently being pursued to promote wide-scale commercialization of polymer electrolyte membrane fuel cell (PEMFC) technology. The membrane electrode assembly (MEA), and, in particular, the electrolyte membrane is considered to be one of the least durable components of a PEMFC. Accordingly, further understanding of how the MEA and the membrane degrade is much needed. The degradation process for fuel cells and related sub-components can be broadly summarized into causes, modes, and effects [1]. The causes resulting in the failure of polymer electrolyte membranes range from manufacturing and design to factors

such as over-compression, MEA sub-component material, and electrolyte membrane thickness variability across the cell [2]. Material property effects such as electrolyte membrane swelling [3,4], and operating conditions such as sub-zero temperatures and extreme conditions of feed stream relative humidity [5–7] also cause degradation. Each cause results in a failure through a specific degradation mode, which can be classified as either mechanical, chemical, or thermal mode [1,2,8].

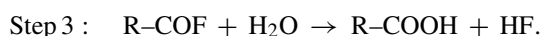
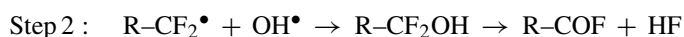
In recent studies by co-authors [9–11], it was observed that the presence of micro-porous layer (MPL) led to a remarkable improvement in the durability of fuel cells. A MPL is a composite of carbon particles and a hydrophobic agent that is coated on one side of the conventional gas diffusion media and can be used on one or both of the anode or cathode electrodes. Without conducting an analysis of the degradation, it was hypothesized that the MPL acted as a protective layer that prevented penetration of sharp carbon fibers into the membranes and, thereby, minimized or prevented mechanical damage of the membrane. Another possibility, which is a topic of this study,

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is that the MPL itself affects the chemical degradation of the MEA.

Chemical degradation of the ionomer membrane generally leads to MEA failure by compromising the integrity of the membrane. In the case of perfluorosulfonic ionomer (PFSI) membranes such as NafionTM, it has been proposed that carboxylic acid end groups left over from the manufacturing process may be susceptible to attack by radical species [12] generated during fuel cell reactions. In particular, hydroxyl radicals are thought to be formed by the decay of hydrogen peroxide which itself is generated within the fuel cell. There is yet some debate as to whether peroxide is predominantly formed by hydrogen crossover, oxygen crossover or as an intermediate in the oxygen reduction reaction. Regardless of the exact mechanism for formation of H₂O₂, its existence in membrane leads to radical generation facilitating the degradation of the ionomer membrane [2,12–15] whose mechanism has been proposed as follows:



As shown above, hydrogen fluoride (HF) is a product of the membrane degradation reaction and may exit the fuel cell in the effluent water. In fact, fluoride ion release rates are often used as a measure of the membrane degradation rate.

Several factors are known to influence chemical degradation and include current density, relative humidity of the inlet streams, and cell temperature. OCV operation is thought to increase the rate of chemical degradation as a result of higher hydrogen and/or oxygen crossover [16–19]. In recent studies, it has been suggested that when an MEA is subjected to extended operation at OCV a platinum band may form in the membrane from an electrochemical deposition process and that degradation will occur within and near the band location [20–22]. A study by Pierpont et al. [23] examined the effect of three load profiles on the degradation of 3 MTM MEAs and reported that the initial fluoride release was inversely correlated to MEA lifetime under the accelerated test conditions. They also reported that high relative humidity increased membrane durability but low average currents led to decrease in MEA lifetime.

There is a general consensus regarding the mechanism of chemical degradation of perfluorosulfonic ionomers leading to the formation of hydrogen fluoride. However, the extent to which the operating conditions such the inlet relative humidity and current density influence the ionomer degradation or affect the fluoride release rate is not completely understood. Furthermore, the role of MPL in enhancing fuel cell durability has not been examined in the context of membrane degradation.

As such, the primary objective of this study was to investigate the influence of MPL on the fluoride release rate, which is a measure of chemical degradation of ionomer membrane. To this end, two fuel cells, each with an MPL on the anode side but one with an additional MPL on the cathode, were studied. The influence of current densities was examined by measuring fluoride release rate at three current densities of

300 mA cm⁻², 500 mA cm⁻² and 700 mA cm⁻². The effect of relative humidity was examined by conducting two sets of experiments wherein the anode/cathode relative humidity were maintained at 100%/60% and 60%/100%, respectively. Changes in ionomer membrane morphology were also investigated via scanning electron microscopy of MEAs.

2. Experimental

2.1. Materials and cell construction

A detailed description of the specific cell configuration and experimental test set-up is presented elsewhere [9–11]. Briefly, the cell had a 100 cm² active area using a catalyst coated membrane (CCM) from Ion Power Inc. The CCM for testing was used as-received without any additional processing steps. Two types of porous transport layer (PTL), commonly known as gas diffusion layers (GDL), were investigated—SGL 10BA and SGL 10BB carbon papers (SGL Carbon Group, Germany). Both SGL 10BA and 10BB carbon papers contain 5 wt% polytetrafluoroethylene (PTFE). The SGL 10BB carbon paper is essentially SGL BA paper with an additional functional layer – a micro-porous layer (MPL) – on one face. The PTFE content of the MPL was 23%. The thicknesses of the 10BA and 10BB carbon papers were 0.37 mm and 0.41 mm, respectively. Thus, it can be inferred that the micro-porous layer is 40 μm thick. The PTLs and the MEAs from the same batch were used in all the tests to minimize variability in the physical and chemical characteristics of the fuel cell components.

Two cell configurations were tested at different current densities, cathode stoichiometries, and cathode/anode relative humidity. The first cell configuration, herein referred to as Cell 1, used a PTL with an MPL on the anode side but no MPL on the cathode side. The second configuration, Cell 2, used PTL with MPL on both anode and cathode sides. For each cell, the cathode stoichiometry was either 2 or 3 and anode/cathode (A/C) relative humidity was adjusted to 100%/60% or 60%/100%. At each level of stoichiometry and relative humidity, the fluoride release rate measurements were made at current densities of 300 mA cm⁻², 500 mA cm⁻², and 700 mA cm⁻². The cell builds and test conditions are summarized in Table 1.

For each cell configuration, at each specific operating condition (A/C relative humidity, A/C stoichiometric ratio, and current density), the effluent water from the anode and cathode streams were collected and stored in polyethylene bottles for fluoride analysis.

2.2. Fluoride ion release

Fluoride ion analysis was carried out with a Dionex ED40 electrochemical detector working with a Dionex GP40 gradient pump. The minimum detectable fluoride ion concentration is 0.011 ppm F⁻. The total time spent and the volume of water collected at each condition was used to determine effluent water flow rates which were then used with fluoride concentration measurements to determine the fluoride release rate.

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