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Performance of individual cells in polymer electrolyte membrane fuel cell stack under-load cycling conditions

A. Bose [a,*], P. Babburi [b,1], R. Kumar [c], D. Myers [c], J. Mawdsley [c], J. Milhuff [c]

[a] Department of Engineering Technology and Texas Center for Superconductivity, University of Houston, Houston, TX 77204, USA
[b] 1500 Harbour Dr, Unit 1J, Wheeling, IL 60090, USA
[c] Chemical Sciences and Engineering Division, Argonne National Laboratory, 9700S Cass Avenue, Argonne, IL 60439, USA

HIGHLIGHTS

- Stack degradation at single cells level was assessed using DOE load cycling protocol.
- An irreversible degradation of stack performance was observed after 480 h.
- Observed kinetic and mass transport losses were largely dominated at the end cells.
- Kinetic losses were primarily caused by the loss of ECSA.
- Durability of ~1700 h can be estimated based on the initial degradation profile.

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ABSTRACT

The performance of a ten-cell 50 cm^2 100 W polymer electrolyte membrane fuel cell (PEMFC) stack was evaluated under dynamic load cycling conditions utilizing the 2005 United States Department of Energy durability test protocol for PEFCs. An enhancement of performance was observed during the first 240 h, while an irreversible degradation of stack performance was observed after 480 h (~4700 cycles). In particular, the stack voltage at 100 mA $cm^{-2}$was decreased by 2.8% after 480 h and individual cell voltage was decreased up to 8%. An analysis of cell overpotentials for activation, Ohmic, and mass transport losses revealed that the predominant source of performance degradation was due to kinetic losses. The loss of catalyst utilization was estimated to be 39% based on the electrochemically active surface area (ECSA) measurements. Electron microscopic images of some of the cells showed growth in cathode Pt particle size from 5.3 to 6.2 nm. However, these microscopic images did not show any membrane damage or electrode thinning. Severe degradation of both the anode and cathode silicone gasket seals was observed during the durability test.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) represent a promising and viable alternative power source for transportation and other applications [1]. PEMFCs offer high power density and greater efficiency at low operating temperatures. A few challenges of this clean energy technology for transportation applications, including the durability of cell stacks, have been highlighted [2,3]. The potential for achieving the automotive application target of 5000 operating hours[4,5] has been extrapolated based on tests of single cells, but the reported durability of existing stacks is considerably shorter, about 2000 h [6]. Several studies have documented causal factors affecting the observed performance degradation at the single cell level [7–9]. Multi-cell stacks, however, encounter conditions and stresses different from those encountered in single cells, including cell-to-cell variations in reactant flows, water distribution, membrane humidification, temperature, and compression [10,11]. There are relatively a few studies of PEMFC stack degradation documented in the extant literature, and these studies have primarily evaluated stacks operating under constant current or constant voltage conditions [9,12–15]. In transportation and many other applications, fuel cell systems must meet wide variations in power demand. For example, average cell voltages may vary rapidly from 0.6 to 0.9 V in the automotive application.

* Corresponding author. Tel.: +1 713 743 5765; fax: +1 713 743 4032.
E-mail address: abbose@uh.edu (A. Bose).
[1] Current address.

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We have taken a systematic approach to understand possible reasons for loss of performance at various stages of cell operations. In our earlier work, we demonstrated that cell performance depends on the curing process during fabrication even when every component of a given cell's composition is kept invariant [16]. The objective of the present work is to analyze sources of stack degradation under varying load conditions using a 100 W 10-cell stack by applying various diagnostic techniques to assess the relative impacts of changes in the electrochemically active surface area (ECSA) of cathode catalyst, Ohmic resistance, and mass transport resistance of individual cells during the durability test. Since the cell performance is largely controlled by the oxygen reduction kinetics, this study was concentrated on cathodes.

2. Experimental

2.1. Stack descriptions and data acquisition

A 10-cell hydrogen–oxygen polymer electrolyte research fuel cell stack with 48.5 cm^2cell active area was obtained from H2ECOnomy (Yerevan, Armenia). The stack contained Nafion115® membrane with 0.5 mg Pt cm^{-2} loading each at the anode and cathode (30% Pt on Vulcan XC-72). The flow-filed was double serpentine. The stack was rated to deliver 100 W peak power at 6 V at a nominal operating temperature of 65 °C, with the anode and cathode at 0.75 and 0.9 bar gauge, respectively. Heating the stack was achieved through thermodynamic and resistive losses. Cooling the stack was achieved through fan cooling facilitated by channels drilled through the centers of the third and seventh bipolar plates. The cells were numbered consecutively from 1 to 10,with Cell 1 proximal to the stack gas inlets and Cell 10 proximal to the gas outlets.

