PERFORMANCE OF AN AMBIENT PRESSURE CELL STACK OPERATING UNDER SYNTHETIC GASOLINE REFORMATE

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INTRODUCTION

Recently, proton exchange membrane fuel cells (PEMFC) have gained worldwide attention as a possible practical replacement to the internal combustion (IC) engine for automotive applications. International Fuel Cells is actively engaged in PEMFC technology using hydrogen as well as reformed gasoline as a fuel source for automotive and stationary applications. Gasoline reformate from a fuel processor arriving at a PEM cell anode is expected to contain small quantities (10-50 ppm) of carbon monoxide. It is well known that CO is a poison to the platinum anode catalyst when present even in small concentrations of ppm in the fuel feed stream. Carbon monoxide adsorbs on active sites on the surface of the catalyst that would otherwise be available to H_2 for dissociation into monoatomic H_{ads} (Tafel step) for subsequent oxidation. In other words, the Tafel reaction which is the slower of the two step Tafel-Volmer reaction mechanism reaches rate limiting conditions earlier due to unavailability of participating reaction sites. The extensive coverage (~80%) at low (65°C) temperatures causes a precipitous drop in anode limiting current and degradation in cell performance referred to as CO poisoning. There are several ways to deal with the residual CO that enters the fuel cell stack. One is to develop new catalysts that are more tolerant to CO either by the mechanism of CO oxidation using OH^- ions at lower potentials. Another is the use of alloys that have components with a lower heat of adsorption to CO. Still a third pathway is to inject small amounts of air into the fuel feed [1,2] so that the CO is oxidized by oxygen at the catalyst surface, thereby recovering surface area for the hydrogen oxidation reaction and raising the cell performance. In the latter case, some hydrogen will also be oxidized, depleting the fuel and, hence, will result in an efficiency loss. A certain amount of heat will also be generated due to the oxidation of both hydrogen and CO.

The reverse shift reaction may also take place, since fuel feed consists of CO_2, which in addition to causing a dilution effect may participate in the production CO or some other reduced form of CO_2 [3]. Thus a poisoning effect due to CO_2 may be observed.

In this paper, we present results on the effect of dilution of fuel, CO, CO_2 poisoning and, its mitigation by air injection, as well as selectivity of air injection.

EXPERIMENTAL

A low loaded (0.10 mg/cm^2 Pt anode; 0.37 mg/cm^2 Pt cathode; Gore 15 micron membrane) as well as a higher loaded "CO tolerant" catalyst (0.40Pt-0.20Ru mg/cm^2 anode; 0.30 mg/cm^2, 0.40 mg/cm^2 cathode on Gore 15 micron membrane) were tested with H_2/CO or synthetic reformate gases at the anode while using air on the cathode. The electrochemically active area of the cell was 327 cm^2. The dry synthetic reformate composition used was CO_2 = 21%, N_2 = 30%, H_2 = 49%. An existing in-house software was used to acquire cell performance data. Special precautions were taken in the experimental test rig to ensure safety in the introduction of air into the fuel stream. Care was taken to ensure that the lower flammable limit (~5% oxygen in hydrogen or ~25% air in hydrogen) was not approached.

Gas chromatographic (GC) mass balance analyses of dry gasses entering and leaving the anode were carried out to determine the CO converted to CO_2 and to better understand the mechanism of CO oxidation particular to this system. GC measurements of dried gases were carried out at the fuel inlet and exit. In these studies CO in pure hydrogen was used rather than synthetic reformate in order to determine both the CO converted as well as CO_2 formed. (The CO_2 formed would not be measurable if synthetic reformate containing 21% CO_2 were used.) Impurities of CO_2 at the inlet, as well as unused oxygen and unoxidized CO (at low air bleeds) at the fuel outlet, were measured. All measurements were repeated 3-4 times for reproducibility.

