INVESTIGATION OF RUTHENIUM DISSOLUTION IN ADVANCED MEMBRANE ELECTRODE ASSEMBLIES FOR DIRECT METHANOL BASED FUEL CELL STACKS

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ABSTRACT

The mechanism of ruthenium dissolution in Direct Methanol Fuel Cell (DMFC) Membrane-Electrode-Assemblies (MEAs) was investigated by preparing various MEAs and subjecting them to continuous operation for a period of 250 hours. All of the MEAs exhibited voltage decay. The voltage decay for MEAs operating at 40 $^{\circ}$C, 0.5 M methanol was in the range of 6 to 48 mV at an applied current of 50-mA/cm^2 and 67 to 150 mV at an applied current of 100-mA/cm^2. The technique of anode polarization was used to determine the source of degradation and revealed that anode performance in these MEAs was constant and that the cathode was more sensitive to duration operation. EDAX analysis was performed on each cell to determine if ruthenium had dissolved from the anode and precipitated onto the cathode, no ruthenium was found on the MEA. This paper discusses stack properties that can promote ruthenium dissolution in DMFC MEAs.

INTRODUCTION

The U. S. Army is presently pursing the development of alternative energy storage devices to power military vehicle test instrumentation. In response to the U. S. Army needs, the Jet Propulsion Laboratory has developed a direct methanol fuel cell (DMFC) based system that was designed to produce 300 Watts of power for 100 hours of continuous operation [1]. The 300-Watt system 80-cell DMFC stack output power decreased from 374 to 178 Watts over a six month period as shown in Figure 1. Stack disassembly revealed that the stack cathode compartments, cathode gas diffusion backing, and various stack components had become contaminated with ruthenium. DMFC membrane-electrode-assembly (MEA) degradation as a result of ruthenium migration in long-term operation has been reported by both the Los Alamos Fuel Cell Group and DuPont [2, 3].
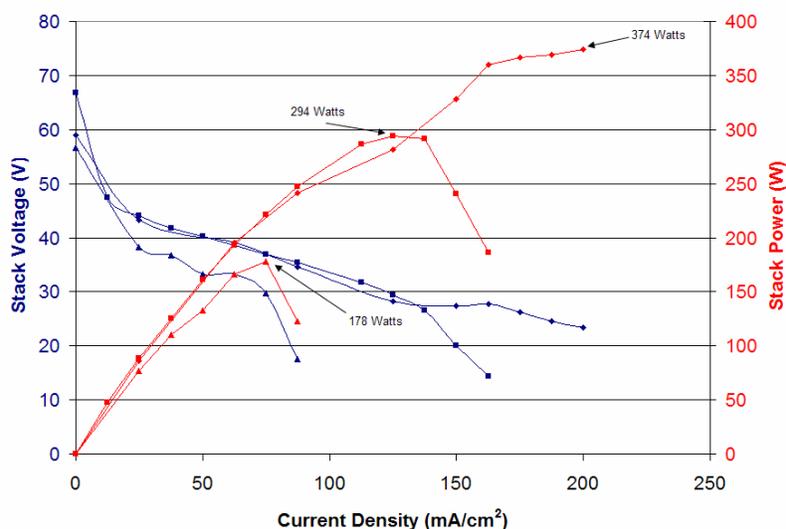
Figure 1. 80-cell DMFC stack performance taken at three month intervals. Stack operating at 60 °C, 0.5M methanol.

An explanation for stack performance loss must account for the ruthenium deposition at the cathode, loss of water-repellency at the cathode and loss of performance. One degradation pathway would be ruthenium dissolution from anode and deposition at the cathode. This degradation mechanism will lower both the anode and cathode potentials. The second degradation pathway would be the loss of hydrophobicity of the cathode. If the cathode loses its hydrophobicity, the cathode would become wetting which would lead to cathode flooding. Such a loss of water-repellency could arise from inadequate Teflon® content or deposition of a hydrophilic material such as ruthenium oxide on the cathode structure. For each of these degradation pathways two mechanisms were proposed:

A. Mechanisms for Ruthenium dissolution:
(A-1) Over discharge caused by shunt currents
(A-2) Instability of platinum-ruthenium commercial catalyst

B. Mechanisms for Loss of hydrophobicity at the cathode:
(B-1) Inadequate Teflon® content
(B-2) Deposition of RuO2 at the cathode from the anode

