A Six-Cell ‘Single-Cell’ Stack for Stack Diagnostics and Membrane Electrode Assembly Evaluation

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ABSTRACT

Polymer electrolyte fuel cells are promising candidates as energy conversion devices in applications from portable power to stationary applications or electric vehicles. In order to achieve practical voltage, power and energy density, stacks are employed for almost all applications. Here, we present a six-cell ‘single cell’ stack in which individual cells can be isolated from the stack by current carrying leads found within each of the bipolar plates. The current carrying leads allow individual cells to be isolated from the rest of the stack, so that cells can either be tested together or independently. The design of the stack, utility for specific applications, including stack diagnostics and membrane electrode assembly (MEA) testing, and some experimental results, obtained using the stack, are presented. Special focus is given in this paper to the area of direct methanol fuel cell (DMFC) stacks, however the equipment and many of the experimental results presented are appropriate for other fuel cell systems.

INTRODUCTION

Polymer electrolyte fuel cells are currently being investigated for a number of applications with milliwatt to kilowatt power requirements. However, single cells are rarely adequate for specific applications so that stacks are typically employed to achieve the voltage, power, and energy density requirements necessary to compete in given applications. The cells in such stacks are usually placed in series with the same current passing through each of the individual cells.

A drawback of such a setup is that under normal conditions, the cell that reaches its mass transport limit first limits the performance of the entire stack. Further compounding this problem, optimized systems tend to operate near mass transport limits (relatively low stoich) because this lowers the balance of plant losses associated with pumps and compressors, and in the case of DMFCs, methanol crossover. In order to ensure optimum stack performance, even flow distribution through the cells is a critical concern in stack design.
While it is possible to monitor and control the flows through individual cells for some externally manifolded stacks, internally manifolded cells are often preferred due to the decreased number of individual parts and ease of assembly. Unfortunately, monitoring or controlling individual flow rates directly in internally manifolded stacks is usually impractical. Modeling of flow through stacks can yield insight, but tolerances of parts and components as well as issues involved with assembly can lead to significant errors. For MEA evaluation using stacks, this can make data interpretation difficult. For example, distinguishing the difference between performance losses due to uneven flow distribution versus individual MEA performance may not be possible. If more information were available on individual cell flow rates, it would lend insight into the performance loss mechanisms of the stack and be a useful tool for designing stacks with more equal flow distribution. Furthermore, if the flow rates through the individual cells can be accurately measured, evaluating individual MEA within a stack configuration becomes much more accurate, offering advantages in the number of MEAs that can be tested (throughput) and the number of test stations required (capital cost).

Here, we present a six-cell 'single cell' stack in which individual cells can be isolated from the stack by individual leads connected to each of the bipolar plates. The primary limitation of such a system is that the leads from each individual cell be capable of carrying the maximum current that the cells were designed for. For this system, the individual bipolar plates have been specially constructed to allow for high currents to be carried through each individual cell. This allows us to test individual cells over a much wider range of operating conditions, operate the stack with some cells removed from operation, and perform diagnostic experiments that are not otherwise possible.

EXPERIMENTAL

Six -celled ‘single-cell’ stack design

The stack, shown in Figure 1, consisted of six cells each of active area 22cm². The unique character of this stack comes from the bipolar plates, shown in Figure 2. The bipolar plates are not a single plate, but rather three components: a 0.036” thick 316 stainless steel current collector and two 0.125” thick graphite plates. Flow fields were machined into the outer faces of the graphite plates, and o-ring grooves were machined near the manifold channels and o-rings were used to isolate the stainless steel current collector from the reactant flow.

Two tabs were on opposite sides of the stainless steel current collectors and connected by spade connectors, one to act as voltage monitor and the other as a current carrier (in Figure 1, the current carrying spade connectors are visible on the left hand side of the Figure). These connections were capable of carrying currents greater than 10 Amps, so testing was limited to less than 0.5 Amps/cm². The focus of this work was DMFC testing so this current limit was sufficient, but for hydrogen fuel cell testing it might be desirable to work at higher current densities. This could be accomplished by moving to a thicker current collector and a higher rated spade connection or by
decreasing the active area of the cells. All the spade connections were made at the same location along the length of the stack (see Figure 1), allowing for easier handling of the stack during testing. However, a high cell pitch (0.310") was necessary to allow adequate space for the connectors, leading to bipolar plates that are much thicker than those used in practical stacks. Thinner plates could be used if one were to stagger the leads.

Figure 1: Six-celled 'single cell' stack with current carrying leads attached to left.

