Steady State and Accelerated Decay Rate Evaluations of Membrane Electrode Assembly of PEM Fuel Cells

Yingjeng James Li, Lung-Yu Sung, Andrew S. Lin, Huan-Jyun Ciou

Abstract—Durability of Membrane Electrode Assembly for Proton Exchange Membrane Fuel Cells was evaluated in both steady state and accelerated decay modes. Steady state mode was carried out at constant current of 800mA/cm² for 2500 hours using air as cathode feed and pure hydrogen as anode feed. The degradation of the cell voltage was 0.015V after such 2500 hrs operation. The degradation rate was therefore calculated to be 6uV/hr. Continuously Vigorous fluctuation of the cell voltage, which was switched between OCV and 0.2V, was employed for the accelerated decay mode. No obvious change in performance of the MEA was observed after 10000 cycles of such operation.

Keywords—Durability, lifetime, membrane electrode assembly, proton exchange membrane fuel cells.

I. INTRODUCTION

 Γ^{UEL} cells receive much attention due to their high energy efficiency in comparison with internal combustion engines. In addition, a fuel cell is a zero emission device if hydrogen is employed as the fuel. Therefore, fuel cells are environmentally friendly and can dramatically reduce the pollution of on-site operation. Among the six types of fuel cells, a Proton Exchange Membrane Fuel Cell (PEMFC) operates at lower temperature and has a higher power density. Suitable power range of PEMFCs extends from tens of watts to hundreds of kilowatts. They are most suitable for applications as the power source for electric vehicles as well as many portable and stationary power demands [1]-[7]. For practical applications, the minimum operation lifetime of a PEMFC for vehicle and stationary power unit is 4,000 and 40,000 hours, respectively. In a stricter point of view, it has to be 8,000 and 80,000 hours, respectively. However, such time could be tedious and bothersome for routine fuel cell's durability evaluation works. Therefore, a "decay rate" or an accelerated aging process is usually applied for evaluating the durability of the membrane electrode assembly (MEA) and/or a fuel cell. There are a few proposals/standards for the durability tests of a fuel cell; however, publicly available data

Yingjeng James Li is with the Department of Chemical Engineering, Ming Chi University of Technology, New Taipei City 24301, Taiwan (corresponding author to provide phone: +886-2-29089899, ext. 4622; fax: +886-2-29082703; e-mail: yjli@mail.mcut.edu.tw).

Lung-Yu Sung is with the Green Energy and Environment Research Laboratories, Industrial Technology Research Institute. Hsinchu 310, Taiwan. (e-mail: RichardSung@itri.org.tw)

Andrew S. Lin is with the Department of Chemical and Materials Engineering, Chang Gung University, Taoyuan City 333, Taiwan (e-mail: Andrew@mail.cgu.edu.tw)

Huan-Jyun Ciou is with the Graduate Institute of Chemical Engineering, Ming Chi University of Technology, New Taipei City 24301, Taiwan (e-mail: a0939082525@gmail.com).

regarding the durability evaluation of MEA for fuel cells are not many [8]-[13]. Here we report the results of two modes of durability evaluation of MEA for PEM fuel cells.

II. EXPERIMENT

A. MEA and Single Cell

The three-layered MEA (Fig. 1), also referred as catalyst (CCM), with active area membrane 5cm*5cm=25cm² was supplied by Yangtze Energy Technologies, Inc. Such MEA was prepared by coating carbon supported platinum catalyst (40% Pt/C supplied from Tanaka) onto DuPont's HP proton exchange membrane. The catalyst loading was 0.2mg Pt/cm² on anode side, and 0.4mg Pt/cm² on cathode side. SGL 10BC carbon papers were applied as the gas diffusion layers (GDLs) for the sample employed for steady state experiment; while CeTech 260GDL carbon papers were applied as the GDLs for the sample employed for accelerated decay experiment. The MEA was assembled into a single cell fuel cell test fixture, which has a triple channel serpentine flow field (Fig. 2). The thicknesses of the gaskets were selected so that the degree of compression of the GDLs was 30-35%. Therefore, the thicknesses of the GDL, after compression, were 70-65% of those of the original GDLs. Accordingly, two different sets of gaskets were employed because the thicknesses of SGL 10BC and CeTech 260 are not the same.

