PROPOSED MECHANISM OF CO MITIGATION IN PEMFCs
BY USING DILUTE H2O2 IN THE ANODE HUMIDIFIER

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ABSTRACT

CO poisoning in proton exchange membrane fuel cells (PEMFCs) can be mitigated by using dilute H2O2 in the anode humidifier. However, mitigation appears to be provided by an “unintended” O2 bleed produced by decomposition of H2O2 in the humidifier, rather than by H2O2 vapors transported from the humidifier to the anode. CO mitigation was effective when significant levels of O2 were present in the anode feed. The effectiveness of CO mitigation disappeared when non-catalytic materials were used to suppress H2O2 decomposition in the humidifier. (Safety Note: H2O2 decomposition in the anode humidifier may produce flammable compositions in the anode feed.)

INTRODUCTION

There is an extensive literature describing how CO poisoning reduces the performance of proton exchange membrane fuel cells (PEMFCs). Recent proceedings provide excellent bibliographies concerning CO tolerance relative to the use of reformate fuels (1,2). Typical performance for a PEMFC operating on impure H2 feed decreases with increasing levels of CO as shown in Figure 1 (3). The electro-oxidation of H2 requires two adjacent Pt sites. CO poisoning is caused by chemisorption of CO onto the anode catalyst, forming a nearly complete CO monolayer which blocks sites for electro-oxidation of H2 (4). H2 oxidation becomes severely polarized as this monolayer approaches complete coverage. This polarization can be reduced by removing a small fraction (typically 5-10%) of the CO from the Pt surface (5,6).

Bleeding small amounts of O2 into H2-rich feeds is reported to mitigate CO poisoning at impurity levels up to 100 ppm CO (7,8). This O2 reacts chemically with the CO, but its selectivity is low. Typically, O2 is fed at roughly 100-200 times the stoichiometric requirement for CO oxidation. The excess O2 consumes H2 fuel via a non-electrochemical reaction. The O2 bleed provides large voltaic improvements which greatly exceed the coulombic losses caused by H2 consumption.

A novel method for mitigating CO poisoning in PEMFCs was recently described wherein dilute 5% H2O2 was used in an anode humidifier to successfully mitigate 100 ppm CO in a H2 rich feed (9). A schematic of Schmidt’s anode humidifier system is shown in Figure 2. A mechanism was proposed which involved vapor transport of the H2O2 from the anode humidifier to the anode where it reacted on a Pt-Ru electro-catalyst via the following reactions:

\[ \text{H}_2\text{O}_2 + \text{M} \rightarrow \text{H}_2\text{O} + \text{M(O)}_{\text{ad}} \]  

[1]
M-CO + M(O)_{an} -> 2 M + CO_{2}  \[2\]

In analyzing this performance, we estimated that the humidified anode feed would contain on the order of 100 ppm H_{2}O_{2}. This suggested that CO oxidation via reactions \[1\] and \[2\] might be more selective than those using the O_{2} bleed. The higher selectivity using H_{2}O_{2} additions could provide a technical and economical advantage over using the O_{2} bleed. For fuel cell powered electric vehicle applications, we estimated that a small bottle (<100 cc) of 30 wt% H_{2}O_{2} would be sufficient to mitigate 100 ppm CO for over 1000 miles of driving range.

Our work essentially reproduced the experimental findings of Schmidt et al. (9), showing successful mitigation of CO poisoning on Pt anodes. In our work, we mitigated approximately 100 ppm CO in the H_{2} feed by using <1% H_{2}O_{2} in the anode humidifier. However more significantly, our data shows that successful mitigation depends on the slow decomposition of H_{2}O_{2} in the humidifier and that suppressing this decomposition suppresses the mitigation effect.

**EXPERIMENTAL**

The membrane electrode assembly (MEA) was prepared by General Motor’s Global Alternative Propulsion Center using a 40 wt% Pt/Vulcan XC-72 at a loading of 0.4 mg Pt/cm^{2} on both sides of a Nafion 112. The MEA was mounted in a Globetech test fixture having 5 cm^{2} active area.

