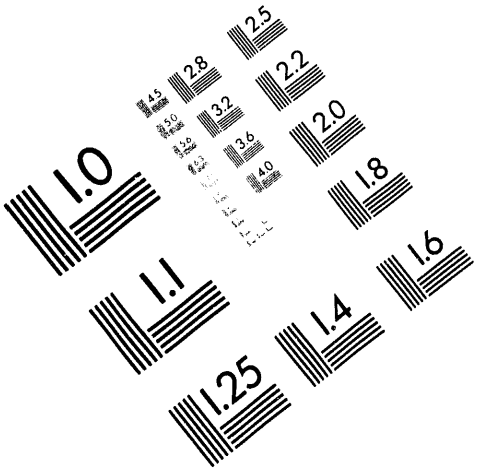

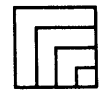

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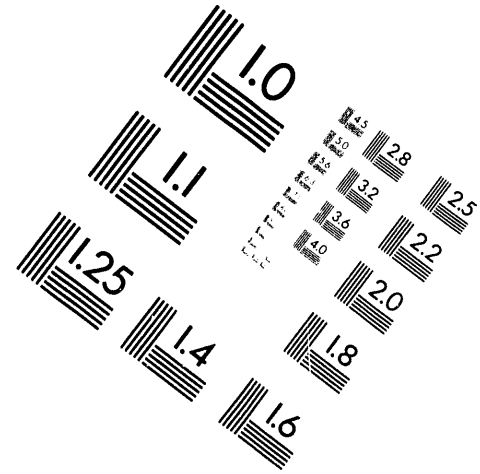

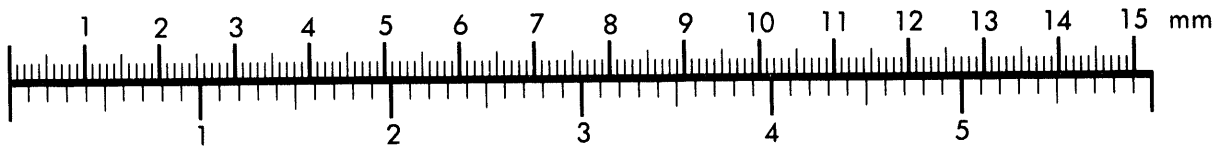

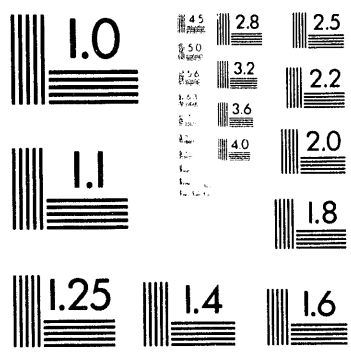

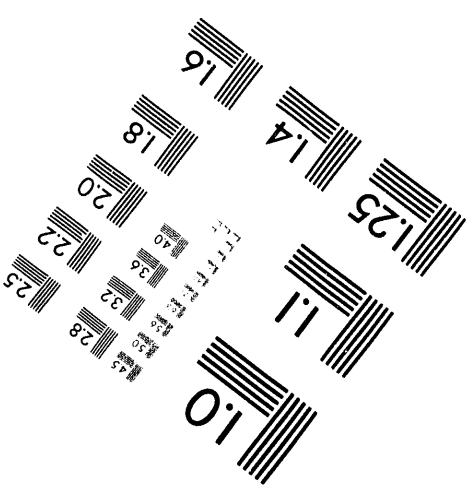

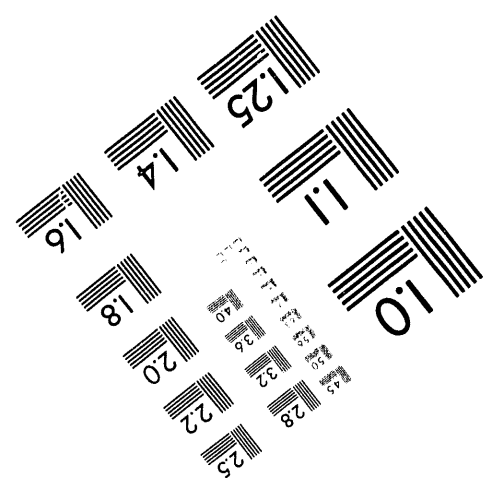

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Title: EFFECT OF OPERATING PARAMETERS AND ANODE GAS IMPURITIES UPON POLYMER ELECTROLYTE FUEL CELLS

