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Effect of dynamic operation on chemical degradation of a polymer electrolyte membrane fuel cell

Minjae Jung*, Keith A. Williams

Department of Mechanical Engineering, 290 Hardaway Hall, Box 870276, The University of Alabama, Tuscaloosa, AL 35487-0276, United States

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ABSTRACT

Dynamic operation is known as one of the factors for accelerating chemical degradation of the polymer electrolyte membrane in a polymer electrolyte membrane fuel cell (PEMFC). However, little effort has been made dealing with the quantification of the degradation process. In this investigation, cyclic current operation is carried out on a fuel cell system, and the frequency effect of cyclic operation on chemical degradation is investigated. The dynamic behavior of a fuel cell system is analyzed first with the modified Randles model, where the charge double layer is modeled by three components; a charge transfer resistance (R_{ct}), and two RC cells for the Warburg impedance. After calculating each parameter value through exponential curve fitting, the dynamic behaviors of the three components are simulated using MATLAB Simulink®. Fluoride release as a function of the frequency of cyclic operation is evaluated by measuring the concentration of fluoride ion in effluent from a fuel cell exhaust. The frequency effect on chemical degradation is explained by comparing the simulated results and the fluoride release results. Two possible reasons for the accelerated degradation at cyclic operation are also suggested.

1. Introduction

The proton exchange membrane fuel cell (PEMFC) has been considered a candidate for future vehicular and stationary applications and has the advantages of high current density, high fuel efficiency, and low temperature operation, although technical problems remain. One of the main issues limiting the application of a PEMFC is membrane degradation which is mainly caused by three factors, mechanical, thermal and chemical degradation [1]. If it is assumed that sufficient temperature control of a fuel cell system can be realized, such that thermal degradation may be neglected, mechanical degradation is thought to be the main cause of early failure [1], and chemical degradation usually results in a significant drop in the performance before the failure [2].

A number of previous research efforts have shown that the chemical degradation is mainly attributed to chemical attack of highly reactive oxygen radicals formed in the fuel cell [1–3]. Although the mechanisms describing how these radicals form and attack the membrane are still unclear, it is now generally considered that the formation of hydrogen peroxide (H_2O_2) plays an important role in the chemical attack. The formation of hydrogen peroxide and reactive oxygen radicals is a multi-step process including oxygen gas crossover and is shown below in Fig. 1 [1,3]. Hydrogen fluoride (HF) is a direct product of the radical attack on the membrane. As such, the rate of chemical degradation can be evaluated by measuring the fluoride content of the effluent from the fuel cell exhaust [4]. As fluoride release continues, the membrane thickness decreases, which is called 'membrane thinning' [4], and eventually, leads to the generation of pin-holes which further degrade the system by allowing hydrogen to pass directly through the membrane and "burn" with oxygen on the platinum catalyst at the cathode side of the fuel cell.

There are several factors that may accelerate the chemical degradation. Severe degradation due to operation with low humidification and operation with an open circuit voltage, but no net current has been reported and investigated by multiple researchers [5–7]. A great deal of research effort has been focused on determining the relation between those factors and membrane degradation, but those relations have not yet been fully clarified. Liu and Case reported that dynamic operation also accelerated the chemical degradation by showing that there is about a one order difference in fluoride release between cyclic operation and constant operation of a PEMFC [8]. However, there has been little further research on the effect of dynamic operation on chemical degradation.

The goal of this research is an examination of the influence of dynamic operation on accelerated degradation of a fuel cell system. The PEMFC used in this research was a Ballard Nexa 1.2 kW fuel cell system, and dynamic operation was realized using a transistor switch controlled by an ON and OFF pulse signal as shown in Fig. 2. In this figure, R_{PL} is a parasitic load resistor composed of the

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* Corresponding author. Tel.: +82 10 5607 1130; fax: +82 31 8056 5518.
E-mail address: aidenian06@gmail.com (M. Jung).

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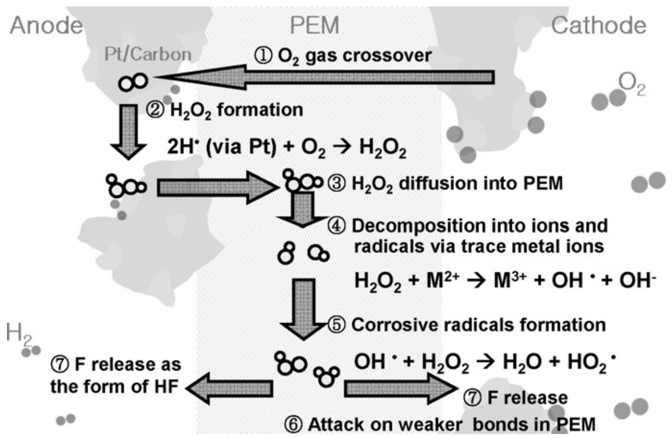

Fig. 1. Mechanism of chemical degradation of a PEM membrane.

