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Post-mortem analysis of a long-term tested proton exchange membrane fuel cell stack under low cathode humidification conditions

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HIGHLIGHTS

- Durability tests for PEMFC stacks are carried out in constant power mode with simulated reformate fuel gases.
- Major degradation mechanisms and patterns in a PEMFC stack are investigated under low cathode humidification.
- Various post-mortem investigations are carried out to disclose the main reasons of failure of the stack.
- Delamination of the catalyst layer of unstable operating MEAs is significant near the cathode gas inlets.
- Degradation is due to the cathode carbon corrosion and membrane failure during the start-up and shut-down process.

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ABSTRACT

During continuous power operation for 2740 h, the major mechanisms and patterns of performance degradation in a polymer electrolyte membrane fuel cell (PEMFC) stack are investigated under low cathode humidification with simulated reformate fuel gases through the use of various physicochemical and electrochemical analysis tools. As operating time increases, the operating voltages and open-circuit voltages (OCVs) of the stack decrease with the large voltage distributions. In the post-mortem analysis of the stack, the delamination of the catalyst layer (CL) of unstable operating membrane electrode assemblies (MEAs) is significant near the cathode gas inlets. This observation is in agreement with the results of OCV, hydrogen crossover current, and anode off-gas measurements. This phenomenon may be due to the acceleration of carbon corrosion in the cathode during the frequent start-up and shut-down process, because the local cathode potential can reach more than 1.5 V in the air/fuel boundary. Additionally, the frequent membrane hydration and dehydration by the accumulation of excess water (through electrochemical reaction) and faster water evaporation (under dry-air cathode conditions and high operating temperatures) may accelerate the interface delamination between the membrane and cathode CL with a substantially uneven distribution of water.

1. Introduction

One of the remaining technical challenges for the commercialization of polymer electrolyte membrane fuel cells (PEMFCs) for portable, stationary, and transport applications is to assure long-term durability and high reliability with reduced system cost [1,2]. The lifetime targets for 2015 set by the U.S. Department of Energy (DOE) is at least 5000 h for automobile applications and 40,000 h for building applications under practical operating conditions. The costs of manufacturing PEMFC systems (including materials) must also be reduced concurrently [3]. Over the last decade, much research has been conducted to improve the long-term durability of PEMFCs by improving membranes, anode/cathode catalysts, bipolar plate materials, balance-of-plants (BOPs), and operating logics (start-up–shut-down) [4–6]. Among these, one of the major cost components in manufacturing PEMFCs for various

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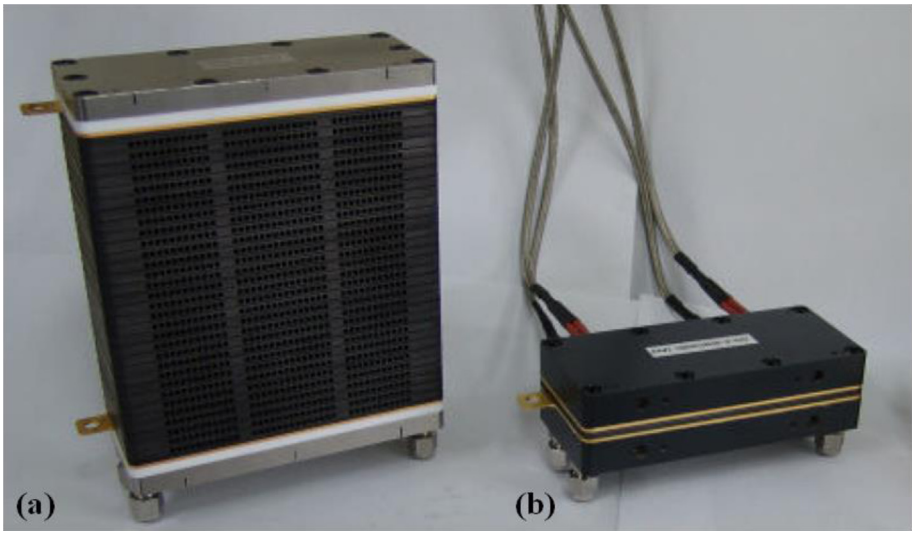