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EFFECT OF OPERATING PARAMETERS AND ANODE GAS IMPURITIES UPON POLYMER ELECTROLYTE FUEL CELLS

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ABSTRACT

PEM fuel cells are actively under development for transportation and other applications. Integration of a PEM fuel cell stack with a methanol reformer requires an understanding of single cell performance under a range of operating conditions using anode gas contaminated with impurities. The effect of temperature, pressure, and anode gas impurities on single cell PEM performance was investigated with platinum black electrodes.

Single cell performance remained unchanged as temperature was varied between 80 and 100°C at 3 atm pressure. High water partial pressures at 120°C produced a mass transfer limiting current. While operation at 120°C did not reverse CO_2 poisoning, anode air addition proved effective. Air injection also decreased CO poisoning at injected concentrations up to 200 ppm CO. Higher single cell tolerance was observed for CH_3OH than CO. Up to 1 mole % CH_3OH in the gas phase reduced the current density by less than 10%.

INTRODUCTION

Electric vehicles are being developed in response to environmental and strategic fuel concerns. Hydrogen-fueled PEM (proton exchange membrane) fuel cells, operating at low temperature, provide an efficient conversion from chemical to electrical energy.

To eliminate the cost, weight, and safety concerns arising from onboard hydrogen storage, methanol reforming is being pursued as an attractive alternative source for hydrogen. The United States Department of Energy and General Motors Corporation, and others are jointly supporting the development of an integrated fuel processing and fuel cell powered electrochemical engine[1]. Gas cleanup to reduce reformer effluent level of CO is also being developed[2]. Since any residual contaminants not removed during the gas cleanup, as well as CO_2, will enter the fuel cell stack, optimization of stack operating conditions and development of impurity tolerant fuel cell catalysts are necessary.

Primary contaminants include CO, CO_2 and CH_3OH, the result of breakthrough in the fuel processing stream. Under most conditions, fuel processing of methanol does not generate significant quantities of methane. Platinum poisoning with CO has been studied extensively for phosphoric acid fuel cells. Since PEM fuel cells operate at lower temperature, deactivation with under 10 ppm CO is observed[3]. Carbon dioxide also produces voltage loss, however. Adsorption of CO_2 on Pt was first documented by Giner[5] in 1963 and was often referred to as reduced CO_2 (r-CO_2). Recent radiotracer studies[6] as well as spectroscopic results[7] indicate that a species other than CO_{ads} is formed. Evidence supports the formation of C-OH, that is triply bonded to platinum. Since maximum surface coverage approaches 0.7 with this species, inhibition of the hydrogen reduction reaction is not as severe as when CO is present. Vassiliev et al.[6] also concluded that the adsorption behavior of CH_3OH is similar to CO_2.

Catalytic poisoning may be reduced or eliminated by (1) higher operating temperatures, the procedure used in phosphoric acid systems, (2) development of tolerant electrocatalysts, and (3) air injection as part of the anode feed[3,4]. The effect of temperature and air injection will be presented here. Use of oxygen to remove adsorbed CO_2 from platinum was first described by Nagy et al.[8] The method was also recently suggested by Ballard as a method for improving PEM cell performance on reformate.

EXPERIMENTAL

A single cell and reference test stand were designed and constructed to provide tight control on operating parameters during PEM measurements. Mass flow controllers regulate gas flow. Humidification is accomplished with HPLC pumps and heated water vaporizers. This method permits rapid, controlled variations in the level of humidification in the inlet steams. The anode gas stream was supersaturated for all tests described here. Cell temperature control is accomplished by constant temperature water circulation through heat exchangers that cover the full test area of the membrane and electrode under test. The cell may be operated over a wide temperature and pressure range.