RESULTS AND DISCUSSION

We report below the data on an MEA in a single cell having 0.1mg/cm^2 anode platinum loading and 0.37 mg/cm^2 cathode loading. Results are reported at 65°C and ambient pressure. Hydrogen utilization was 90% and air utilization 30% at 647 mA/cm^2. Figure 1 shows a "calibration" performance curve using pure H_2, performance curve with 20 ppm CO in H_2, and 0.5% air injection. The anode polarization loss at 400 mA/cm^2 was >300 mV. A complete performance curve was obtained at 0.25% air bleed. The air injection reduced the polarization to ~250 mV. At 647 mA/cm^2, the air injection was increased in discrete steps up to 2.5% at which point the performance loss reached a minimum ~20 mV. Figure 2 shows the discrete steps in which the air bleed was increased at 647 mA/cm^2. In the last two steps, the CO is shut off after which the air bleed of 2.5% is shut off. A ~5-10 mV increase in performance is observed when the CO is turned off.

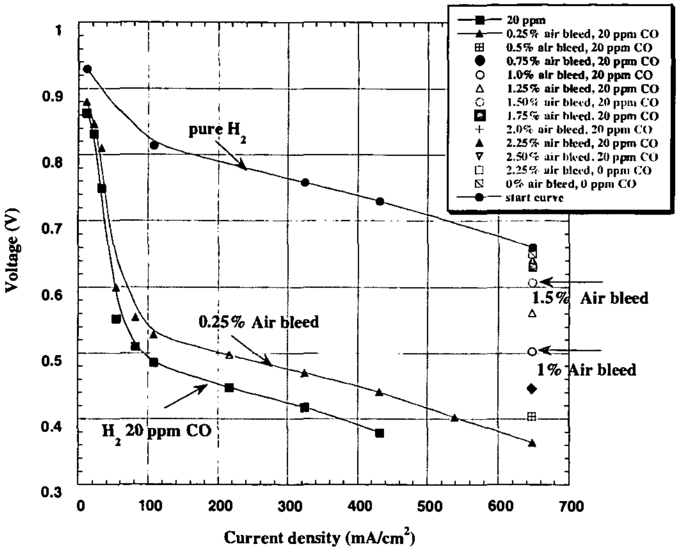

Figure 1 Performance curves depicting the loss in performance with the introduction of 20 ppm CO and the mitigation of CO poisoning with the use of an air bleed in the fuel feed stream. A complete curve with 0.25% air bleed is plotted as well as gain in performance with increasing air bleed at 647 mA/cm^2 at 65°C and 100 kPa.

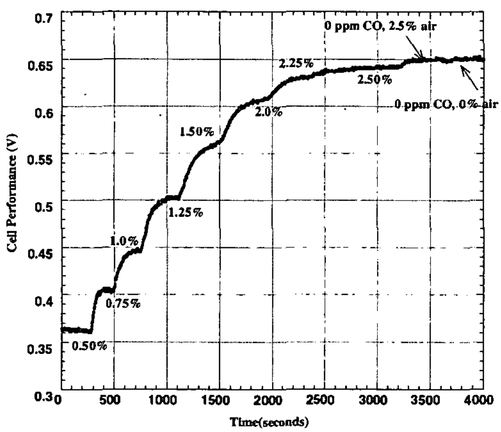

Figure 2 Details of the enhancement in performance during the step wise increase in air bleed at 647 mA/cm^2 of figure 2 at 65°C and 100 kPa.

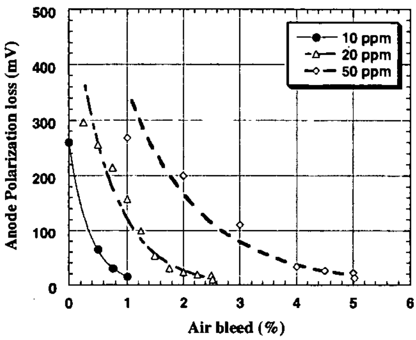

Figure 3 Variation of anode polarization with air bleed as a percentage of total anode fuel flow at 65°C and 100 kPa. (anode platinum loading 0.1 mg/cm^2)

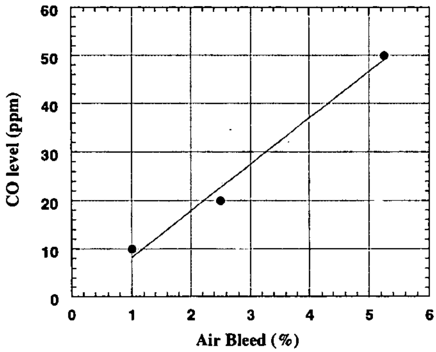

Figure 4 Dependence of the % air bleed required to raise the performance of a CO poisoned MEA (anode platinum loading 0.1 mg/cm^2) to within 10-15 mV of its hydrogen–air performance at 65°C and 100 kPa.