A fuel cell (FC) test stand (Scribner 850e) was used to measure polarization curves, control the hydrogen and oxygen flow rates, humidity levels, and monitor temperatures. To enable monitoring of the individual cell performances and conditions, voltage and thermocouple leads are incorporated into each bipolar plate and a thermocouple into one of the cooling channels. The temperature of the stack was monitored in the innermost air cooling hole. Altogether these 10 voltage leads and 12 thermocouples are connected to a multi-meter (Agilent Datalogger), and were monitored on a computer using the Agilent Datalogger software. The individual cell voltages were monitored by the digital multi-meter.

2.2. Stack performance verification and dynamic load test protocol

The initial stack performance was verified under operating conditions recommended by the vendor. These conditions include stack temperature of 65 °C, hydrogen input and humidifier temperature of 50 °C, oxygen input and humidifier temperature of 55 °C, constant flow of 1.24 SLPM hydrogen at 0.75 bar gauge, and 1.18 SLPM oxygen at 0.9 bar gauge. These flow rates equate to hydrogen and oxygen stoichiometry of 1.05 and 2.0, respectively, at 100 W, the rated power of the stack. At the start of a test, the stack was heated to the operating temperature of 65 °C by holding it at a constant potential of 7.0 V before applying the desired test protocol, during which the stack temperature usually decreased. The initial stack polarization curve was identical to that provided by the vendor.

The dynamic load cycling protocol established by the U.S. Department of Energy (DOE) was used to assess the long-term performance of PEMFC stacks under conditions reflecting the automotive application [8,17]. Briefly, the test protocol involves cyclically stepping through a series of currents with periodic interruption of the cycling for polarization measurements and diagnostics. According to the protocol, the definition of stack end-of-life is a decay of ≥10% of the average cell voltage at all current densities. The various steps in the dynamic load test protocol are shown Table 1 [8,17]. The current densities at the various steps are defined by the measured current densities at the specified cell voltages obtained in the initial stack polarization measurement. The initial stack polarization curve was used to establish the current steps for the load test profile at stack voltages of 8.8, 8.0, 7.5, 6.5, and 6.0 V. The current values at these voltages are designated as C_{88}, C_{80}, C_{75}, C_{65}, and C_{60}, respectively, as listed in Table 1. These current densities and time intervals were then used for the load cycling tests. Constant stoichiometric flow ratios of 1.05 for H_2 and 2.0 for O_2 were used during each step. The current density, fuel and oxidant gas inlet flow rates, temperatures, and humidifier temperatures were controlled, and the corresponding individual cell voltages and temperatures were recorded. The dynamic testing was interrupted at 240 h and 480 h to perform diagnostic tests, as discussed below.

Table 1
DOE-recommended generalized current density vs. time for the dynamic load test protocol [8,16].

Step	Duration (s)	C_{XX}	Step	Duration (s)	C_{XX}
1	15	OCV	9	20	C_{75}
2	25	C_{80}	10	15	C_{88}
3	20	C_{75}	11	35	C_{80}
4	15	C_{88}	12	20	C_{60}
5	24	C_{80}	13	35	C_{65}
6	20	C_{75}	14	8	C_{88}
7	15	C_{88}	15	35	C_{75}
8	25	C_{80}	16	40	C_{88}

Abbreviations used: XX=stack voltage*10 (V),Cxx refers to current densities at various cell voltages (for example, C80 is the current density at a cell voltage of 0.8 V), and OCV = open circuit voltage.

2.3. In-situ diagnostics

After 240 h and 480 h of dynamic load cycling, stack polarization curves were measured in the controlled-current mode. The increasing current portions of these curves are shown in Fig. 1. The maximum current density was constrained to ~300 mA cm^{-2} due to gas flow rate limitations inherent in the test equipment. The total resistance of the stack was obtained by using the current interrupt

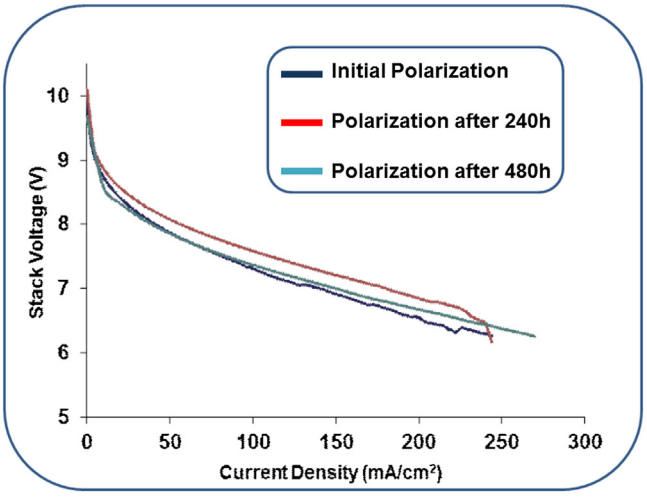

Fig. 1. Polarization curves for the 10-cell stack recorded at 0, 240, and 480 h of dynamic stress testing. Test conditions: pressures, anode/cathode, 0.75/0.9 bar gauge; temperatures, cell = 65 °C, H_2 humidifier = 50 °C, O_2 humidifier = 55 °C; stoichiometry, H_2/O_2 = 1.05/2.0.