The membrane electrode assemblies (MEAs), provided by DOW Chemical Co, were constructed using DOW XUS-1304.20 membrane at a platinum loading of 4 mg/cm^2. Active area of the MEAs was 46.5 cm^2.

Tests were performed with equal gas pressure on both the anode and cathode. Higher gas stoichiometry was needed in this study than in subsequent work for effective water removal. Anode values were 2 to 4 while cathode rates were 4 to 6 unless otherwise noted.

An initial MEA performance of 0.7 volts at 1 amp/cm^2 was obtained. During testing, an MEA was removed and reinserted in the test cell. This procedure generally led to a performance decrease. Consequently, this trend is shown—a reduction in maximum cell performance and variations between figures are reported.

A gas chromatograph (GC), model HP-5890, configured with methanizer and FID detector, allowed measurement of carbon monoxide concentrations to less than 1 ppm. This GC was configured with an auto-sampler valve for in-line sampling of gas effluent streams from the cell. In-line sampling was found to be necessary. About 10 ppm CO formed from the reverse gas shift reaction at room temperature over a period of hours.

RESULTS AND DISCUSSION

Temperature and Pressure Effects

It was anticipated that higher operating temperature would decrease CO_2 adsorption on Pt. In addition, waste heat available at higher temperatures from a stack may be used more efficiently in feed stream vaporization.

Tests were performed under 3 atm total pressure at 80, 100 and 120°C. As apparent from **Fig. 1**, essentially identical cell performance was obtained on pure hydrogen at 80 and 100°C. Maintaining effective anode humidification becomes more difficult at high temperature and thus humidification losses are more important than factors that increase performance at higher temperature.

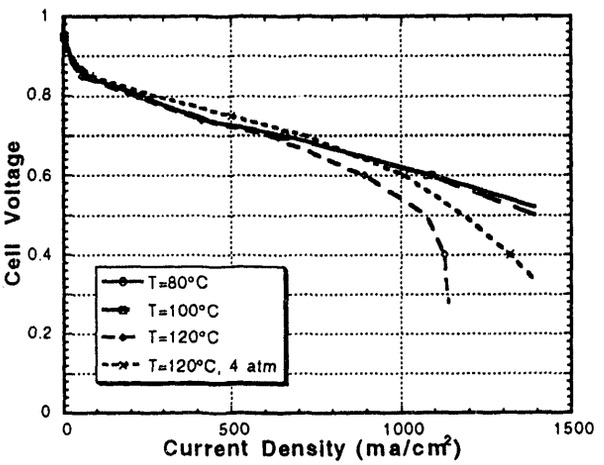

Fig 1. Effect of elevated temperature upon single cell performance, A/C pressure = 3/3 atm.

At 120°C, an apparent mass transfer limit is reached at 1.1 amp/cm^2. Electrode modeling efforts have shown that the high water partial pressure under these conditions reduces the oxygen mole fraction and leads to this limit. This hypothesis was confirmed by increasing total absolute pressure to 4 atm. Under these conditions, the mass transfer limit disappeared.

A similar series of measurements was performed at 1 atm pressure (**Fig 2**). While comparable performance is seen at 70 and 80°C, a mass transfer limit is apparent at elevated temperature where the boiling point of water is approached. At a given pressure, operating

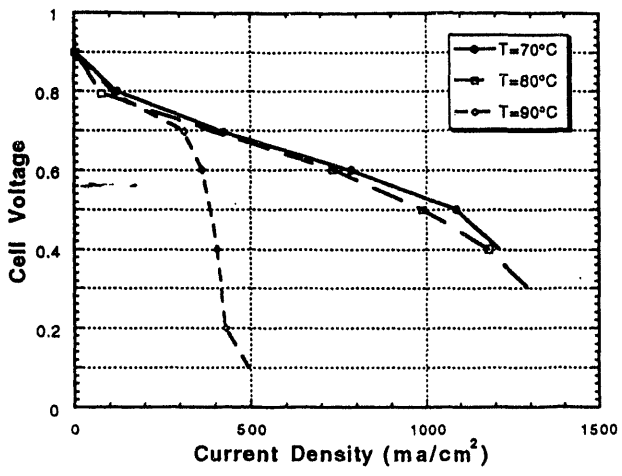

Fig 2. Effect of operating temperature upon single cell performance, A/C pressure = 1/1 atm.

temperature is limited to 10 to 20°C below the boiling point of water.