The rate at which the performance was enhanced (or anode polarization/cell loss decreased) with increasing % air bleed at 647 mA/cm^2 is shown in figure 3. The performance loss decreases at an exponential rate with % air bleed. Figure 4 summarizes the approximate amount of %air needed to be injected for different CO amounts in the fuel stream for performance recovery to within ~20 mV. The ratio of air bleed (21% oxygen) to CO level is a constant at about 200 and is a measure of the selectivity of the CO oxidation.

Mass Balance on low loaded (0.10 mg/cm^2 Pt anode) Pt anode

As described in the experimental section gas chromatographic studies were conducted to determine the mass balance of CO, air, and impurities (CO_2 ~8 ppm) entering and exiting the anode. The air bled in also contains 0.04% CO_2. The gases measured at the inlet and exit are dry gases. At 20 ppm CO inlet conditions with 2% air injection, the mass balance is shown in table 1. We observed that oxygen in the air bleed is not fully utilized and exits the anode along with CO_2 and even unoxidized CO at low air bleeds. The selectivity of CO oxidation based on the mass balance is of the order of 100:1.

TABLE 1 20ppm CO in hydrogen, 65°C, V_{OC}, 2% air bleed

	Inlet Flow	Exit Flow	|Inlet-Exit|
CO ppm	20.4	0.0	20.4
CO_2 ppm	15.0	43.1	28.1
N_2%	1.51	1.60	0.10
O_2%	0.43	0.11	0.30
CO oxidized	=20.4ppm		
O_2 used	=0.30% = 3000ppm		
O_2 unused	=0.11% = 1100ppm		

Figure 5 shows three performance curves, namely the hydrogen-air curve, 50% hydrogen and 50% nitrogen, 49% hydrogen, 30% N_2, and 21% CO_2. (simulated reformate with no CO). The losses due to dilution by N_2 at 647 mA/cm^2 is ~25 mV and the additional loss due to CO_2 poisoning is ~ 70 mV. At 647 mA/cm^2 air was bled into the anode in small increments until the cell performance was recovered. At 0.6% air bleed the performance reaches to within 10-15 mV of the maximum possible diluted performance. Further air bleed did not result in any performance gain. Figure 6 shows the effect of air bleed when the anode is subject to simulated reformate + 10 ppm CO. Combining the results in figures 6 and 7, it appears that the air bleed required for recovering the performance is approximately the sum of that required for CO_2 and CO individually and is ~1.75%.

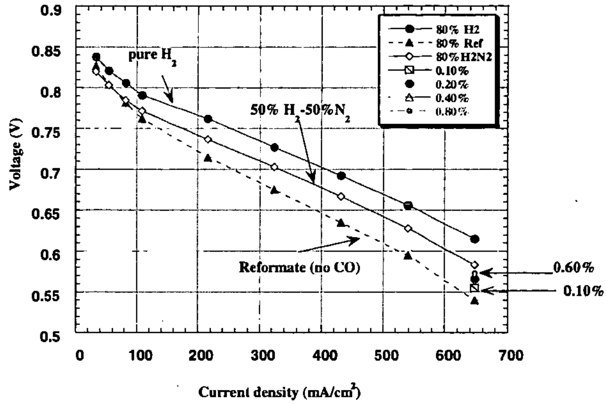

Figure 5 Single Cell Stack Performance with anode gas compositions of pure H_2, H_2-N_2 and simulated reformate containing 49%H_2:21%CO2:30%N_2
+ Air Bleed (% of total anode flow)

High loaded Pt-Ru anodes (0.40Pt-0.20Ru mg/cm^2)

Figure 7 compares the effect of reformate with 10 ppm CO with and without air bleed at 538 mA/cm^2 with time. The air bleed required for this Pt-Ru catalyst with 10 ppm CO in reformate is of the order of 0.6% and less than that for a lower loaded Pt anode (1%) for the same CO ppm in reformate.