Physical examination of the stack MEAs had shown that ruthenium dissolved from the anode and deposited on the cathode. Also, there was evidence of shunt current activity (electrolysis and arcing) on the bipolar plates and the end plates. Shunt currents with poor reactant distribution can lead to over-discharge of some of the cells and consequent ruthenium dissolution (Mechanism A-1). Thus, mechanism A1 was already plausible. It is important to know if the anode catalyst used in the MEAs was inherently unstable under normal operating conditions (Mechanism A-2), as suggested by other reports[1,2]. It was not clear if there was any loss of hydrophobicity from inadequate Teflon® in the cathode backing layer (Mechanism B-1). The deposition of ruthenium on the cathode structure would certainly render the cathode hydrophilic resulting in performance loss (Mechanism B-2).

The focus of this paper will be to present data from recent experiments on MEA duration testing and discuss the possible mechanism for ruthenium dissolution as it relates to the specific stack design employed in the 300-Watt system. The MEA degradation studies focused on the instability of platinum-ruthenium commercial catalyst (Mechanism A-2) and inadequate Teflon® content (Mechanism B-1).

EXPERIMENTAL

Membrane Electrode Assembly Fabrication

MEA studies in single cells were conducted to determine the stability of the anode catalyst and the effect of Teflon® content on the long-term hydrophobicity of the cathode. Single cells cannot sustain shunt currents and therefore the effect to shunt currents can be separated from other causes of degradation. It was hypothesized that some catalysts could be inherently unstable if they had high ruthenium oxide content. Therefore, three types of anode catalyst were evaluated. These were, Johnson-Matthey Pt-Ru catalyst as received that was rich in ruthenium oxide (JM), JPL Pt-Ru catalyst that was largely metallic (JPL), and a "reduced" Johnson-Matthey catalyst that was largely metallic since the oxide was reduced with hydrogen gas at 225°C (JMR). While 5% Teflon® in the backing layer at the cathode is adequate to achieve sufficient water-repellency, it was suspected that additional Teflon® (as high as 15%) may provide sustained water repellency during long duration operation. To investigate these effects, four MEAs were prepared; the composition of each MEA is shown as Table 1.

Table 1. Membrane-electrode-assembly compositions

MEA	Anode Catalyst	Cathode Paper Teflon Content
JPL	JPL	15%
JM	JM	15%
JMR	JM*	15%
JM-STD	JM	5%

All MEAs were 25-cm^2 active area fabricated in-house by the Jet Propulsion Laboratory Direct Deposit Technique [4, 5]. The MEAs where fabricated with Johnson-Matthey Fuel Cell Grade Pt-Black cathode catalyst. The nominal catalyst loadings for each MEA were range of 8 to 12 mg/cm^2 per electrode and were fabricated using the same hot-press conditions. JM-STD is the standard (or control) MEA that had the same composition as that used in the 80-cell stack.

Testing Methodology

The single cells were operated in a test stand for over 250 hours. An in-house designed methanol sensor was used to control fuel concentration during the test. The data was collected using a LabVIEW® based automated data acquisition system. An initial current-voltage cell characterization was taken of each cell to form the performance baseline. The cells were then operated in the duration test stand with 40 °C, 0.5 M methanol at an applied current of 60-mA/cm^2 for a period greater than 250 hours. At the completion of the 250-hour test, a second set of current-voltage cell characterization were taken to determine performance degradation. Anode polarization experiments [6, 7] were the final electrochemical experiments performed on cells.

In the anode polarization experiment, nitrogen is fed to the cathode thereby converting the cathode into a dynamic hydrogen electrode. When the cell is polarized in anode polarization mode, the resultant curve will be anode potential (E_a) vs. current density at the chosen operating temperature of the cell. The cathode potential (E_c) can be determined by added the cell potential (V_{cell}). A schematic for the anode polarization experiment is shown as Figure 2. Anode polarization experiments are only performed at the end of the experimental series to prevent any anode degradation that may occur as a result of polarizing the anode to high potentials. To ensure that the polarization experiments do not compromise the anode catalyst, the anode polarization potential is kept to a maximum of 650 mV versus the Normal Hydrogen Electrode (NHE).
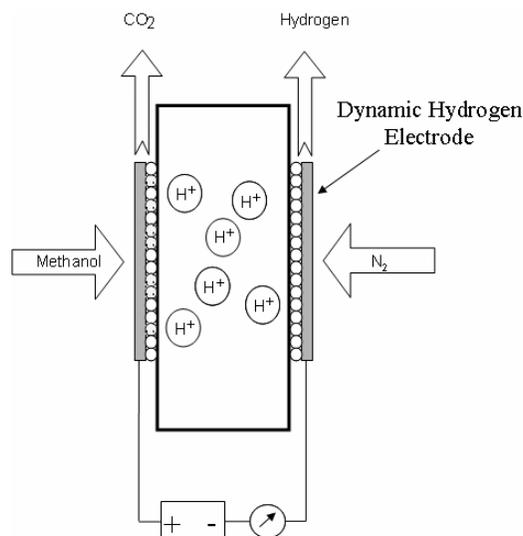

