FUEL CELL PLATINUM UTILIZATION[i]

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Abstract

Long range, zero emission vehicles will require the development of low cost, hydrogen/air fuel cells. Of all fuel cell types, the proton exchange membrane (PEMFC) system is presently the strongest candidate. The PEMFC uses platinum as a catalyst for the electrode. Current electrode loading levels will require substantially more platinum per vehicle than is presently used in the internal combustion engine 3-way catalytic converter. Due to its limited supply and resultant economics, the platinum catalyst must be replaced or the loading level must be significantly reduced. This paper presents performance data on low platinum loading PEMFCs from the Center for Electrochemical Systems and Hydrogen Research (CESHR). The effects of platinum loading, and the effect reactant operating pressure are presented and described.

Introduction

Electric vehicles will play a significant role in solving energy and environmental problems. The new clean air laws in California mandate the sale of zero emission vehicles by 1998, (2% of total vehicle sales increasing to 10% by the year 2005). The only vehicle power systems that can meet the zero emission requirement are battery or fuel cell power systems with on-board hydrogen. Initial sales requirements will be met by battery powered vehicles for use in an urban setting (range of less than 150 miles/day). Long range general purpose vehicles will require fuel cells. Of all fuel cell types, the proton exchange membrane fuel cell (PEMFC) system is presently the strongest candidate.

The energy crisis in 1973 stimulated the development of batteries and fuel cells as power sources for electric vehicles. The R&D expenditure since 1973 for developing advanced batteries for electric vehicles has exceed that of fuel cells by at least a factor of ten. Recent fuel cell developments indicate that the PEMFC may be a the first fuel cell to be commercialized for vehicle use. Even though the attainable power and energy densities in PEMFCs may be sufficient to serve as a sole power source for electric vehicles, a hybrid propulsion system (i.e. a PEMFC with advanced batteries) appears more attractive due to lower capital cost[1].

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Platinum Utilization

Platinum utilization is defined in this paper as the number of peak kilo Watts (kW) produced per gram of platinum (kW/gram). As a result, utilization is affected by the amount of platinum used in the electrode preparation and the specific performance of the electrode membrane assembly.

Fuel Cell Platinum Utilization (kW/grams)

Depends On:

- Electrode Platinum Loading - grams/cm^2
- Electrode Membrane Performance - Watts/cm^2

Electrode Membrane Performance Depends On:

- Membrane Characteristics
- Electrode Characteristics (structure)
- Electrode Platinum Loading
- Reactant Gas Pressure (O_2 partial pressure)
- Operational Temperature
- Gas Humidity
- Bipolar Plate Design (flow/contact resistance)
- Auxiliary Power Requirements (compressor, pumps etc.)

The relationship between platinum loading and performance is complex, electrode membrane performance will increase with platinum loading however utilization may decline. Commercially available PEMFCs use high platinum loading (about 4 mg/cm^2) in each electrode (8 mg per cm^2 of membrane area). Experimental low platinum loading electrodes can use as little as 0.1 mg/cm^2(0.2 mg per cm^2 of membrane area). Electrode membrane performance can range between 0.2 and 1.0 W/cm^2 depending on conditions. This results in a possible platinum utilization range of 0.025 to 5 kW/g.

The following table illustrates the influence that platinum utilization will have on the quantity and cost of platinum on a per vehicle basis. The two fuel cell power values represent an author estimate of the power necessary for a midsize car. The 90 kW is a peak power for a fuel cell only vehicle while the 30 kW value is for a fuel cell/battery hybrid.

- Platinum Cost per gram $12 (communities value)
- Average 3 way catalytic converter uses 3 grams - $35

Utilization kW/g	90 kW Fuel Cell		30 kW Fuel Cell	
	grams	Cost	grams	Cost
0.025	3600	$43,200	1200	$14,400
0.25	360	$4,320	120	$1440
1.0	90	$1,080	30	$360
10	9	$108	3	$36

Table 1. Fuel Cell Platinum Utilization/Cost Comparison

The table indicates that platinum would be prohibitively expensive for utilization's of 0.025 and 0.25 kW/g. At 1 kW/g the 30 kW fuel cell/battery hybrid may be possible, at 10 kW/g platinum cost is no longer an issue and for the 30 kW fuel cell/battery hybrid is approximately equal to a internal combustion engine 3 way catalytic converter.