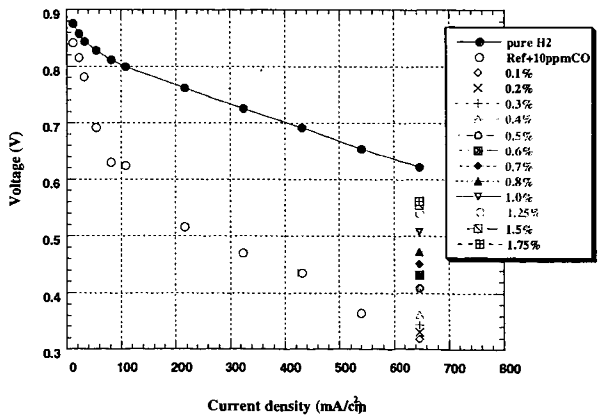

Figure 6 Performance curves showing the effect of reformate containing 10 ppm CO and step increases in air bleed at 647 mA/cm^2 that recovers the poisoning losses.

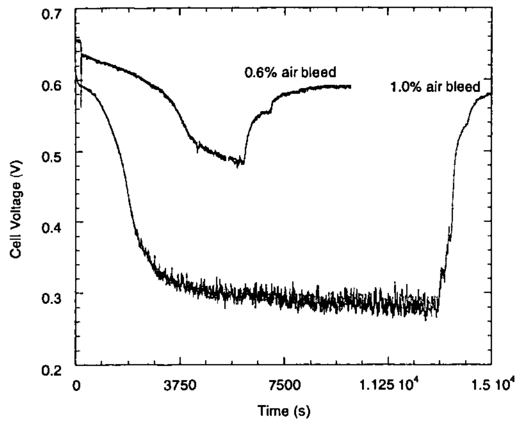

Figure 7 Comparison of cell voltage at constant current density of 647mA/cm^2 versus time. The upper curve corresponds to a Pt-Ru anode of 0.4-0.2 mg/cm^2 loading and the lower curve corresponds to anode with a Pt loading of 0.3 mg/cm^2. Both cathodes had 0.3 mg/cm^2 of Pt. The PtRu anode shows lower anode polarization losses and a lower air bleed of 0.60% is required to mitigate the poisoning.The cell temperature and pressure are 65°C and 100 kPa.

Voltage Oscillations

In the process of assessing the CO tolerant properties of different anode catalysts by testing for MEA performance, we observe an oscillatory phenomena. At high current densities and/or high CO ppms, the performance of the fuel cell fluctuates systematically with a relatively fixed amplitude and period. Air bled into such an oscillating system causes the oscillations to decline in frequency and eventually dampens out the amplitude. The period of oscillation is quite definite; if air is bled in, the period increases until finally oscillations cease in time when the air bleed is sufficient. With very low anode loadings of 0.1mg/cm^2 oscillations were not observed. Although the total number of available sites is reduced with a lower loading, the fraction of available sites for hydrogen oxidation stays the same following an adsorption isotherm. When the number of available sites are very low, the instrumentation is not sensitive enough to measure low amplitude oscillations.

CONCLUSIONS

The air bleed required to regain the performance and alleviate carbon monoxide poisoning was determined for different CO concentrations in hydrogen. Air injection was also found to recover losses caused by the much milder CO_2 poisoning. The air bleed to recover performance loss due to the combined effect of CO and CO_2 was found to be additive. In the presence of reformate with 10 ppm CO only ~ 0.5% air bleed was required for a higher (0.4Pt-0.2Ru mg/cm^2) loaded Pt-Ru anode. Mass balance of the CO and converted CO_2 as well as excess oxygen were measured using gas chromatography. The amount of air bleed will affect the fuel efficiency of the stack and power plant.

REFERENCES

1. S. Gottesfeld and J. Pafford, *J. Electrochem Soc.*, **1988**, 135, 2651
2. D. Sutton, Report at the **1992** *Fuel Cell Seminar*, Tucson , AZ.
3. J. Giner, *Electrochim. Acta*, **1963**, 8, 857