Figure 2. Schematic of the a DMFC operated in anode polarization mode

After electrochemical evaluation, each cell was disassembled and visually inspected for changes to the membrane and gas diffusion backings. For the final analysis, MEAs were sectioned and surveyed using EDAX to determine possible ruthenium dissolution and ruthenium migration from the anode to the cathode.

RESULTS and DISCUSSION

Current-Voltage Performance

Testing in the single cell test stand revealed irreversible voltage decay for all the cells, the test results are shown as Figure 3 and are summarized at select current densities in Table 2. The results indicated that the MEAs fabricated with the *as received* Johnson-Matthey catalyst (JM, JM-STD) performed the best after the durability test. The performance decline is reported as 67 and 96-mV at 100-mA/cm^2 for MEA JM and JM-STD, respectively. It is noted that at an applied load of 50 mA/cm^2, MEA JM and JM-STD shown a performance decline of 6 mV. The MEAs fabricated with JPL's Pt-Ru catalyst (JPL) and the "reduced" Johnson Matthey catalyst (JMR) showed the greater performance decline. The performance decline at 100-mA/cm^2 for MEA JPL and JMR are 150 and 107 mV and 48 and 30 mV at 50-mA/cm^2, respectively.
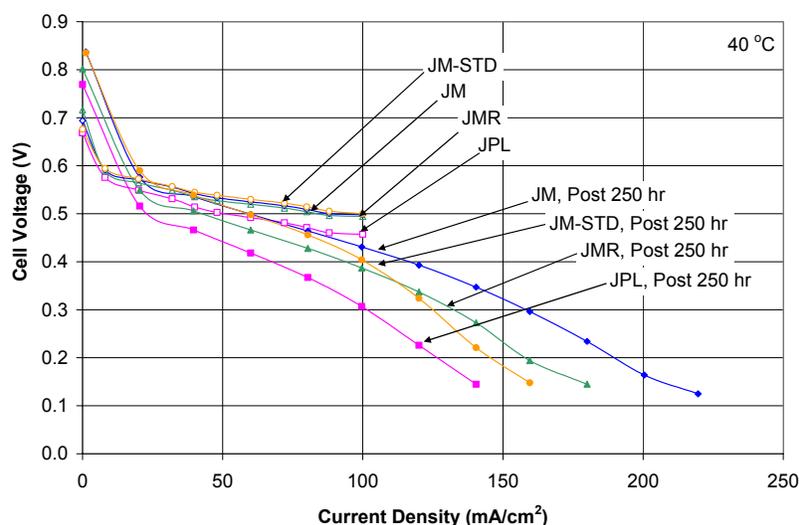
Figure 3. Current-voltage characterization plots for MEAs before and after 250 hour testing. Cell operated at 40 ^{o}C, 0.5M methanol.

Table 2. MEA performance analysis, post 250 hour duration experiment. Performance measured for cells operating at 40 ^{o}C, 0.5M methanol.

