Journal of Power Sources 304 (2016) 64–73

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Proton exchange membrane fuel cell degradation: A parametric analysis using Computational Fluid Dynamics

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HIGHLIGHTS

- Numerical investigation of PEM fuel cell degradation using CFD.
- A comprehensive parametric analysis on PEM fuel cell degradation.
- Numerical estimation of overall degradation using experimental data.
- About 17% performance loss with a degraded PEM fuel cell in two years.

ARTICLE INFO

Article history:
Received 1 July 2015
Received in revised form 8 October 2015
Accepted 9 November 2015
Available online 21 November 2015

Keywords:
PEM fuel cell degradation
Computational Fluid Dynamics
Parametric analysis

ABSTRACT

A Polymer Electrolyte Membrane (PEM) fuel cell is numerically investigated both as fresh and as degraded with the help of observed degradation patterns reported in the literature. The fresh fuel cell model is validated and verified with the data from the literature. Modifying the model by varying the parameters affected by degradation, a degraded PEM fuel cell model is created. The degraded fuel cell is parametrically analyzed by using a commercial Computational Fluid Dynamics (CFD) software. The investigated parameters are the membrane equivalent weight, the Catalyst Layer (CL) porosity and viscous resistance, the Gas Diffusion Layer (GDL) porosity and viscous resistance, and the bipolar plate contact resistance. It is shown for the first time that PEM fuel cell overall degradation can be numerically estimated by combining experimental data from degraded individual components. By comparing the simulation results for the fresh and the degraded PEM fuel cells for two years of operation, it is concluded that the effects of overall degradation on cell potential is significant – estimated to be 17% around the operating point of the fuel cell at 0.95 V open circuit voltage and 70 °C operating temperature.

1. Introduction

Performance of a Polymer Electrolyte Membrane (PEM) fuel cell degrades over time mainly due to undesired reactions and corrosive environment related to load cycling between low and high cell voltages, operation at low humidity and high temperature, and fluctuations in temperature and humidity (as discussed in Ref. [1], among others). Robustness of a PEM fuel cell can be defined as the capability of the PEM fuel cell to resist against permanent degradation in performance. Robustness includes reliability, stability and durability of the fuel cell, and has been extensively discussed in the literature [2–8]. Reliability is mainly related to the quality of Membrane Electrode Assembly (MEA) of the fuel cell, and it can be improved by improving the manufacturing processes. Stability is related to recovery from MEA performance loss that may happen during continuous operation due to operating conditions and reversible changes in materials. Currently, most of the problems related to reliability and stability of PEM fuel cells have been solved at a high cost. Accordingly, cost and durability stands as the two key issues for commercialization of PEM fuel cells. Performance degradation over time needs to be further investigated for both estimating and improving durability.

In the current literature, e.g. Ref. [9], attention is mainly focused on investigating the individual factors affecting PEM fuel cell durability to improve the lifetime of fuel cells without increasing the cost or decreasing the performance. Wu et al. [10] stated that durability of the fuel cell is negatively affected by degradation mechanisms. Decrease in durability can be related to non-operative natural degradation of fuel cells that may occur during storage and recoverable or unrecoverable degradation of fuel cells that may occur during their operation.

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http://dx.doi.org/10.1016/j.jpowsour.2015.11.042
0378-7753/

Recently, different aspects of PEM fuel cell degradation have been investigated by considering natural degradation and recoverable degradation phenomena. Among others, Zhan et al. [11] investigated natural degradation and stimulated recovery of PEM fuel cells by analyzing performance degradation of a PEM fuel cell stack over a storage-duration of 40,000 h. It was concluded that natural degradation of PEM fuel cells is primarily caused by dehydration of the membrane. Wang et al. [12] studied recoverable degradation of PEM fuel cells under various operating conditions, mainly concentrating on the effects of relative humidity under drive cycle. It was reported that, after 5 h of operation time, the cell performance was decreased for the both anode and cathode sides. It was observed that the performance loss was mostly recovered after one night rest at high humidity operating conditions. Zhang et al. [13] conducted a study on the degradation mechanisms of catalyst layers of PEM fuel cells and emphasized that recoverable losses are associated with the reduction of Platinum Oxide inside the catalyst layer.

Unrecoverable fuel cell degradation occurring over time has been related to permanent changes in properties of individual fuel cell components that have been reported in various studies in the literature. Each of these experimental studies concentrated on an individual component and investigated the changes in the parameters of that component. In order to estimate the overall degradation, however, these changes need to be considered together. This can only be done with a numerical simulation because it is impossible to measure all of these parameters at the same time in a single experiment.