B. Operation Condition

The temperature of the single cell, humidifiers, and gas feed tubing are all set at 65°C. The flow rate is 1.2 stoics for hydrogen (anode) and 3.0 stoics for air (cathode). The gas outlets on the test fixture were set open so that the experiment was carried out at ambient pressure for the steady state operation. However, in order to pick up the gas flows for loading following, the pressure was set at 35kPa for the accelerated decay experiment. The measurements were performed employed a Tension Energy Inc. Fuel Cell Test Station, model number TEI-P600-1AANAS.

C. Steady State Operation

The cell was set to undergo electric loading at constant current of 20 Amperes. Such current corresponds to a current density of 800mA/cm². The operation was 24hr non-stop during weekdays. It was shut down during weekends owing to safety consideration. The experiment was carried out until a total of 2500 hours were accumulated.



Fig. 1 Three-layered MEA, i.e. CCM, supplied by Yangtze Energy Technologies, Inc. was employed in this study

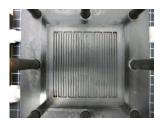


Fig. 2 MEA test fixture employed in this study has a triple channel serpentine flow field and an area of 25cm²

D.Accelerated Decay Operation

Accelerated mode was carried out by switching the voltage of the single cell between OCV and 0.2V. The durations held at OCV and 0.2V were 20 and 40 seconds, respectively. Such setting represents the cycle time of one minute per cycle. The cell was allowed to undergo consecutive 500 cycles each operation day. Polarization curves were taken before and after the cycling. Such operation was accumulated for 20 days so that there were 10,000 cycles and 40 polarization curves.

III. RESULTS AND DISCUSSION

A. Steady State Operation

The results of the steady state operation are shown in Fig. 3. During the course of steady state operation, the fuel cell test station encountered humidifier dry-out for four times. Such dry outs correspond to the decrease of performance of the MEA. However, MEA's performance was restored when the fuel cell test station's humidifiers were refilled with water. In addition, permanent damage was not found for MEA experienced such dry operation conditions. From Fig. 3, the cell voltage at 800mA/cm^2 current density decrease from 0.630 V at the beginning to 0.615 V after 2500 hours of accumulated operation. According to this, its decay rate is $6 \mu \text{V/hr}$. Such decay rate represents a relative good and acceptable performance.

B. Accelerated Decay Study

In this study, we employed one of the most extreme operation conditions for evaluation of the durability of MEA. As illustrated in the experimental section, the operations were under vigorous variations both in electric loading and gas flow rates. A total of 10000 such cycles were performed. Part of the data was shown in Fig. 4, in which 9501st-to-10000th cycles and two polarization scans, one before and the other one after the cycling were illustrated. These two polarization scans are

redrawn as curves of voltage versus current density as in Fig. 5.

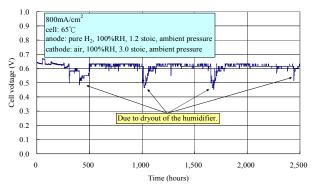


Fig. 3 Steady state durability test results of the membrane electrode assembly

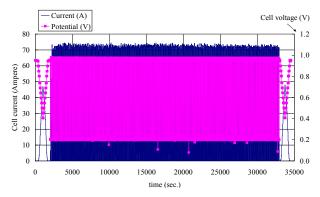


Fig. 4 Representative results of the 500 OCV-0.2V cycling. Results shown here are the data of 9501-10000 cycles

A total of 20 sets of cycling and 40 polarization curves were recorded. Cell current density at 0.7V, 0.6V, and 0.5V before and after the cycling were summarized in Table I. During the cycling, there was a slight decay in current density at a certain operation voltage. For example, by comparing the current densities at 0.7V of the cell before the cycling (the 2^{nd} column in Table I), we can calculate the decay rate to be $4.8\mu A/cycle$ (Fig. 6 (a) red line). However, the decay rate will be only $1.0\mu A/cycle$ if calculated from the least decayed curve, which is the polarization at 0.7V after cycling (Fig. 6 (b) blue line). Figs. 6 (b) and (c) show the variation of MEA current density at 0.6V and 0.5V, respectively.

Efforts had been paid to understand the degradation mechanism of the proton exchange membrane employed for fuel cell application [14]-[22]. Sethuraman et al. [22] showed that frequent start-stop cycles, which associate with frequent wetup-dryout cycles, can cause mechanical stress to the membrane and affect the stability and durability of the MEA. However, it also has been pointed out that the gradual washout of the hydrophobic component in the gas diffusion media by the gas flow can be the major cause of degradation of the overall performance of a fuel cell. Losing the hydrophobic component, the GDL will pick-up water which hinder the transport of reacting gases [23], [24]. Such phenomenon

usually can be observed by examining the low voltage portion of the polarization curves.