MEA	Formulation	Performance Decline (mV)		Performance Decline (mW/cm^2)	
		50 mA/cm^2	100 mA/cm^2	50 mA/cm^2	100 mA/cm^2
JPL	Anode: JPL Cathode: 15% Teflon	48	150	2.4	15
JM	Anode: Johnson Matthey Cathode: 15% Teflon	6	67	0.3	6.7
JMR	Anode: Reduced Johnson Matthey Cathode: 15% Teflon	30	107	1.5	10.7
JM-STD	Anode: Johnson Matthey Cathode: 5% Teflon (Standard)	6	96	0.3	9.6

The current-voltage characterization for the MEA JPL is shown as Figure 4. The initial cell performance at 60 ^{o}C, 0.5M methanol and an applied load of 100-mA/cm^2 is 0.5 Volts. The cell degradation, under the same operating conditions, measured after the 250-hour durability experiment is 61 mV. The rate of voltage decay and power density loss for this MEA is 0.00024-V/hr and 44-mW/cm^2, respectively. The performance loss for the JPL MEA is 12%. The voltage decay observed in this MEA is comparable to previous performance under similar conditions [8] with the exception that losses in this case were irreversible. In the 80-cell stack, we had observed more than 50% loss in performance in less than 100 hours of testing and thus the observations in the 250-hour test did not account for the major loss in performance. Further analysis of the losses in the MEA performance was carried out by separating the polarization losses at the anode from that at the cathode.
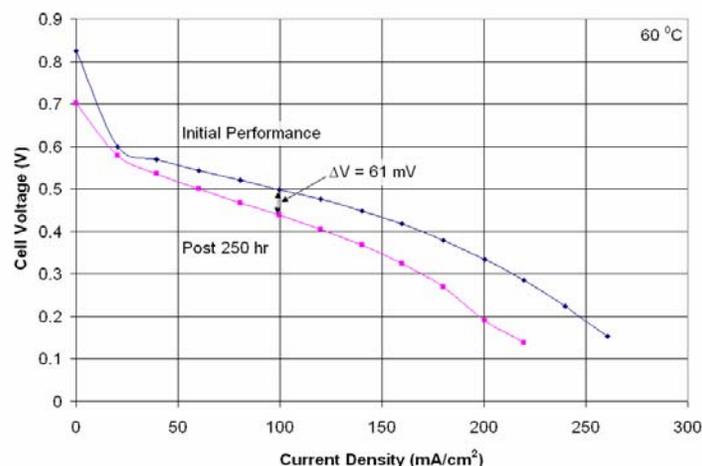
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Figure 4. JPL MEA cell voltage as a function of applied current. The plot was taken for a cell operating at 60 ^{o}C, 0.5M methanol.

Electrode Analysis

Anode polarization experiments were performed on the cells after the current voltage data was obtained. The anode polarization plots for the MEA after the 250-hour test are shown as figure 3. For comparison purposes, an MEA fabricated with Johnson Matthey catalyst with the same catalyst loadings and fabrication technique used to fabricate the other MEAs and has been included initial anode performance and is labeled "Fresh" in Figure 5. The Tafel slopes, measured in the kinetically controlled region, ranged from 110 to 150-mV/decade. The anode performance of each MEA, after the 250-hour durability testing, was similar to that of the freshly prepared MEA. The anode performance of the MEA fabricated with the reduced Johnson Matthey catalyst was similar to the MEA fabricated with the JPL Pt-Ru catalyst. The anode performance of the Johnson Matthey Pt-Ru remained unchanged after the 250-hour test. The data from the anode polarization experiments reveals that at 250 hours of testing, the anode catalyst is stable in DMFC operation.
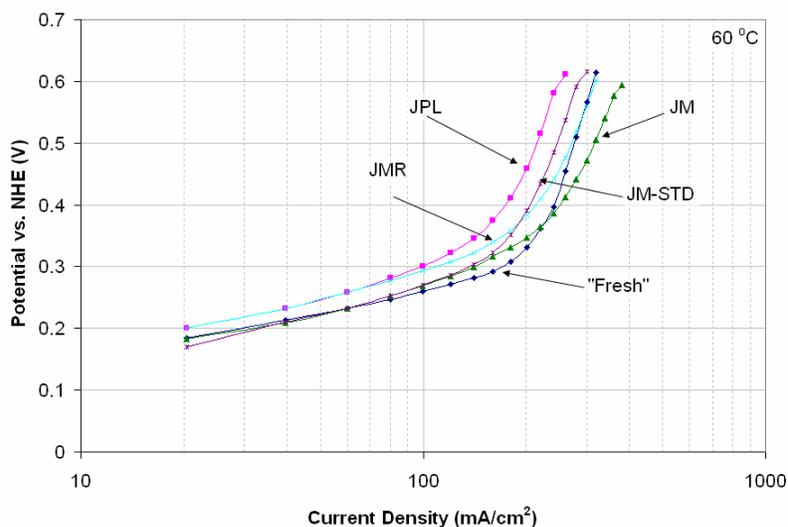

