

THE EFFECTS OF FUEL IMPURITIES ON PEM FUEL CELL PERFORMANCE

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Power generation with polymer electrolyte membrane fuel cells (PEMFC), particularly those designed for domestic and transportation applications, will likely operate on hydrogen reformed from hydrocarbons. The primary sources of H_2 can be methane (from natural gas), gasoline or diesel fuel. Unfortunately, the reforming process generates impurities that may negatively affect FC performance. The effects of CO impurity have received most of the attention. However, there are other impurities that also may be detrimental to FC operation. Here we present the effects of ammonia, hydrogen sulfide, methane and ethylene.

Two structural domains of the membrane and electrode assembly (MEA) are usually affected by the presence of a harmful impurity. First, the impurity may decrease the ionic conductivity in the catalyst layer or in the bulk membrane. Second, the impurity may chemisorb onto the anode catalyst surface, suppressing the catalyst activity for H_2 oxidation. Catalyst poisoning by CO is the best known example of this kind of effect.

Fuel reforming processes [1] generally involve the reaction of a fuel source with air. The simultaneous presence of N_2 and H_2 may generate NH_3 in concentrations of 30 to 90 ppm [1]. The effect of NH_3 on performance depends on the impurity concentration and the time of anode exposure [2]. Higher concentrations result in more rapid performance decreases. If the cell is exposed to ammonia for about 1 hour and then returned to neat H_2 , it will recover its original performance very slowly (about 12 hrs). This behavior is quite different from that of CO, which can be quickly purged from the anode with pure H_2 , resulting in complete performance restoration within a few minutes. Longer exposure times (e.g. >15 hrs) to ammonia result in severe and irreversible losses in performance. It seems that replacement of H^+ ions by NH_4^+ ions, first within the anode catalyst layer and then in the membrane, is the primary reason for cell current losses.

H_2S also adversely affects FC performance. Figure 1 depicts the current density changes in a FC exposed to both 1 and 3 ppm H_2S while operating at a constant voltage of 0.5 V. As expected, the greater the contamination level the faster the current density drops. Eventually in each case the cell becomes totally disabled. The effect H_2S appears to be cumulative, because even sub-ppm H_2S levels will decrease the FC performance if the exposure is long enough. We have recorded slow current droppings to about 20% of the initial value after exposure to concentrations of H_2S of 200 parts per billion (10^9) for 650 hours. Exposure to higher concentrations of H_2S may bring catastrophic consequences. We have exposed cell anodes to H_2S burps of the order of 8 ppm, and observed that the current at 0.5 V dropped from 1.1 to 0.3 $A\ cm^{-2}$ in just few minutes.

Figure 2 shows the effect of H_2S on cell polarization. Curves **b** and **c** in this figure were

recorded after 4 and 21 hours of exposure to 1 ppm H_2S , respectively, while keeping the cell at a constant voltage of 0.5 V. Regardless impurity concentration and running time, replacing the contaminated fuel stream with pure H_2 does not allow any recovery as observed with CO poisoning. Cyclic voltammetry (CV) indicates that H_2S chemisorbs very strongly onto Pt catalyst surface and high voltages are required for full cleansing of the H_2S -poisoned active sites. After full anode poisoning with H_2S (curve **c**), the electrode was subjected to CV (up to 1.4 V) and then the polarization curve **d** (with neat H_2) was recorded. The complete cell performance recovery is apparent from this curve. A more extended discussion on H_2S catalyst poisoning and cleaning will be presented.

We also tested methane (0.5 % by vol.) and ethylene (50 ppm) as potential fuel impurities and we found no effects on performance.

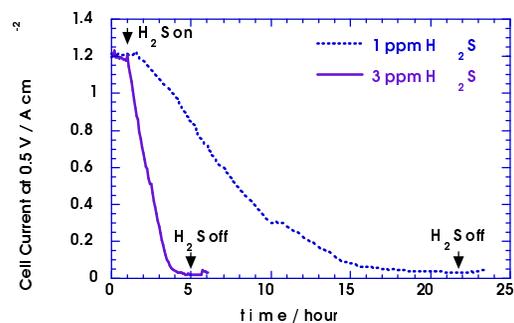
References

1. "Multi-Fuel Reformers for Fuel Cells Used in Transportation". Phase I, Final Report, May 1994 by Arthur D. Little, Inc for US DOE-OTT
2. F. A. Uribe, T. Zawodzinski Jr., and S. Gottesfeld, in *Proton Conducting Membrane Fuel Cells II*, S. Gottesfeld and T. Fuller, Editors PV 98-27, p. 229, The Electrochemical Society Proceedings Series, Pennington, NJ (1999).

Acknowledgment

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Figure 1. Effect of 1 and 3 ppm H_2S on anode FC performance at 0.5 V and 80 °C. Cell size 5 cm^2 .



Loadings 0.2 mg Pt cm^{-2} on each electrode.

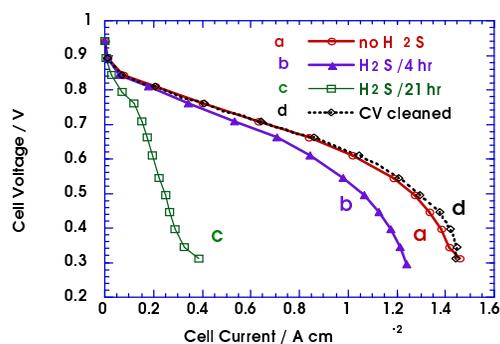


Figure 2. Effect of 1 ppm H_2S on FC performance after 4 hours (**b**) and 21 hours (**c**) of exposure. Curve (**d**) recorded after electrochemical cleaning the H_2S -poisoned anode. Curve (**a**) recorded with neat H_2 . (Same cell as above at 80 °C).