Figure 1: Current carrying bipolar plate for six celled 'single cell' stack.

A six-cell stack was chosen as a balance between having enough cells to determine reproducibility, being able to isolate issues associated with stack location (end cells vs. interior cells), and ease of data acquisition and manufacture. Six cells allowed
us to test either three sets of two identical MEAs or two sets of three identical MEAs and isolate these MEAs from each other. The typical arrangements were cells 1 & 4, 2 & 5, 3 & 6 for the three sets of two identical MEAs and cells 1 & 3 & 5, 2 & 4 & 6 for the two sets of three identical MEAs.

**Fuel cell experiments**

**MEA fabrication** - MEAs were prepared from standard catalyst inks containing either unsupported platinum or platinum-ruthenium, water, and Nafion 1100 solution. These inks were mixed by sonication and then applied to the membranes by direct painting. All the membranes tested had identical electrodes. Nafion 117 films were pretreated by boiling for 1.5 hours in each step in 3% H₂O₂, deionized water, 0.5 M H₂SO₄, and again in deionized water.

**Polarization curves** - Current versus voltage performance of the stacks on MeOH/air or H₂/air were obtained. One significant advantage of this stack was the ability to obtain performance of individual cells, thereby extending the current range and learning about the mass transport limits of individual cells.

**Anode polarization** - Current versus voltage performance of the stacks on MeOH/H₂ were obtained. For DMFCs, this data yields quantitative data about the anode performance (1). One significant advantage of this stack was the ability to obtain performance of individual cells, thereby extending the current range and learning about the mass transport limits of individual cells.

**CO stripping** - CO (99.3% purity, 1.8 L min⁻¹) was adsorbed at 0.1 V versus H₂ for 15 minutes at 25°C. The gaseous CO was removed with purging N₂ (6.0 L min⁻¹) for 30 minutes. The beauty of the ‘Single Cell’ stack configuration is the possibility of stripping off the adsorbed CO for one cell while keeping the CO adsorbed in the remaining five cells at 0.1 V. The CO could then be consecutively removed for each catalyst surface by a linear potential sweep from 0.1 to 0.8 V with a scan rate of 2.3 mV s⁻¹. The stripping charge was determined from the peak area under the peak associated with CO adsorption and the scan rate (2,3). This measurement was not possible using a traditional stack.

**Limiting current methanol crossover** - Current versus voltage performance of the stacks on MeOH/N₂ were obtained. From this data open circuit methanol crossover through each individual cell could be measured (1). Because the MEAs presented here were identical, the data obtained were approximately equal and will not be discussed, but it is another example of a measurement not possible using a traditional stack.

**High frequency resistance** - High frequency resistances were also measured. While these can also be measured in traditional stacks, even cells that have been short-circuited still give meaningful resistances.
Lifetime studies – Stacks were held at a constant current and the voltage change of the individual cells over time was recorded. This is a traditional stack test, however, because of the addition of the current collecting bipolar plates, some of the aforementioned fuel cell tests could be run periodically during the life test to isolate the loss mechanisms associated with declining performance.

RESULTS AND DISCUSSION

For purposes of illustration, a specific six-cell ‘single-cell’ test case is presented here. In this case, three sets of two identical cells (1 & 4, 2 & 5, 3 & 6) were prepared. This arrangement allowed us to test duplicate cells and decouple issues associated with cell location. The MEAs were of the same catalyst loading and all were on Nafion 117. At the beginning of our testing, cells 2 & 5 had developed severe flow problems due to specific differences in processing. While even single cell failure is catastrophic for MEA testing within traditional stacks, due to the construction of our stack we were still able to test cells 1, 3, 4 & 6, by short-circuiting cells 2 & 5. Thereby salvaging the time and effort needed to prepare and assemble the stack.

The purpose of this stack was to understand DMFC MEA degradation for MEAs prepared by different processing routes. Therefore, a DMFC lifetime experiment was run at 2 amps for 360 hours and the voltage response of the cells was recorded as a function of time, see Figure 3. The operating conditions for the stack are 1M methanol at a flow rate of 18 mL/min preheated to 80C for the anode, and 2.14 L/min air humidified to 90C without backpressure inside an oven at 80C. The first 20 hours of the lifetest were used as a ‘break-in’ period and data were not recorded. The lifetest was stopped periodically, after 20, 120 and 339 hours, so that the cell performances could be evaluated as a function of time. These breaks are visible in Figure 3 as cell performance is recovered following the intermittent testing. It is worth noting that the cathode humidifying bottle in the test station affected cell performance between 20 and 120 hours. After the faulty bottle was replaced (120 hours), the performance of the cells improved significantly and performance was much more even.