fuel cell control system and balance of plant (cooling fan, compressor, solenoid valves), and R_L is an exterior load resistor. Different operation conditions were modified by changing the frequency of the pulse signal. For the sake of this work, the dynamic behavior of PEMFC was first investigated. The Nexa system was modeled by a simplified Randles model for which parameters were evaluated using curve-fits and the dynamic behavior of the fuel cell system as the pulse input was varied was simulated using MATLAB software. The rate of chemical degradation during operation with different frequencies was determined by measuring the concentration of fluoride ions released in the water drained from the fuel cell system using a fluoride ion selective electrode. The fluoride is usually released from both the anode and the cathode, and the release rate is determined using the effluent collected from both sides [2]. However, the product water of the Nexa system is just from the cathode side because the system has a dead end structure where the anode outlet is blocked. Accumulation of nitrogen and water vapor in the hydrogen stream gradually increases with time, so the anode is purged to flush out inert constituents periodically [9]. It is believed that the fluoride released from the anode would be exhausted with the anode gas when it is purged, and there is also fluoride exhausted in the form of a gas from the cathode. Without consideration of the amount of these fluoride gases, it is very difficult to determine absolute amount of the fluoride released from fuel cells. In this research, the value of the fluoride emission rate measured using the ion selective electrode does not mean the absolute value of the total HF emission from the fuel cell system. The rate of chemical degradation is compared by comparing the fluoride release rate of the tests at different operating frequencies. Finally, the frequency effects on both simulated dynamic behavior and chemical degradation were compared and their close relationship was shown.

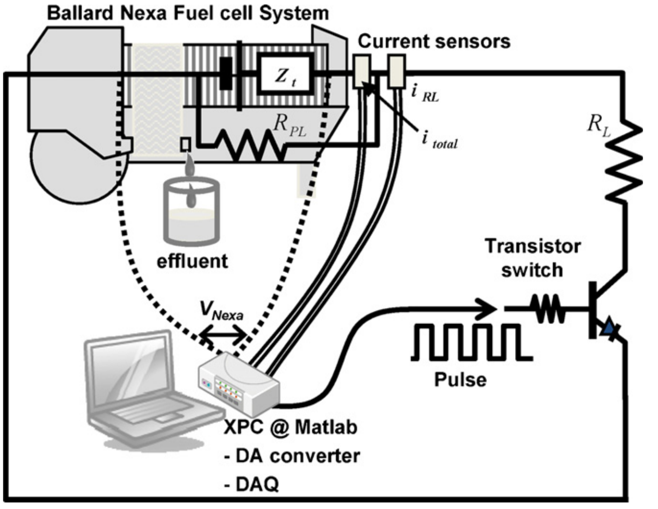

Fig. 2. Experimental setup for dynamic operation of the Ballard Nexa fuel cell system. Z_t is a total impedance of the Nexa system.

2. Experimental setup

The schematic diagram of the Ballard Nexa fuel cell system is seen in Fig. 2. To dissipate the fuel cell power, a 0.77 Ω resistor with a 1 kW power dissipation rating was implemented by parallel connection of a 1 Ω and three 10 Ω resistors (FSE-1000, Huntington Electric Inc.). The duty ratio of the pulse signal was fixed at 15% and 50% in which the 15% duty cycle means 15% externally loaded and 85% parasitic load only, and the pulse frequency was varied from 0.0005 Hz to 1 kHz. A transistor switch was constructed to perform the step loading and unloading of the system using a high-current complementary transistor (MJ11032) and a diode. The switch signal and data acquisition were realized using a standard DAQ card controlled using the MathWorks software package XPC. Fluoride release rates during operation of the fuel cell system were evaluated by collecting effluent from the exhaust and measuring the fluoride ion concentration using a fluoride ion selective electrode (Hach, Model No. 51928; a concentration range for the measurement is from 0.01 mg L^{-1} F to saturated solutions, and a slope change for the concentration is -58 ± 3 mV per decade [10]). Preparation of a standard solution and calibration were performed by the direct measurement method as described in its manual [10]. The fluoride release rate was calculated by measuring the fluoride concentration and condensation rate of the cathode product water.

3. Results

3.1. Modeling and simulation

The voltage and current changes during cyclic operation are shown in Fig. 3. The stack current cannot be completely turned off because there is always a parasitic load current (i_{RPL}), so the cyclic operation condition in this research has no open circuit condition. Furthermore, under the assumption of well-controlled humidification of the Nexa system, the only accelerating degradation factor in this experiment is assumed to be the dynamic operation.

The equivalent circuit in Fig. 4 is used to model the fuel cell system as described in a previous effort [11] in which the charge double layer is modeled by three pairs of resistors and capacitors

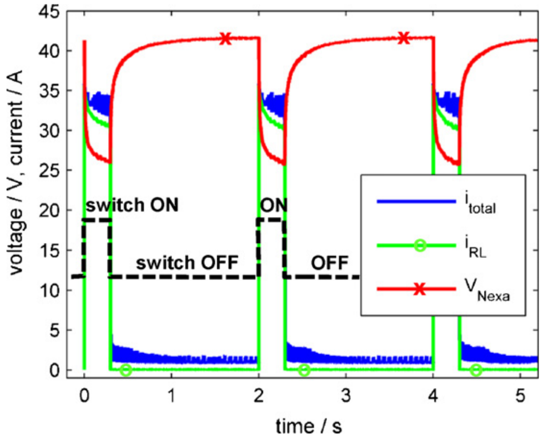

Fig. 3. Voltage and current changes during cyclic operation.