Fig. 1. Exterior view of the (a) 32-cell and (b) single-cell PEMFC stack. The closest cell from the gas inlet (bottom) was designated as #1 (bottom) and the far-end cell (up) from the gas inlet was designated as #32.

applications is the catalyst and bipolar plate. Extensive works have carried out to reduce the cost via the use of more effective supports (*e.g.* graphene, nanofibers, and nanoparticles) and novel composite catalysts (Pt alloys with various transition metals) with less precious metal loadings, and high-performance membrane electrode assemblies (MEAs) with better fabrication methods and electrode structure [7,8]. Low-cost bipolar materials such as composite materials or other conductive metals have also been considered as alternatives to graphite plates, in terms of the conductivity, gas permeability, corrosion resistance, ease of manufacturability, thinness, and light weight [9].

Another way to realize cost-savings for PEMFC systems is to remove the external gas humidification parts on the cathode side [10]. It is possible to minimize the complexity, size, and number of balance-of-plants (BOPs) in PEMFC systems. The high humidification of gas causes additional energy losses due to the heating of the humidifier and control of the water balance [11]. Additionally, at subzero temperatures, detrimental effects by ice formation on PEFMCs (*e.g.* in the MEAs and humidification parts) in the cathode part can be reduced during the storage and operation of the system. Low-humidified fuels, however, may reduce the lifetime of PEMFCs with reduced power density due to the dehydration and mechanical stress of the membrane by uneven water distribution between both the electrodes in the MEA.

Hence, this study aims at assessing the major mechanisms and patterns of performance degradation in a PEMFC stack (including membranes, electrodes, bipolar plates, and seals) operating continuously for thousands of hours under low cathode humidification through the use of various physicochemical and electrochemical analysis tools. Although many efforts have been made on understanding PEMFC behavior under low-humidification conditions, they have mainly focused on stable stack performance without humidifying the gas streams through the specific design of a stack flow-field or proper operating conditions [11–13]. In addition, it is imperative that the long-term durability of PEMFC stack be evaluated as a function of time under realistic operating conditions to enter the energy market, since single-cell evaluation cannot represent the characteristics of a PEMFC system in terms of energy and thermal efficiency due to the non-uniformity in potential, temperature, and flow distributions [14].

The CO tolerance of a PEMFC stack is also investigated with liquefied petroleum gas (LPG) reformed hydrogen gas containing a few ppm of CO in the anode for various power applications. At present, LPG is easily accessible and available without major infrastructure investment. Most previous research has mainly been conducted in mild operating conditions using hydrogen fuel, full humidification, and constant operation mode regarding voltage or current. This work contributes to recognizing various degradation sources occurring under harsh PEMFC operation conditions to realize stable stack performance in a real operation mode for a targeted lifetime.

2. Experimental

2.1. Stack preparations

Membrane electrode assemblies (MEAs) were prepared by a commercial catalyst-coated membrane (CCM; Gore MESGA Primea Series, USA) with Pt–Ru/C (anode) and Pt/C (cathode) catalysts. The Pt loadings were 0.4 $mgcm^{-2}$ for both electrodes, and SGL carbon papers (35BC Germany) were used as gas diffusion layers (GDLs). The active area of the electrode was 51.6 cm^2 for MEAs in the stack. The PEMFC stack was composed of 32 single cells connected in series with machined-graphite flow-distribution plates (Ildo F & C, Korea). A planar PEMFC stack is shown in Fig. 1, where the closest cell from the gas inlet is designated as #1 (the lowest cell), and the cell at the far end from the gas inlet was designated as #32 (the highest cell). The flow channels of the cathode and anode were designed as quadruple and dual serpentine-type fields, respectively, and their width and depth were 0.3 mm and 1.0 mm, respectively. Ethylene propylene diene monomer (EPDM; Don-A Hwa Sung Co, Korea) was used for the gasket between each single cell for its chemical resistibility and stability. The six cooling fans (GB0535AEV2-8, Sunon, Taiwan) were set up on the front of the stack for quick removal of the heat generated by high-temperature humidified fuel and electrochemical reactions inside the stack. Cell voltage probes were installed on the side of the stack to read the voltage variation of 32 cells.

2.2. Stack durability test

A durability test was carried out with the PEMFC stack using a fuel cell test station (Arbin Instruments, USA) equipped with an electrical load, mass flow controllers (MFCs), temperature-variable