CO_2 Adsorption

Single cell performance was measured at 80, 100, and 120°C with pure hydrogen, 25% N_2 and 25% CO_2. Typical results are given by **Fig 3**. The nitrogen curve represents the effect of H_2 dilution on performance.

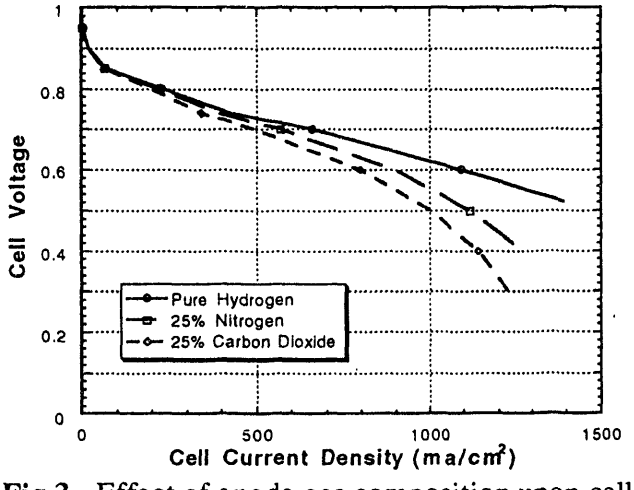

Fig 3. Effect of anode gas composition upon cell performance at 80°C, 3 atm pressure.

With CO_2, an additional voltage loss is apparent and may be attributed to Pt surface coverage by the adsorbed CO_2 species. Table 1 summarizes these data.

Conditions Temp(°C)/ Press(atm)	H_2 (volts)	V-25% N_2 V-pure H_2 @1 amp/cm^2	V-25% CO_2 V-pure H_2 @1 amp/cm^2
80/3	0.62	0.887	0.806
100/3	0.62	0.952	0.581
120/3	0.54	0.944	0.611
120/4	0.605	0.843	0.678

Table 1. Effect of N_2 and CO_2 dilution upon cell voltage normalized to pure H_2 performance.

At 80°C, a 20 percent decrease in voltage is seen with CO_2, calculated at 1.0 amp/cm^2. At elevated temperature, a 30 to 40% penalty exists. Therefore, the effect of CO_2 poisoning appears to increase slightly with temperature on a pure Pt electrocatalyst.

On-line GC measurements were used to determine whether the voltage loss resulted from low concentrations of CO, either because of CO contamination in the feed CO_2 or from CO production by the MEA, the result of catalytic promotion of the reverse-shift reaction. While the cathode was totally flooded with N_2, H_2 and CO_2 flowed through the anode at low flow rate. The feed or anode vent stream showed no sign of CO (< 1 ppm). Neither was CO found in the anode effluent of working single cells. In concurrence, Johnson et al.[9] found no trace of CO following CO_2 adsoption on Pt in acidic solution. Thus, CO_2 poisoning may be attributed to formation of r-CO_2 as described in the literature.

Air injection was explored as a method for reversing the adverse effects of CO_2 adsorption. Baseline curves for cell performance were obtained on pure hydrogen, 25%N_2 and 25% CO_2 . **Fig. 4** illustrates the variation in performance. With injection of 2% air, cell performance returned to the 25% N_2 case indicating effective removal of r-CO_2 from the platinum black catalyst. Further tests showed that as little as 0.18% oxygen was effective in anode activation.