Figure 5. Anode polarization plots for various MEAs operating at 60 ^{o}C, 0.5M methanol, corrected for internal resistance

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The data from the anode polarization experiments was used to separate the cathode performance from cell voltage for the JPL MEA. The cathode polarization for the JPL MEA as a function of applied current density is shown as Figure 6. The initial cathode performance was in the range of 0.82 Volts versus NHE and is flat during the polarization. After the 250 hours of operation, the cathode performance is below 0.8 Volts and now appears to be operating under mass transfer limitations. The loss in cathode potential at an applied current of 100-mA/cm^2 is 59 mV. Comparing the cathode degradation to cell degradation reported in Figure 4 show that the cathode is more affected than the anode by long-term operation in a DMFC.
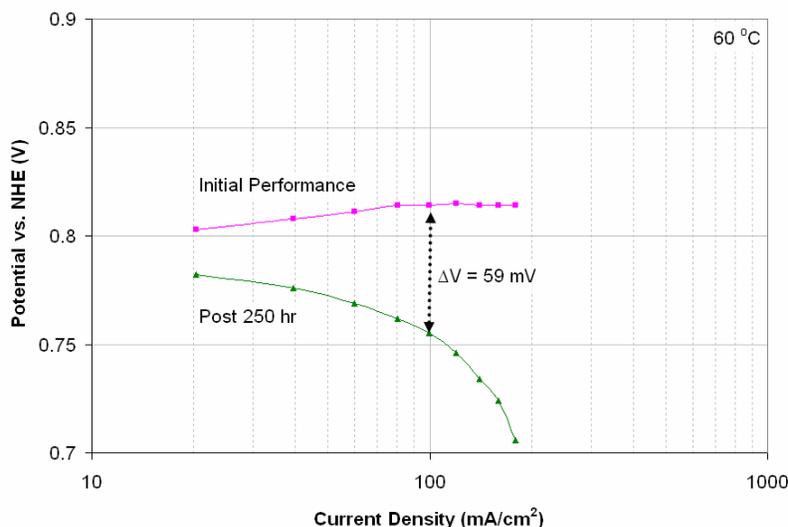

Figure 6. IR corrected cathode polarization plots for the JPL MEA before and after the 250 hour duration experiments. The polarization plots were taken for the cell operating at 60 ^{o}C, 0.5M methanol.

Cell Disassembly

After electrochemical testing each of the cells were disassembled and inspected. Water droplets were used to examine the wettability of the MEA cathodes after the 250-hour test. The electrode structures compared in Figure 7 are 15% Teflon content paper before and after duration testing, 5% Teflon content paper after duration testing, and paper with no Teflon content. The hydrophobic character of the paper appears to be affected only slightly by the extended testing. Both the 15% and 5% paper did show a slight reduction of hydrophobicity after the long-duration test. However, these structures were still largely hydrophobic when compared to the MEAs that were removed from the 80-cell stack. Based on the results of the 250 hour test, the MEAs made from the Johnson-Matthey anode catalyst (JM, JM-STD) and the 15% paper showed the lesser performance decline.
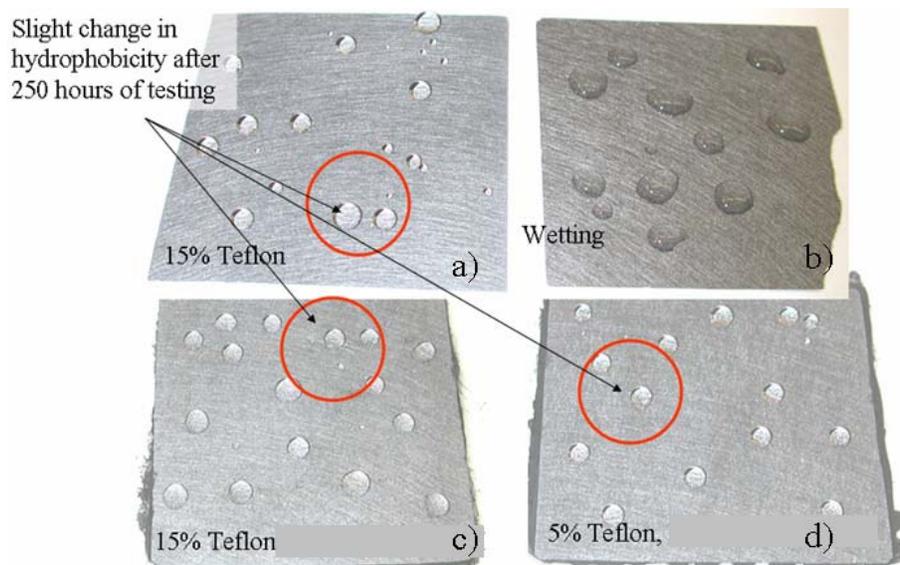
Figure 7. Comparison of wettability of the various backing paper structures, a) 15% Teflon treated prior to operation, b) wetting, c) 15% Teflon treated post duration testing, d) 5% Teflon treated post duration testing.