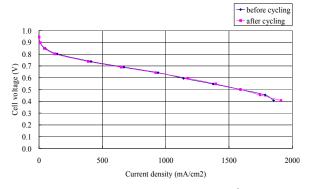


Fig. 5 MEA Polarization performed before the 9501st cycle and after the 10000th cycle

 $TABLE\ I$ Current density of the mea at 0.7v, 0.6v, and 0.5v before and after the cycling

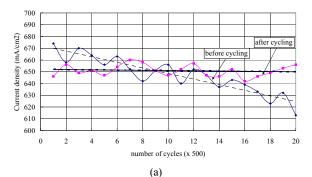
| THE CYCLING | | | | | | | |
|--|---|------|------|------------------|---|------|------|
| n th day of operation | current density (mA/cm²) before cycling | | | number of cycles | current density (mA/cm²) after cycling | | |
| | 0.7V | 0.6V | 0.5V | 0,0103 | 0.7V | 0.6V | 0.5V |
| 1 | 674 | 1180 | 1617 | 1-500 | 646 | 1148 | 1575 |
| 2 | 658 | 1162 | 1589 | 510-1000 | 656 | 1149 | 1591 |
| 3 | 670 | 1168 | 1590 | 1001-1500 | 649 | 1176 | 1591 |
| 4 | 664 | 1164 | 1578 | 1501-2000 | 651 | 1176 | 1590 |
| 5 | 656 | 1161 | 1570 | 2001-2500 | 647 | 1150 | 1574 |
| 6 | 663 | 1165 | 1579 | 2501-3000 | 654 | 1170 | 1577 |
| 7 | 652 | 1152 | 1571 | 3001-3500 | 660 | 1180 | 1590 |
| 8 | 642 | 1147 | 1555 | 3501-4000 | 658 | 1160 | 1582 |
| 9 | 651 | 1152 | 1570 | 4001-4500 | 651 | 1170 | 1575 |
| 10 | 656 | 1154 | 1575 | 4501-5000 | 647 | 1145 | 1570 |
| 11 | 640 | 1145 | 1546 | 5001-5500 | 652 | 1168 | 1575 |
| 12 | 652 | 1152 | 1568 | 5501-6000 | 657 | 1174 | 1585 |
| 13 | 647 | 1149 | 1560 | 6001-6500 | 647 | 1152 | 1577 |
| 14 | 637 | 1143 | 1540 | 6501-7000 | 646 | 1150 | 1573 |
| 15 | 643 | 1149 | 1560 | 7001-7500 | 652 | 1148 | 1572 |
| 16 | 639 | 1146 | 1550 | 7501-8000 | 642 | 1140 | 1569 |
| 17 | 633 | 1142 | 1535 | 8001-8500 | 646 | 1150 | 1576 |
| 18 | 623 | 1139 | 1520 | 8501-9000 | 649 | 1158 | 1581 |
| 19 | 632 | 1142 | 1524 | 9001-9500 | 653 | 1160 | 1573 |
| 20 | 613 | 1144 | 1521 | 9501-10000 | 656 | 1163 | 1577 |
| average | 647 | 1153 | 1561 | | 651 | 1159 | 1579 |

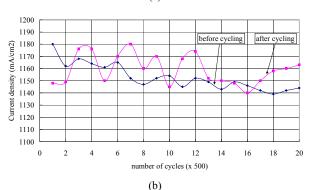
As the lifetime evaluation of the MEA is still ongoing. Here in this paper we report the overall performance of the MEA throughout the durability test to date. Detailed examinations such as catalyst activity by CV, ionic conducting behavior by AC impedance, hydrogen crossover by linear sweep voltammetry will be followed.

IV. CONCLUSION

In this work, we have performed a steady state operation and an accelerated decay mode with vigorous vibration in both current density and gas flows for the evaluation of the durability of the MEA supplied by Yangtze Energy Technologies, Inc. The steady state mode showed that the

decay rate of the MEA is $6\mu V/hr$, while the accelerated decay mode employed in this study showed that there is $4.8\mu A/cycle$ decay at the 0.7V region when performed before each set of cycling; however, there is negligible decay at the same 0.7V when performed after the cycling. In general, the MEA investigated in this study represents a stable and reliable performance.