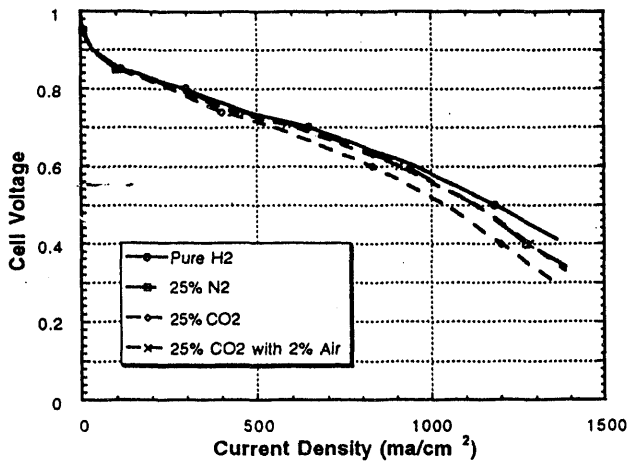

Fig 4. Reversal of CO_2 poisoning by anode air injection at 80°C, 3 atm pressure, A/C stoich.= 1.4/3.0.

CO Poisoning

The maximum level of CO that can be tolerated in the fuel cell determines fuel stream pre treatment requirements. Because air injection appears desirable during reformation operation, the requirements for complete CO removal might be loosened. This effect was investigated by studying the amounts of CO that can be effectively processed with anode air injection. Given a set level of CO in the anode feed, air concentration was increased until greater than 90% of the current density was recovered at 0.6 volts. Fig.5 illustrates in the form of a surface plot the degree of current recovery versus oxygen injection.

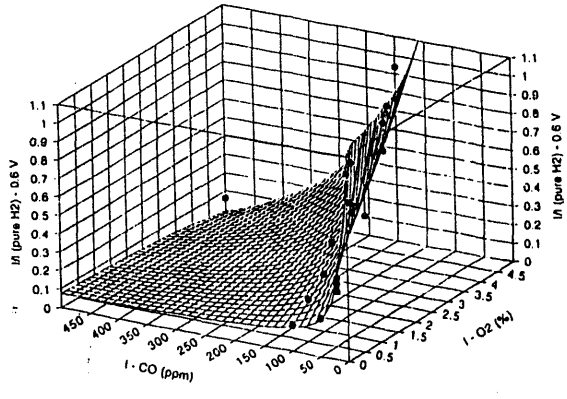

Fig 5. Effect of CO and anode air injection upon cell current at 80°C, 3 atm pressure.

The improvement in cell performance is readily apparent when small air levels are injected. Normalized current density, defined as I / I for pure H_2 greater than 0.9, is applied in Fig. 6 to differentiate between poisoned and recovered performance.

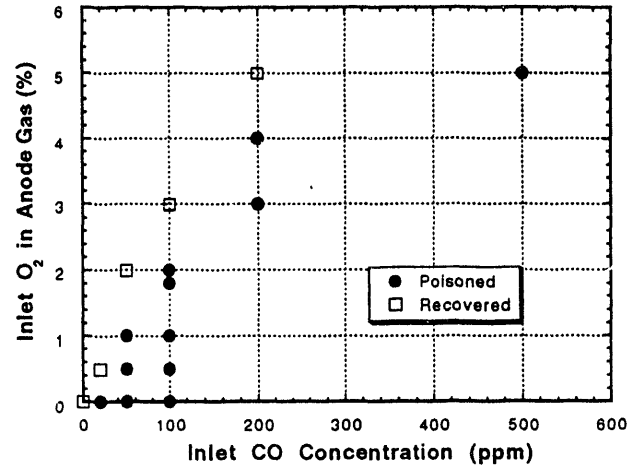

Fig 6. Impact of CO and anode air injection upon normalized current density at 80°C, 3 atm pressure.

An O_2 concentration of 2 to 3% is needed to recover cell performance with 100 ppm of CO in the feed. This level is comparable to the amount required for Pt/C catalysts at lower platinum loading[3]. At the flammability limit of 5% O_2—the highest safe operating condition—adverse effects of CO can be reversed for as high a concentration of 200 ppm.

During these experiments, the effluent gas composition was monitored for oxygen. For a given inlet concentration of CO, an O_2 concentration below a critical level yielded little oxygen or CO consumption. Above this level, re-activation of the catalyst surface was indicated by current recovery. GC data also indicated higher consumption of oxygen, reduction of CO to less than 20 ppm, and production of CO_2 – reactions expected on platinum catalytic sites.