EDAX Analysis

The ruthenium and platinum distribution across the MEA was investigated using EDAX analysis. All four of the MEAs subjected to the 250-hour test were studied using EDAX analysis. The results for the MEA fabricated with JPL anode catalyst is shown as Figure 8, these results are typical of all the MEAs tested. EDAX analysis focused on detecting carbon, oxygen, ruthenium, platinum, and fluorine. As highlighted in figure 8, within the detectable limit of the EDAX technique, no ruthenium was found at the cathode. Thus, the EDAX analysis has shown that the commercial platinum-ruthenium catalyst, the JPL catalyst and the reduced JM catalyst are all stable during the 250-hour DMFC operation and that catalyst stability is not likely to be an issue for normal long duration operation.
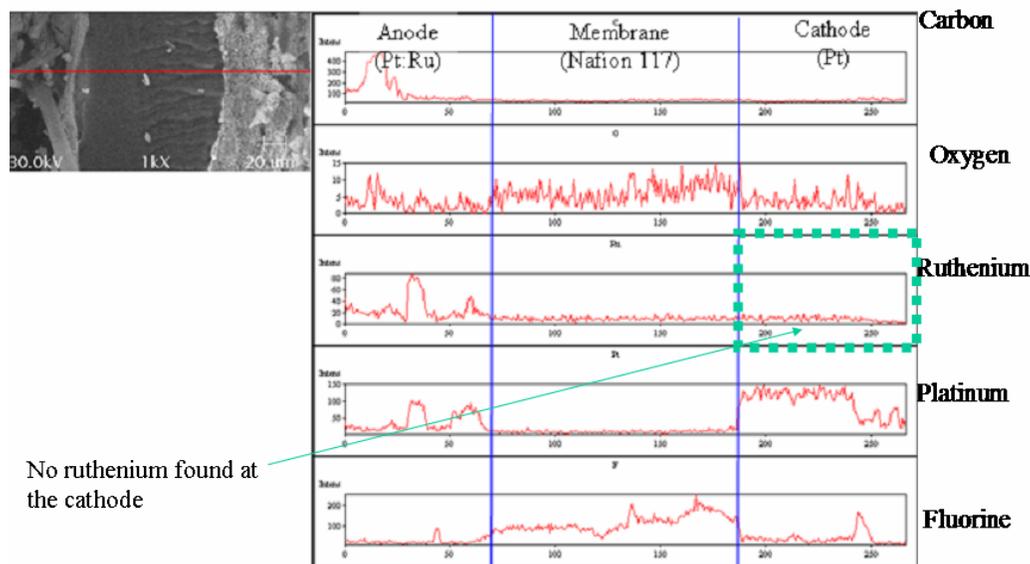