Performance tests were run using a commercial Globetech GT-120 test station which controls gas flow rates, pressures and humidifier temperatures. The cell was run at 80°C and ambient pressure at both electrodes. Humidifiers were approximately 60-70% filled with liquid. Our initial anode humidifier used Globetech’s standard 1000 mL heated stainless steel humidifier bottle. In subsequent testing, this was replaced by a heated polypropylene (PP) humidifier chamber. The PP humidifier was made from a Nalgene 250 mL narrow mouth square bottle. The lines connecting the humidifier to the fuel cell were changed from stainless steel to polyethylene (PE). The temperature of the PP humidifier was controlled by partially immersing it in a water bath heated on a hot plate. The cathode humidifier was always run at 82°C. The anode humidifier was controlled between 25° and 45°C in various experiments. House H_{2} was used for the anode feed after passing through a butyl lithium getter (Supelco, OMI 2 Indicator Tube). Cylinders of impure H_{2} were research grade, prepared by MG Products. House air was used for the cathode feed.

Performance curves for the fuel cell were run using a power supply and an HP 6050A System DC Electronic Load. Test protocol held the anode and cathode flow rates constant during performance measurements. The cell was held at constant potential for 60 seconds prior to recording each current. Transients were allowed to stabilize for at least 30 minutes, after switching from pure to impure H_{2} or changing the H_{2}O_{2} concentration in the anode humidifier. H_{2}O_{2} (J.T. Baker, 30 wt%, Reagent Grade) was diluted with deionized H_{2}O between 0.5 and 15 wt%.

Gas analysis was performed on a Wasson modified HP 5890 GC. Anode feed samples were collected in a double-valved stainless steel sample bomb. Anode gases were allowed to flow through the humidifier for at least 90 minutes prior to sampling. GC
analysis for N₂ confirmed that the sampling procedure had not been contaminated with traces of air.

RESULTS AND DISCUSSION

Our initial performance curves for pure and impure H₂, with and without H₂O₂, are plotted in Figure 3. Without H₂O₂, the performance on impure H₂ containing 96 ppm CO was severely degraded. However, with 0.75 vol% H₂O₂ in the stainless steel humidifier, performance was restored, approaching that for pure H₂. This performance mitigation is comparable to that reported in previously by Schmidt et al. using Pt-Ru anodes (9).

We observed small gas bubbles in the sight glass of the stainless steel anode humidifier. This suggested that H₂O₂ might be decomposing via [3] to form O₂ in the humidifier, with the reaction being catalyzed by the metallic walls in the humidifier. (Schmidt et al. also suggest the possibility of H₂O₂ decomposing in their humidifier and stainless steel anode feed lines.) We analyzed the anode feed (100 mL/min., humidifier temperature = 45°C) using a GC, and found approximately 2% O₂ in H₂. This O₂ level is in the range reported to be effective for CO mitigation using the O₂ bleed (7,8).

\[ 2 \text{H}_2\text{O}_2 \rightarrow 2 \text{H}_2\text{O} + \text{O}_2 \]  \[ \text{[3]} \]

At this point, a PP humidifier and PE feed lines were substituted at the anode in order to suppress H₂O₂ decomposition, as shown schematically in Figure 4. Qualitatively, almost no bubbles were observed on the walls of the PP vessel, showing that this material did not catalyze H₂O₂ decomposition at temperatures up to 50°C.

The H₂O₂ treatment became ineffective at mitigating CO poisoning (96 ppm) when using the PP humidifier, even when the humidifier contained as much as 15 wt% H₂O₂ at 45°C. GC analysis of the feed gases from the PP humidifier showed that the O₂ was now below measurable levels (less than 10 ppm).