High frequency resistances (HFR) were also recorded during the lifetest, see Figure 4. The cells showed little change in resistance, except for cell 6, which showed a slightly elevated HFR between 20 and 120 hours. This elevated HFR was likely related to the cathode humidifying bottle and because cell 6 faced the cathode endplate it would tend to be more susceptible to cathode flow effects.

During breaks in the lifetest, various single cell and stack measurements were performed to evaluate the performance of the individual MEAs. Here, we will focus on anode polarization and CO stripping on the anode.
Figure 3: Voltage response of cells 1, 3, 4 and 6 at 2 amps for a 360-hour lifetest

Figure 4: High frequency resistance of cells 1, 3, 4 and 6 at 2 amps
Figure 5 shows a typical CO stripping response for a CO-free DMFC anode versus a DMFC anode that has been saturated with adsorbed CO. The area under the peak is proportional to the amount of CO that has been adsorbed by the surface, or in other words, the active catalyst surface area. By quantifying the changes in active surface area as a function of lifetime in the stack, the degradation mechanisms associated with declining performance can be better understood.

![Graph](image_url)

Figure 5: Typical anode CO stripping responses for a DMFC anode exposed to CO and a CO-free surface at 80°C. CO (99.3%) was adsorbed for 15 min and 1.8 L min\(^{-1}\). Gaseous CO was removed with purging \(N_2\) (6.0 L min\(^{-1}\)) for 30 min. The adsorbed CO was oxidatively removed with a single potential sweep from 0.1 V to 0.8 V, scan rate 2.3 mV s\(^{-1}\).

The changes in the anode CO stripping charge as a function of time are shown in Table 1. A significant decrease in the total stripping charge was shown for each of the electrodes, with an average decrease of an 8% after 120 hours and 13% after 339 hours. The numbers presented in these tables represent the average of two separate stripping experiments. Interestingly, the numbers from cell to cell and between scans show good consistency and reproducibility. The data suggest that one possible loss mechanism in the system is loss of active catalyst surface area on the anode as a function of time.

Anode polarization data complements the CO stripping data presented above. Figure 6 represents the average anode polarization of cells 1, 3, 4 and 6 as a function of time. From Figure 6, it is obvious that over time a higher potential is required to give the same current density at earlier times. These results are tabulated for single cells in Table 2 in terms of current density at 0.3 volts. The results in Table 2 show qualitative agreement with those shown in Table 1 for CO stripping, with the current density associated with the anode polarization at 0.3 V decreasing on average 14% after 120 hours and 19% after 339 hours. While the decreases in current density are not as uniform.
for cell to cell as the decrease in active surface area, this might not be surprising because interpreting losses in current density at a specific voltage are not as straight forward as interpreting losses in active surface area.

| cell # | Charge [C] | S.C. (C) |
|-------|------------|----------|
|       | 20 h | 120 h | % loss | 339 h | % loss |
| 1     | 47.6 | 43.4 | 9   | 41.2  | 13     |
| 4     | 42.3 | 38.7 | 9   | 36.8  | 13     |
| 3     | 42.4 | 40.0 | 6   | 36.6  | 14     |
| 6     | 45.1 | 41.6 | 8   | 39.1  | 13     |
| Average | 44.4 | 40.9 | 8   | 38.4  | 13     |

Table 1: Anode CO stripping charge for cells 1, 3, 4 and 6 as a function of time

|          | Curr.Dens. @ 0.3V | C.D. (0.3V) |
|----------|-------------------|-------------|
| cell #   | 20 h  | 120 h | % decrease | 339 h | % decrease |
| 1        | 132   | 116   | 12          | 107   | 19         |
| 4        | 136   | 115   | 15          | 105   | 23         |
| 3        | 145   | 121   | 17          | 113   | 22         |
| 6        | 140   | 125   | 10          | 124   | 11         |
| Average  | 138   | 119   | 14          | 112   | 19         |

Table 2: Anode polarization for cells 1, 3, 4 and 6 as a function of time
CONCLUSIONS

The six-cell 'single cell' stack in which individual cells could be isolated from the stack by current carrying leads found within each of the bipolar plates was found to be useful in the lifetime testing of DMFC stacks presented here. The stack has shown utility in screening multiple MEAs without requiring multiple test stations, and can also be used as a diagnostic tool in stack design.

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