Figure 8. Cross-section EDAX analysis of JPL MEA

Mechanism of Stack Degradation

The loss in performance observed in the 250-hour durability testing of various MEAs showed a maximum 12% loss in performance. Thus, the observations from the 250-hr test did not account for the 50% loss in performance observed in the stack. These results suggest that any instability that might exist with the commercial platinum-ruthenium catalyst or the 5% Teflon content in the cathode paper does not explain the excessive ruthenium dissolution and the loss of hydrophobicity of the cathode of the MEAs in the 80-cell stack. Consequently, the degradation in stack performance found in the 80-cell stack of the 300-Watt system is attributed to over-discharge of the anode. Such over-discharge would arise from shunt currents sustained in the stack as a result of the stack design. The 80-cell stack is shown as Figure 9.
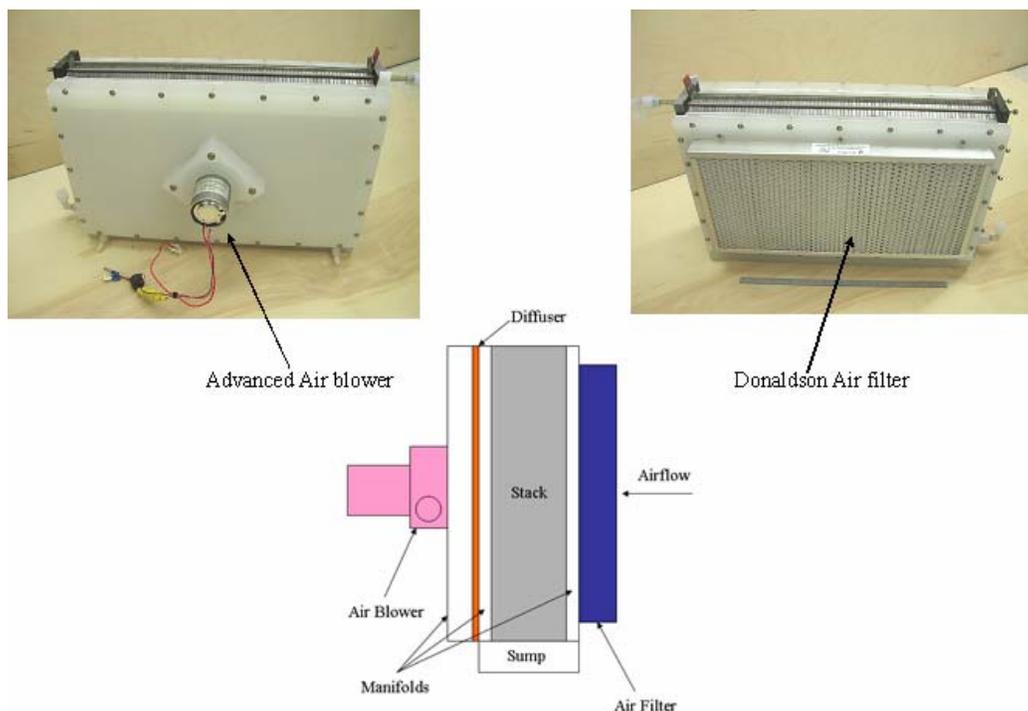

Figure 9. 80-Cell DMFC stack built for the 300-Watt power source

In the 80-cell stack, air is drawn into the stack through an air filter which is mounted to an open-to-air cathode face. In this stack design, the cathode compartments always have continuous access to air. Also, the liquid manifold of methanol solution saturated with carbon dioxide provides a path for shunt currents. When the stack voltage is over 1.23 V, electrolysis currents can be sustained through the manifold, and these are called shunt currents. The shunt currents are powered by the fuel cell reaction. These shunt currents lead to electrolysis of water. When the manifold and the cells are supplied with fuel during normal operation, the shunt current is just a parasitic loss and not a cause for concern. However, when the fuel distribution and oxidant distribution is not uniform in the stack, this can have deleterious consequences. Under these circumstances those cells with an adequate fuel and oxidant supply will have a high positive voltage, and others will a low cell voltage. However, the total stack voltage for an 80-cell stack may be still high enough to sustain electrolysis as shown in Figure 10. These electrolysis currents (also termed shunt currents) will flow through all the cells and will result in over-discharging (driving the voltage to negative values) those cells with a low supply of fuel.
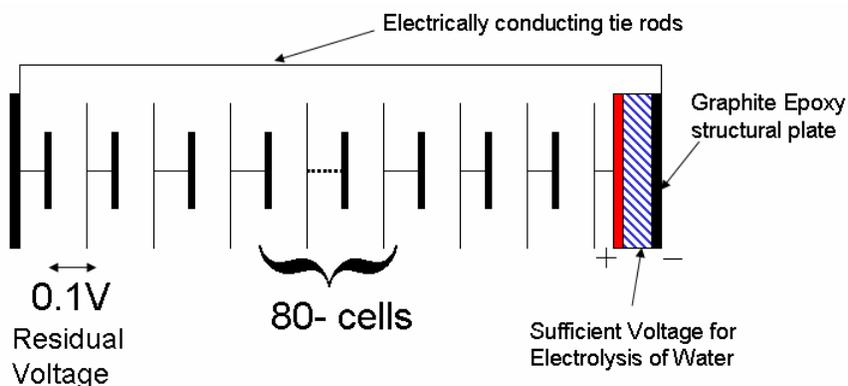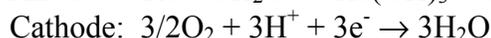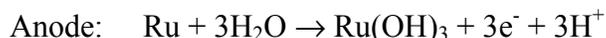
Figure 10. Electrolysis and Over-discharge in a DMFC stack

