

LA-UR- 98-4128

Approved for public release;
distribution is unlimited.

Title:

CORROSION TESTING OF STAINLESS STEEL FUEL CELL HARDWARE

Author(s):

Mahlon S. Wilson - MST-11
Christine Zawodzinski - MST-11
Shimshon Gottesfeld - MS-11

Submitted to:

1998 Fuel Cell Seminar
Palm Springs, CA
November 1998

RECEIVED
AUG 18 1999
OSTI

Los Alamos

NATIONAL LABORATORY

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the University of California for the U.S. Department of Energy under contract W-7405-ENG-36. By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy. The Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

This hardware has been successfully demonstrated in a 2000 h life-test of a single PEFC operating on pressurized and humidified H₂/air (3) and more recently has been implemented in short stacks of 2-4 cells (2). In the 2000 h life-test, the fuel cell was operated continuously at 0.5 V and its performance over the time period was monitored through polarization curves and high frequency resistance (HFR) measurements. If the metal hardware was corroding, it would be expected that the HFR would increase over time due to metal ion uptake by the membrane, accompanied by a corresponding loss in cell performance. For about the first 1700 hours, the cell maintained a power density output of 0.45-0.5 W/cm², after which it exhibited some loss in performance due to problems associated with flooding in one of the hardware components, the design of which has since been corrected. The HFR remained steady over the entire 2000 hour period, with only minor fluctuations which were probably a direct result of water management within the cell. Overall, the cell performed very well, and upon taking it apart, no visual evidence of corrosion of the hardware was observed.

Chemical analysis tests were carried out on the cell water and membrane/electrode assembly (MEA). Water was collected from the cell outlets of the 2000 h cell and from a short stack. The water was analyzed by ICP-MS and ICP-ES for metals such as Ni, Cr, Mo, and Fe. Table 1 shows the data obtained from the 2000 h test cell and a 4-cell stack.

Table 1: Comparison of inlet and outlet water for 2000 h life-test cell and 4-cell stack based on 316 SS metal hardware components.

Sample	Ni (ppm)	Cr (ppm)	Mo (ppm)	Fe (ppm)
Cathode inlet H ₂ O from test station	0.190 ± 0.030	< 0.005	< 0.005	< 0.040
Cathode outlet H ₂ O from 2000 h cell	0.011 ± 0.005	< 0.005	< 0.005	< 0.040
Cathode outlet H ₂ O from 4-cell stack	0.035 ± 0.009	0.050 ± 0.020	0.007 ± 0.005	0.740 ± 0.07
Anode inlet H ₂ O from test station	0.220 ± 0.030	< 0.005	0.006 ± 0.005	< 0.040
Anode outlet H ₂ O from 4-cell stack	0.034 ± 0.005	0.007 ± 0.005	0.008 ± 0.005	0.180 ± 0.04

We discovered that the deionized inlet water contained appreciable amounts of nickel. The source of the Ni was most likely contamination of the water as it traveled through extensive plumbing lines. This was readily observed when a demineralizer cartridge that changes color when saturated was added to the water line and began to change color within days of use. We then substituted 18 MΩ water collected directly from the DI tap to bypass the piping. However, the fuel cell test stations, which contain humidifier bottles made of 304 SS, could also be a potential source of contamination. Thus, Mo concentrations of the outlet water are of prime interest because Mo is unique to 316 SS. The data show that essentially no Mo was detected in either the 2000 h cell water or the stack water. The 2000 h cell water was essentially metal-ion free, while water from the 4-cell stack did show some elevated levels of Fe and Cr. This may be an indicator of possible corrosion due to shunt currents in the manifold regions of the cell. Corrosion can occur in these areas when water ionically shorts across several cells. At the single cell level, as in the 2000 h cell, this effect is minimized, but in a stack it is exacerbated due to the higher voltages involved.

Despite such possible difficulties, the metals concentrations in the effluents were either quite low or at the detection limit. A primary concern with even low levels of metal ions is uptake by the membrane where it can have an adverse effect on membrane conductivity. Initially, the MEAs

from these cells were analyzed by EDAX and found to contain no metals such as Cr or Mo. However, for trace analysis, EDAX provides mainly qualitative data and can not differentiate Ni and Fe from the background of the instrument's stainless steel components. For this reason, the MEAs also were analyzed by XRF spectroscopy, a much more sensitive technique. Trace amounts of Ni, Mn, and Cr, as well as somewhat higher levels of Fe were detected, but Mo was not present. Some Ca and Zn that may have come from the cell water supply was also found in the stack MEA. While detectable amounts of these metals found their way to the MEA, we still need to quantify the uptake rate and its effect to more fully understand the ramifications.

To further assess the corrosion resistance of 316 SS, two types of tests were conducted under conditions harsher than would be expected in a typical PEFC environment. In the first test, pieces of 316 SS foil (0.002" thick, 1 in² each, 4 foils per sample bottle) were immersed in solutions of water or dilute sulfuric acid of varying acidity (pH 2 - 5) for 500 hours. The solutions were maintained at 80°C by means of a water bath and were continuously sparged with either hydrogen or air. At the end of the test period, the metal samples were dried and weighed, and the solutions were analyzed by ICP-MS and ICP-ES for the presence of Ni, Cr, Mo, and Fe.

The corrosion rates of the metal, determined based on weight loss of the samples, were consistently $<0.34 \mu\text{/yr}$, regardless of the nature of the test solution or sparge gas. However, the ICP analyses indicated a strong relationship between the amount of metals in solution and the pH. Figures 2 and 3 show metals content versus pH for the hydrogen-sparged solutions and air-sparged solutions, respectively.