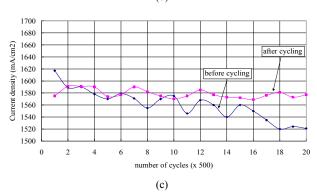


Fig. 6 Changes of MEA current density before and after accelerated decay cycling. (a) at 0.7V, (b) at 0.6V, (c) at 0.5V

ACKNOWLEDGMENT

This research was financially supported by Bureau of Energy of the Ministry of Economic Affairs (MOEA) and Ming Chi University of Technology, Taiwan. We also greatly appreciate the assistance given by the Fuel Cell Laboratory of GEL/ITRI (Green Energy and Environmental Laboratories/Industrial Technology Research Institute) in the long-term durability test. Thanks were also given to Yangtze Energy Technologies, Inc. for providing MEA samples for this work.

REFERENCES

- [1] E. Antolini, J. Appl. Electrochem. 34 (2004) 563-576.
- [2] M. Conte, A. Iacobazzi, M. Ronchetti, R. Vellone, J. Power Sources 100 (2001) 171–187.
- [3] F. Jing, M. Hou, W. Shi, J. Fu, H. Yu, P. Ming, B. Yi, J. Power Sources 166 (2007) 172–176.
- [4] S. Litster, G. McLean, J. Power Sources 130 (2004) 61-76.
- [5] S. Maass, F. Finsterwalder, G. Frank, R. Hartmann, C. Merten, J. Power Sources, 176 (2008) 444–451.
- [6] Mehta, J.S. Cooper, J. Power Sources 114 (2003) 32-53.
- [7] K. Scott, A.K. Shukla, Rev. Environ. Sci. Bio/Technology 3 (2004) 273–280
- [8] D.P. Wilkinson, J. St-Pierre, in Handbook of Fuel Cells, vol. 3, John Wiley & Sons Ltd., 2003, pp.611-626.
- [9] O. Yamazaki, M. Echigo, T. Tabata, Abstracts from Fuel Cell Seminar, 2002, Palm Springs, CA, November, 2002, pp. 105–108.
- [10] M. Hicks, D. Ylitalo, Abstracts from Fuel Cell Seminar 2003, Miami Beach, FL, November, 2003, pp. 97–99.
- [11] S.J.C. Cleghorn, J.A. Kolde, Abstract from Fuel Cell Seminar 2003, Miami Beach, FL, November 2003, pp. 832–835.
- [12] M. Takahashi, N. Kusunose, M. Aoki, A. Seya, Abstracts from Fuel Cell
- Seminar 2002, Palm Springs, CA, November 2002, pp. 74–77.

 [13] S.D. Knight, K.M. Colbow, J. St-Pierre, D. Wilkinson, J. Power Sources 127 (2004) 127–134.
- [14] C. Iojoiu, E. Guilminot, F. Maillard, M. Chatenet, J.-Y. Sanchez, E. Claude, E. Rossinot, J. Electrochem. Soc. 154 (2007) B1115–B1120.
- [15] C. Chen, G. Levitin, D.W. Hess, T.F. Fuller, J. Power Sources 169 (2007) 288–295.
- [16] E. Guilminot, A. Corcella, M. Chatenet, F. Maillard, F. Charlot, G. Berthome, C. Iojoiu, J.-Y. Sanchez, E. Rossinot, E. Claude, J.
- Electrochem. Soc. 154 (2007) B1106–B1114.
 [17] J. Healy, C.Hayden, T. Xie, K. Olson, R.Waldo, M. Brundage, H. Gasteiger, J.Abbott, Fuel Cells 5 (2005) 302–308.
- [18] T. Kinumoto, M. Inaba, Y. Nakayama, K. Ogata, R. Umebayashi, A. Tasaka, Y. Iriyama, T. Abe, Z. Ogumi, J. Power Sources 158 (2006) 1222–1228.
- [19] S. Kundu, M.W. Fowler, L.C. Simon, S. Grot, J. Power Sources 157 (2006) 650–656.
- [20] S. Kundu, L.C. Simon, M.W. Fowler, Polym. Degrad. Stab. 93 (2008) 214–224.
- [21] H. Tang, S. Peikang, S.P. Jiang, F. Wang, M. Pan, J. Power Sources 170 (2007) 85–92.
- [22] V.A. Sethuraman, J.W. Weidner, A.T. Haug, L.V. Protsailob, J. Electrochem. Soc. 155 (2008) B119–B124.
- [23] J. St-Pierre, N. Jia, J. New Mater. Electrochem. Syst. 5 (2002) 263–271.
- [24] S.J.C. Cleghorn *, D.K. Mayfield D.A. Moore, J.C. Moore, G. Rusch, T.W. Sherman, N.T. Sisofo, U. Beuscher, Journal of Power Sources 158 (2006) 446–454.