Thus, in the absence of fuel, the cells would be driven into polarity reversal, and the anode will be raised to potentials greater than 0.8 V, the cathode potential in the presence of air. When the anode potential is higher than 0.8V, the dissolution of ruthenium can occur. These processes and reactions are summarized as follows:

1. Reactions without methanol at the anode:
    Anode: $Ru + 3H_2O \rightarrow Ru(OH)_3 + 3e^- + 3H^+$
    Cathode: $3/2O_2 + 3H^+ + 3e^- \rightarrow 3H_2O$
2. Ru^{3+} migrates through the Nafion membrane
3. Ruthenium reaction at the Cathode:
          $2Ru(OH)_3 + 1/2O_2 \rightarrow 2RuO_2 + 3H_2O$
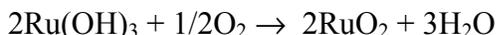
Thus, the most probable cause of the ruthenium dissolution observed in the 300-Watt system stack was attributed to the over-discharge of the cells.

CONCLUSIONS

Durability testing was performed in single cell MEAs to determine the pathway of cell degradation. The tests showed that degradation in DMFC MEAs occurs in short periods of operation (250 hours). Electrode polarization analysis revealed that the MEA performance loss is attributed to the changes in the cathode. EDAX analysis of MEA cross-sections and water drop experiments on the MEA cathodes showed that the performance degradation could not be attributed to either large scale ruthenium dissolution or dramatic changes in the hydrophobicity of the cathode backing papers. Thus, dissolution of ruthenium observed in the 80-cell stack was attributed to over-discharge of the anode. The open-to-air cathode stack design used in the study was capable of sustaining shunt currents across the stack at all times because of the plentiful access to air. When shunt currents are forced through cells where methanol is absent from the anode compartment, the anode potential reaches values where ruthenium in the platinum-ruthenium anode catalyst starts to dissolve. Over-discharge is the most plausible explanation for the substantial amounts of ruthenium observed at the cathode in the 80-cell stack. Ruthenium dissolution in a DMFC stack can be prevented by developing internally manifolded stacks that seal reactant compartments and bring cell voltages to zero quickly when not in operation.

ACKNOWLEDGEMENTS

REFERENCES

1. T. Valdez, A. Abtahi, F. Clara, M.L. Young, and S. Narayanan, Direct Methanol Fuel Cell System for Armored Vehicle Applications, 2004 Joint International Meeting of the Electrochemical Society, Abstract# 1486, 2004

2. Abdou , "Direct Methanol Fuel Cell MEAs", Abstract #264, Fuel Cell Seminar, San Antonio, Nov 1-4, 2004.

3. P. Piela, C. Eickes, E. Brosha, F. Garzon and P. Zelenay, Ruthenium Crossover in Direct Methanol Fuel Cell, J. of The Electrochemical Society, 151 (12) A2053-A2059, 2004

4. Narayanan et al, Patent No: 6221,523, Direct Deposit of Catalyst on the Membrane of Direct Feed Fuel Cells.

5. T. I. Valdez and S. R. Narayanan, Effect of Fabrication Technique on Direct Methanol Fuel Cells Designed to Operate at Low Airflow. Proceeding to the 202nd Electrochemical Society Meeting, to be published. (2005)

6. T. I. Valdez and S. R. Narayanan, Recent Studies on Methanol Crossover in Liquid-Feed Direct Methanol Fuel Cells, Proton Conducting Membrane Fuel Cells II, The Electrochemical Society proceedings volume 98-27, Edited by S. Gottesfeld and T.F. Fuller, 1998, Pages 380-387

7. J T. Mueller and P. M. Urban, J of Power Sources, 75, 139-143, 1998

8. T. I. Valdez, S. R. Narayanan and N. Rohatgi, Development of a 150-Watt direct methanol fuel cell system, 15th Annual Battery Conference on Application Advances Proceedings, Long Beach, CA., 2000, Pages 37-40