CH_3OH Poisoning

The effect of methanol contamination on single cell performance was measured to determine the consequences of methanol breakthrough upon reformer/fuel cell system performance. Methanol was fed to the anode vaporizer as aqueous solutions.

Solutions of methanol and water are non-ideal. To represent the fugacity of methanol, the gas phase was assumed to be ideal. For a constant pressure experiment, the fugacity of methanol may be represented by the mole fraction of methanol in the gas phase. This value was calculated based upon the concentration of methanol in water, water solution feed rate, hydrogen gas flow rate, and activity coefficients calculated from the literature.

In contrast to CO performance, the MEA performed well even with high levels of CH_3OH in the gas phase. Cell current at 0.6 volts was normalized versus performance with pure H_2 and plotted in **Fig. 7**.

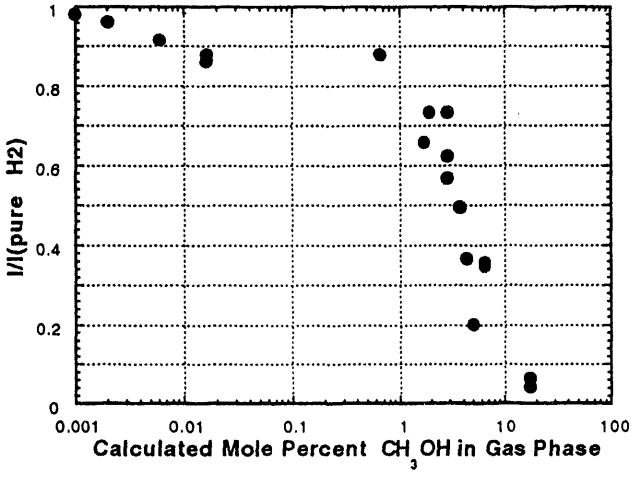

Fig 7. Effect of methanol injection to the anode upon normalized cell current at 80°C, 3 atm. Only a 10% drop in current is seen with up to 1 mole % CH_3OH in the gas phase. Above 1% CH_3OH, cell performance drops significantly.

Air injection to the anode was attempted to reverse methanol poisoning. Inlet oxygen concentrations up to 4 mole % were injected with 6 mole % methanol in the gas phase. None of these strategies resulted in improvement.

Cathode gas composition was also monitored while injecting up to 4.3 % methanol in the gas phase. Interestingly enough, the CO_2 level increased from 300 ppm, expected in the inlet air, to as much as 1.2%. Since oxygen reduction kinetics is ~5 orders of magnitude slower than the rate of hydrogen oxidation on Pt, the presence of methanol at the cathode can be very detrimental to cell performance. Reduced platinum cathode performance has been reported in the literature[10].

CONCLUSIONS

1. While cell performance was similar at 80 and 100°C, an apparent mass transfer limit is apparent at 120°C and 3 atm pressure. High steam mole fractions appear responsible. Atmospheric pressure operation also indicates that maximum cell temperature is limited to 10 to 20°C below the boiling point of water.

2. Increasing cell temperatures up to 120°C has no influence on CO_2-adsoption voltage loss on a platinum black anode.

3. Carbon dioxide poisoning can be reversed with even small quantities of anode oxygen injection, as low as 0.18% oxygen. Carbon dioxide deactivation does not appear to be the result of CO emanating through the reverse - shift mechanism. This finding supports evidence in the literature for the formation of a "reduced" CO_2 species unrelated to CO adsorption.

4. At CO concentrations up to 200 ppm, poisoning can be reversed on platinum black electrodes by air addition. Effluent analysis shows that when the anode is re-activated, CO concentration decreases to less than 20 ppm by oxidization to CO_2.

5. Anode tolerance for CH_3OH was greater than for CO. Only 10 percent drop in current density (constant voltage) was apparent with 1 mole % CH_3OH in the gas phase. Oxygen injection in the anode had no effect on reducing the deactivation. Some deactivation occurs at the cathode from diffusion of methanol through the membrane, poisoning oxygen reduction kinetics.

ACKNOWLEDGMENTS

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