A novel method was developed at Los Alamos National Laboratory to create low platinum loading electrodes in PEMFCs and still maintain performances close to those with high loading. This procedure was used at CESHR to attain the data presented in the following section. The procedure is roughly as follows:

(i) impregnation of a proton conductor into the electrode structure to enhance the three-dimensional reaction zone just as when using a liquid electrolyte;

(ii) hot-pressing of the proton conductor-impregnated electrodes to the proton conducting membranes at a temperature close to that of the glass transition temperature;

(iii) localization of platinum near the front surfaces of the electrodes by using thinner active layers and depositing a very thin layer of platinum on the front surface.

CESHR AIR BREATHING FUEL CELL DATA

The CESHR fuel cell experimental data and analysis is presented in the following text and Figures 1 through 6. All data was taken in early 1991 using a single test cell with 5 cm^2 electrodes. The electrode membrane assemblies were fabricated using porous gas diffusion electrodes and proton conducting polymer membranes (Dow Chemical, 125 μm thickness). The fabrication method and a schematic of the test cell is provided in reference[2]. The fuel cell gases were humidified and temperature regulated. The performance evaluation was conducted using a computer controlled power supply and a data acquisition unit.

All data is presented in the form of polarization and performance curves. The polarization curves show the cell voltage and electrode current density relationship. The performance curves present the electrode power density (voltage x current density) and the chemical to electrical efficiency based on the lower heating value of hydrogen (equal to 1.25 volts).

The following four sections present the data and are entitled; 1) Effect of Electrode Platinum Loading, 2) Effect of operating pressure, 3) Energy of Air Compression, 4) Net Effect of Operating Pressure.

1) Effect of Electrode Platinum Loading

In Figure 1 polarization data is presented that compares high and low platinum loading electrodes on air. The platinum loading presented are 10.0 and 0.45 mg/cm^2 of electrode area. This translates to 20.0 and 0.9 mg/cm^2 of membrane material and is considered as being very high and low values.

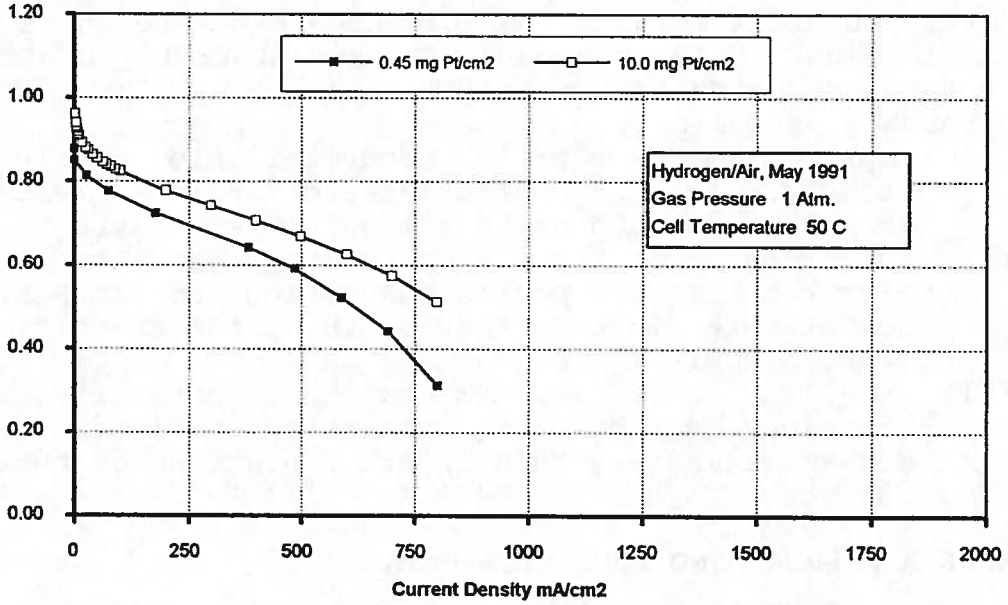

Figure 1. Polarity - Electrode Platinum Loading Comparison

The polarization curve of a fuel cell is typically characterized by three regions an initial region followed by a linear region, and finally a mass transfer limited region. Consider the Figure 1, 0.45 mg Pt/cm^2 case:

1. The initial region (0 to 100 mA/cm^2) shows an initial steep drop in the cell potential due to slow cathode kinetics. With sufficient voltage drop (0.1 to 0.15 volts) the kinetics improve and are no longer limiting.