In this study, a fresh PEM fuel cell is numerically modeled; the model is validated; the validated model is modified with degraded properties; and then the effects of the degraded properties on the performance of the fuel cell parametrically investigated with a set of simulations. The investigated parameters are the membrane equivalent weight, the Catalyst Layer (CL) porosity and viscous resistance, the Gas Diffusion Layer (GDL) porosity and viscous resistance, and the bipolar plate contact resistance.

2. PEM fuel cell degradation and related fuel cell parameters

In the literature, it is noted that it may be hard to evaluate long-term performance and durability of PEM fuel cells since not all degradation mechanisms of PEM fuel cell components are completely understood (Schmittinger and Vahidi [14]); nevertheless, the observed degradation patterns of various components may give a near complete view and the already available data can be used for obtaining degradation estimates.

In the following subsections, degradation mechanisms of PEM fuel cells are discussed in detail for each fuel cell component.

2.1. Membrane degradation

According to Zhang et al. [15], membrane degradation mainly depends on operating conditions of the PEM fuel cell: temperature, humidity, freeze-thaw cycle, transient operation and start-up/shut-down cycle.

Mechanical degradation, thermal degradation and chemical degradation are the three main degradation mechanisms of the membrane of a fuel cell. Tang et al. [16] stated that the main reason of the mechanical degradation and failure of the membrane is repeating dimensional changes and stress cycles. Dimensional changes results from thermal changes and stress cycles from sequential start-up and shut-down processes. On the cathode side, membrane is exposed to a severely oxidizing environment, whereas on the anode side, membrane is exposed to a chemically reducing environment. Furthermore, peroxy and hydroperoxy radicals, which are formed inside the fuel cell, attack to the membrane. Collier et al. [17] stated that these attacks mainly results in chemical degradation of the membrane. According to Lie et al. [18], it will possible to encounter with performance loss and serious failures due to membrane thinning and pinhole formation when chemical degradation is combined with mechanical and thermal degradation. Thermal degradation mainly caused by thermal stresses and degradation of the membrane usually speeds up with the increasing temperature.

The membrane experiences hydration and temperature variations when fuel cell operates in fluctuating operating conditions. In contrast, when fuel cell operates in on-off operating condition with its maximum available capacity, fuel cell degradation from hygro-thermal fatigue loading gets reduced [19].

Additionally, as the PEM fuel cell operates, the carbon particles and Polytetrafluoroethylene (PTFE) of the cell are exposed to chemical attack and electrochemical oxidation. The loss of carbon particles and PTFE leads to changes in physical characteristics of the fuel cell components. As a result, the performance of the fuel cell decreases.

Performance of a PEM fuel cell is directly related to the membrane. The membrane is modeled by the equations presented below.

The membrane phase conductivity is modeled using the following equation [20].

$$\sigma_{mem} = \beta(0.514\lambda - 0.326)^{\omega} e^{1268\left(\frac{1}{303} - \frac{1}{T_{cell}}\right)} \quad (1)$$

where λ designates the water content of the membrane and defined by Eqs. (2) and (3), which is obtained using the correlation suggested by Springer et al. [20]. Here, two model constants, ω and β are introduced by ANSYS Fluent for generality [21].

$$\lambda = 0.043 + 17.18a - 39.85a^2 + 36a^3 \quad (a < 1) \quad (2)$$

$$\lambda = 14 + 1.4(a - 1) \quad (a > 1) \quad (3)$$

where a is the water activity that is given by the following equation:

$$a = \frac{P_{wv}}{P_{sat}} + 2s \quad (4)$$

where s is the water saturation ratio or the water volume fraction [22].

From Eqs. (1)–(4), it is observed that the membrane performance is directly related with the water content and the water activity. However, degradation of the membrane can be directly observed from one of the physical characteristics of the membrane, which is called the equivalent weight. Equivalent weight is a parameter of the back diffusion flux equation given by the following equation:

$$J_w^{diff} = -\frac{\rho_m}{M_m} M_{h_2o} D_l \nabla\lambda \quad (5)$$

where ρ_m and M_m are the density and the equivalent weight of the membrane. M_m is valid for a dry membrane.

Equivalent weight is the inverse of Ion-Exchange Capacity (IEC). IEC is given in units of moles of titratable protons per gram of dry ionomer [23]. Equivalent weight changes as a function of degradation time and can be taken as 1132 kg/kmol for a degraded membrane [24], whereas a fresh membrane has an equivalent weight value of 1100 kg/kmol (Nafion 1100 series is selected as the membrane).