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Fuel Cell Perfluorinated Sulfonic Acid Membrane Degradation Correlating Accelerated and Lifetime Testing

Marianne P. Rodgers, R. Paul Brooker, Nahid Mohajeri, Leonard J. Bonville, H. Russell Kunz, Darlene K. Slattery, James M. Fenton
Florida Solar Energy Center-University of Central Florida
1679 Clearlake Road, Coca, FL 32922

Introduction

Proton exchange membrane (PEM) fuel cell durability is a major impediment to their widespread commercialization. Fuel cell components must endure a wide range of operating and cyclic conditions, which adds complexity to the fuel cell system and impacts its durability.

Understanding and mitigation of fuel cell failure mechanisms is accomplished by lifetime and accelerated testing. Knowledge of the degradation mechanisms is necessary to guarantee that the test protocols do not ignore potential degradation mechanisms or introduce mechanisms that do not occur during regular operation. To establish a universal procedure to determine and predict the durability of PEM fuel cell components in practical applications, it is desirable to assess the extent to which accelerated stress tests (ASTs) amplify cell degradation compared to lifetime tests.(1)

Membrane Decay

Failure of PEMs is a result of many factors, including manufacturing/design issues,(2) material characteristics, (3-6) and operational conditions.(7,8) These factors result in failure through thermal, mechanical, and chemical modes, of which chemical and mechanical degradation are generally considered the most important.

Chemical degradation – PEMs are attacked by radicals formed by the reaction of hydrogen and oxygen on the surface of platinum. In addition to the electrodes, radical formation occurs on the Pt particles that migrate into the PEM during fuel cell operation. Membrane chemical decay is accelerated by several test methods, including running tests at open circuit.

Mechanical degradation – Mechanical failure is often life-limiting and is related to chemical decay, which damages the mechanical integrity of the membranes. Membrane mechanical decay results from the formation and growth of a small number of defects. As fuel cell operating conditions change, the constrained PEM swells and shrinks. This can result in mechanical failure and/or delamination of the catalyst layer. Mechanical decay is accelerated by relative humidity cycling.

Fuel Cell Tests

Lifetime Tests – Lifetime tests are typically carried out in static conditions with the voltage or current density held constant for hundreds or thousands of hours.

Accelerated Stress Testing – Lifetime tests are not always practical because of the time and resources involved. However, accelerated degradation conditions can be used to determine membrane degradation characteristics. (9,10)

Drive Cycle Tests – To simulate automotive applications, drive cycle tests are used in which power density is continuously and cyclically varied. Because these tests are performed under real operating conditions, they provide the most relevant PEM lifetime data.

Results from Lifetime and Accelerated Testing

The failure modes observed after a literature survey of lifetime tests, including fluorine and sulfur loss, hydrogen crossover, PEM thinning, electrical shorts, increased resistance, catalyst degradation, electrochemically active area reduction, and Pt particle size increase appear to be consistent with the understood degradation mechanisms.

The failure modes observed after ASTs, including membrane thinning, hydrogen crossover, fluoride and sulfate ion detection, and growth of catalyst clusters were quite similar to those observed for the lifetime tests, demonstrating that the ASTs offer suitable accelerating conditions. After the ASTs, additional degradation modes that were not described in the lifetime tests, including pinhole formation, tearing, and creep, were also observed. Degradation rates for the ASTs were considerably higher than those from the lifetime tests, which is unsurprising and signifies accelerated degradation.

The observed degradation modes were consistent with the specific AST used. For example, RH cycling, which is intended to increase mechanical degradation of PEMs, resulted in increased hydrogen crossover, creep, and fatigue.(4,11) When open circuit voltage was used, degradation modes included radical formation and increased gas crossover.(4,12,13)

Conclusions

This study demonstrates that the AST protocols reproduce the failure mechanisms associated with testing in real time without introducing new failure mechanisms. It is difficult to conclusively assess the acceleration factors of ASTs because each test had different materials and hardware, lifetime and accelerated test protocol, and methods and measurements to characterize degradation. It is desirable that standard materials, tests, and methods are used to accurately assess the amplifications of degradation.

References

1. MP Rodgers, RP Brooker, N Mohajeri, LJ Bonville, HR Kunz, DK Slattery, JM Fenton, *J Electrochem Soc*, **159**, F338 (2012).
2. AB LaConti, M Hamdan, RC McDonald, in *Handbook of Fuel Cells: Fundamentals, Technology and Applications*, W Vielstich, A Lamm, H Gasteiger Editors, p. 647, John Wiley & Sons, Chichester, England (2003).
3. CH Paik, T Skiba, V Mittal, S Motupally, T Jarvi, *ECS Meeting Abstracts*, **501**, 771 (2006).
4. MF Mathias, R Makharia, HA Gasteiger, JJ Conley, TJ Fuller, C Gittleman, S Kocha, D Miller, C Mittelsteadt, T Xie, *Electrochem Soc Interface*, **14** (2005).
5. MP Rodgers, BP Pearman, N Mohajeri, LJ Bonville, DK Slattery, *Electrochim Acta*, **100**, 180 (2013).
6. MP Rodgers, N Mohajeri, LJ Bonville, DK Slattery, *J Electrochem Soc*, **159**, B564 (2012).
7. DP Wilkinson, J St-Pierre, in *Handbook of Fuel Cells: Fundamentals, Technology and Applications*, W Vielstich, HA Gasteiger, A Lamm Editors, p. 611, John Wiley & Sons, Chichester, England (2003).
8. E Endoh, S Terazono, H Widjaja, Y Takimoto, *Electrochem Solid-State Let.*, **7**, A209 (2004).
9. R Borup, J Meyers, B Pivovar, YS Kim, R Mukundan, N Garland, D Myers, M Wilson, F Garzon, D Wood, P Zelenay, K More, K Stroh, T Zawodzinski, J Boncella, JE McGrath, M Inaba, K Miyatake, M Hori, K Ota, Z Ogumi, S Miyata, A Nishikata, Z Siroma, Y Uchimoto, K Yasuda, K Kimijima, N Iwashita, *Chem Rev*, **107**, 3904 (2007).
10. X-Z Yuan, H Li, S Zhang, J Martin, H Wang, *J Power Sources*, **196**, 9107.
11. B Lakshmanan, W Huang, D Olmeijer, JW Weidner, *Electrochem Solid-State Lett*, **6**, A282 (2003).
12. L Protsailo in *DOE Hydrogen Program Review*, Arlington, VA (2006).
13. T Kazuhiro, K Kentaro, T Shohji, H Shuichiro, *Electrochem Solid-State Lett*, **9**, A475 (2006).