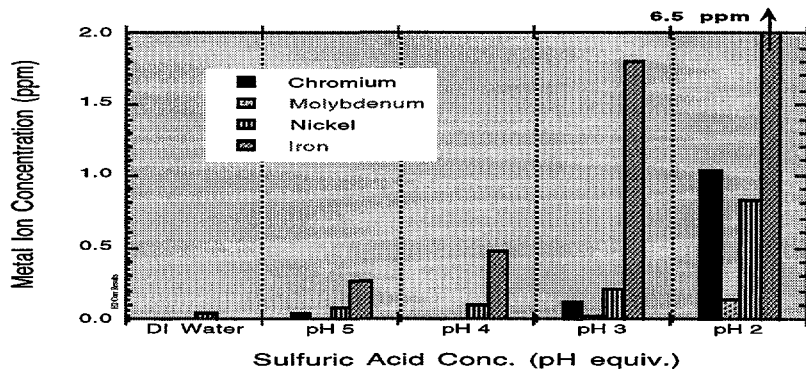


Figure 2: Metal ion concentration versus pH of test solution for H₂-sparged samples.

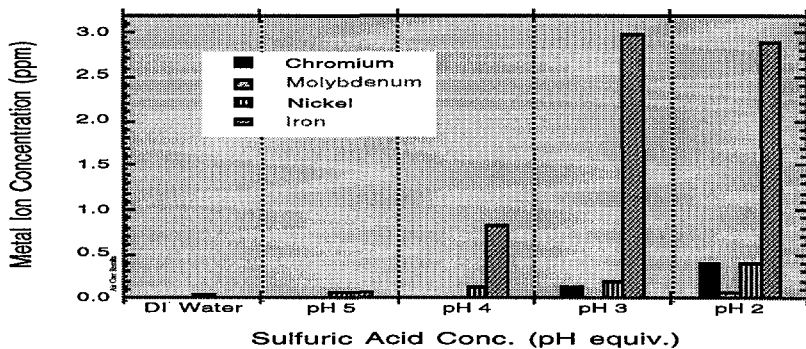


Figure 3: Metal ion concentration versus pH of test solution for air-sparged samples.

The data clearly show that as the pH of the test solution was decreased, the concentrations of metals found in solution significantly increased. Additionally, the data show some dependence on the sparge gas as well. Though the pH appears to be the predominant factor influencing corrosion of the metal, the presence of hydrogen contributes to the process. This is perhaps best illustrated by the chromium and molybdenum data. In the air-sparged samples, Cr remains undetected above pH 3, while Mo is virtually non-existent at all pHs. In the hydrogen-sparged samples, however, Cr appears at pH 5 and both Cr and Mo are clearly detected at pH 2 in much higher concentrations than in the air-sparged samples. Overall, these data suggest that if the pH of the water within in the fuel cell can be maintained above pH 5, 316 SS based metal hardware should not significantly corrode. Water samples from our cells previously discussed were all in the range of pH 6 - 7.

Another test that we conducted involved continuously holding a single cell at open-circuit voltage (0.94 V) for 120 hours. In this case, the cell intentionally was assembled without gas diffusion backings so that the perforated foil (Figure 1) of the metal hardware directly contacted the membrane. Additionally, the membrane (NafionTM 112) was left uncatalyzed to maximize metal to membrane contact. Other operating conditions were as described for regular cell testing. At the end of the test period, the cell was taken apart and examined. Though the hardware itself appeared the same except for a bit of light gold discoloration in a few spots, the membrane was significantly discolored. The EDAX analysis showed the presence of copper, which could have leached from gold-coated copper current collector plates or from unprotected manifold regions of the irridized aluminum alloy endplates employed. Though the EDAX analysis showed no traces of other metals, XRF analysis did detect the presence of other metals that are common to stainless steel. In a properly designed fuel cell, where stainless steel parts do not contact the membrane, this effect should be minimized.

In general, we have found that 316 SS can be corrosion-resistant under the normal operating conditions of a PEFC if a number of conditions are satisfied. The most influential factor appears to be the pH of the cell water. Maintaining it above pH 5, by avoiding any sources of acidity, appears to suppress corrosion. Additionally, direct metal contact with the membrane must be avoided. Because of this, we use polysulfone frames to avoid metal-to-membrane contact in the non-active areas of the cell. In the active area, the carbon cloth backings are cut slightly larger than the perforated foils and screens to prevent contact along the edges. Lastly, the presence and effect of shunt currents, particularly in large-scale stacks, is a potential problem that must be minimized by appropriate design if full-scale implementation of SS hardware is to be successfully realized.

Acknowledgments

This work was supported by the Hydrogen Program of the U. S. Department of Energy, Office of Utility Technologies.

References

1. R. K. A. M. Mallant, F. G. H. Koene, C. W. G. Verhoeve and A. Ruiter, "Solid Polymer Fuel Cell Research at ECN", Program and Abstracts of the Fuel Cell Seminar, San Diego, CA, pp. 503 - 506, Nov. 94.
2. C. Zawodzinski, M. S. Wilson, and S. Gottesfeld, "Metal Screen and Foil Hardware for Polymer Electrolyte Fuel Cells" in Proton Conducting Membrane Fuel Cells [2nd International Symposium], Electrochemical Society Proceedings Series, Vol. 98-27, 1998.
3. C. Zawodzinski, M. S. Wilson, and S. Gottesfeld, "Stainless Steel Wire Mesh Flow-fields for Polymer Electrolyte Fuel Cells", Program and Abstracts of the Fuel Cell Seminar, Orlando, FL, p. 659 - 662, Nov. 1996.