This change in O₂ content of the anode feed gases is best explained by a slow decomposition of H₂O₂ in the reservoir. Metallic surfaces are known to catalyze H₂O₂ decomposition, while polyolefinic materials are not likely to catalyze this reaction. The effective CO mitigation when using the stainless steel humidifier and the loss of mitigation when using the polypropylene humidifier is best explained by the well known O₂ bleed effect rather than by the vapor transfer of H₂O₂ from the humidifier to the anode. Our interpretation is that an unintended O₂ bleed provided the primary mechanism for CO mitigation when using the stainless steel humidifier. Furthermore, if the CO mitigation mechanism involved a vapor transfer of H₂O₂ from the humidifier to the electrode, there is no reason to expect that changing the material of the humidifier would affect the CO mitigation.

In further support of our interpretation, the literature describes H₂O₂ reduction on Pt, Ru and Pt-Ru electrodes as proceeding via a two electron reduction, with H₂O being the final product (10). This suggests that reaction [1], the formation of stable M(O)ad, is unlikely.
Finally, our proposed O\textsubscript{2} bleed mechanism will not be economically attractive in PEMFCs. Compared to air, H\textsubscript{2}O\textsubscript{2} is an expensive source of O\textsubscript{2}. The low selectivity for O\textsubscript{2} bleed (~1%) would require costly amounts of H\textsubscript{2}O\textsubscript{2} to achieve CO mitigation.

**Safety Note:** Decomposition of H\textsubscript{2}O\textsubscript{2} in heated metallic humidifiers can proceed at unknown rates. This decomposition has the potential to produce flammable mixtures of H\textsubscript{2} and O\textsubscript{2} in the anode feed, which should be avoided. The lower flammable limit for pure O\textsubscript{2} in H\textsubscript{2} is 6.1 vol\% (11).

**REFERENCES**

1. D.P. Wilkinson and D. Thompsett, in Proceedings of the 2\textsuperscript{nd} International Symposium on New Materials for Fuel Cell and Modern Battery Systems, Montreal, Canada, 266, (1997).
2. S.J. Cooper, A.G. Gunner, G. Hoogers and D. Thompsett, ibid, p. 286.
3. R.J. Bellows, E. Marucchi-Soos and D.T. Buckley, *Electrode Materials and Processes for Energy Conversion and Storage IV*, PV 97-13, 1-14, Electrochemical Society Proceedings, Pennington, NJ (1997).
4. P. Stonehart and P.N. Ross, Cat. Rev.-Sci. Eng., 12, 1-35 (1975).
5. H.A. Gasteiger, N.M. Markovic and P.N. Ross, *J. Phys. Chem.*, 99, 16757, (1995).
6. T. Springer, T. Zawodzinski and S. Gottesfeld, *Electrode Materials and Processes for Energy Conversion and Storage IV*, PV 97-13, 15-24, Electrochemical Society Proceedings, Pennington, NJ (1997).
7. S. Gottesfeld and J. Pafford, *J. Electrochem. Soc.*, 135, 2651-2652 (1988).
8. D.P. Wilkinson, H.H. Voss, J. Dudley, G.J. Lamont, and V. Basura, U.S. Patent 5,432,021, (1995) and U.S. Patent 5,482,680, (1996).
9. V.M. Schmidt, H.-F. Oetjen, and J. Divisek, *J. Electrochem. Soc.*, 144, L237-238, (1997).
10. K. Kinoshita, “Electrochemical Oxygen Technology”, John Wiley & Sons, Inc., New York, 1992, Chapter 2, pp.19-112.
11. Handbook of Physics and Chemistry, 45th Edition, R.C. Weast, Ed., p. D-55, Chemical Rubber Company, (1964).
Figure 1: PEMFC Performance on H₂/Air on Pt Anodes, 80°C, 0.3 mg Pt/cm²

Figure 2: CO Mitigation using H₂O₂ in Anode Humidifier (Schmidt)
Figure 3: Steady state performance of PEMFC on pure and impure H₂, T_{cell} = 80°C; catalyst loading = 0.4 mg Pt/cm²

Figure 4: CO Mitigation using H₂O₂ in Polyolefin Humidifier