2. The linear region (100 to 500 mA/cm²) is characterized by a linear voltage drop primarily due to ionic resistance in the electrolyte.
3. As the current density further increases, the polarization curve enters the mass transfer limited region (500+ mA/cm²). Cell potential drops off rapidly primarily due to the inability of oxygen to reach reaction sites fast enough. This inability may be caused by a combination of an oxygen gradient through the electrode, process water blockage and/or nitrogen blanketing.

Figure 1 shows that higher platinum loading increases the cell voltage at a given current density. The curves at the beginning of the linear region have an offset of approximately 60 mV but the spread increases to > 100 mV as the potential drops due to mass transfer limitations. This may be explained by the higher platinum loading having more reaction sites available, thus mass transfer limitations occur at a high current density.

Figure 2 presents the Figure 1 data in a performance curve form. The ordinate is electrode power density in W/cm² and is an indication of how compact the fuel cell could be constructed. A higher electrode power density means less surface electrode area will be needed to achieve a given power level. The abscissa is electrode efficiency based on the lower heating value of hydrogen. Higher efficiency translates to greater fuel economy thus a smaller on-board hydrogen storage system and or a longer vehicle range.

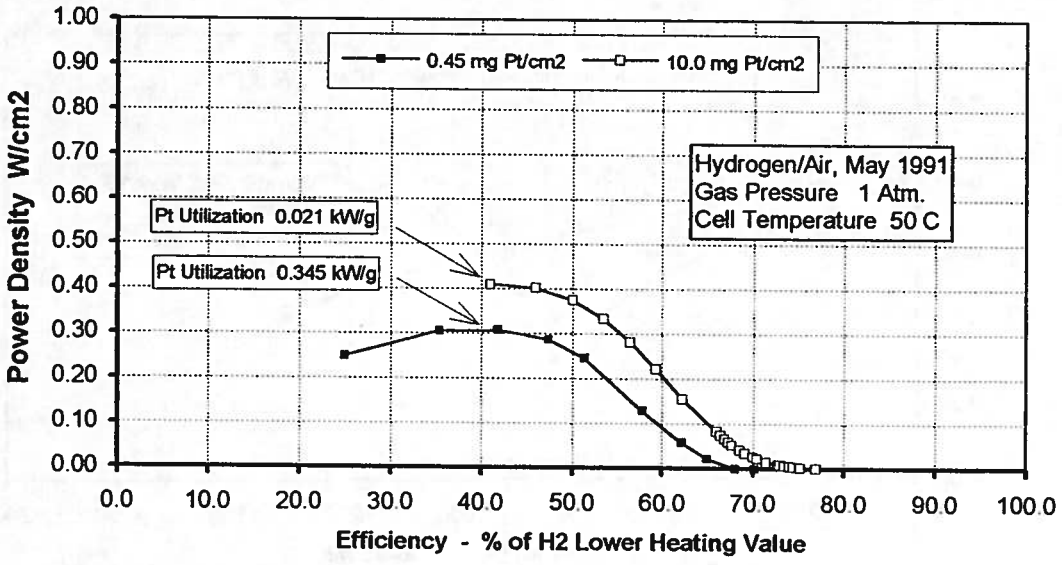

Figure 2. Performance - Electrode Platinum Loading Comparison

The curves indicate that there is a trade off between power density and efficiency. A higher power density is achieved at a lower efficiency, a peak is reached where the power density and efficiency both decline.

The figure shows that higher platinum loading increases the fuel cell power density and efficiency. The high platinum loading case increases the peak power density by approximately 33% (from 0.3 to 0.4 W/cm²). However this is accomplished at great cost to platinum utilization, 0.021 kW per gram of platinum compared to 0.345 kW/g for the low platinum loading case (factor of 16). Considering a hybrid vehicle (fuel cell battery combination) may require 30 kW of fuel cell power this translates to 1429 grams and 87 grams respectively. This indicates that higher platinum utilization is achieved by lowering the electrode loading and accepting a relatively small reduction in power density which translates to a proportionately larger electrode area to achieve the same number of kW.

Cyclic voltametry was performed at CESHR to determine the electrochemical active surface area of the 0.45 mg Pt/cm² electrodes. The active area was found to be about 15% to 20% of the total platinum area available (particle size dependent) leaving significant opportunity for further increases in performance[3].

2) Effect of Operating Pressure

In Figure 3 polarization curves are presented for operating pressures of 1 and 5 atmospheres utilizing low platinum loading electrodes.

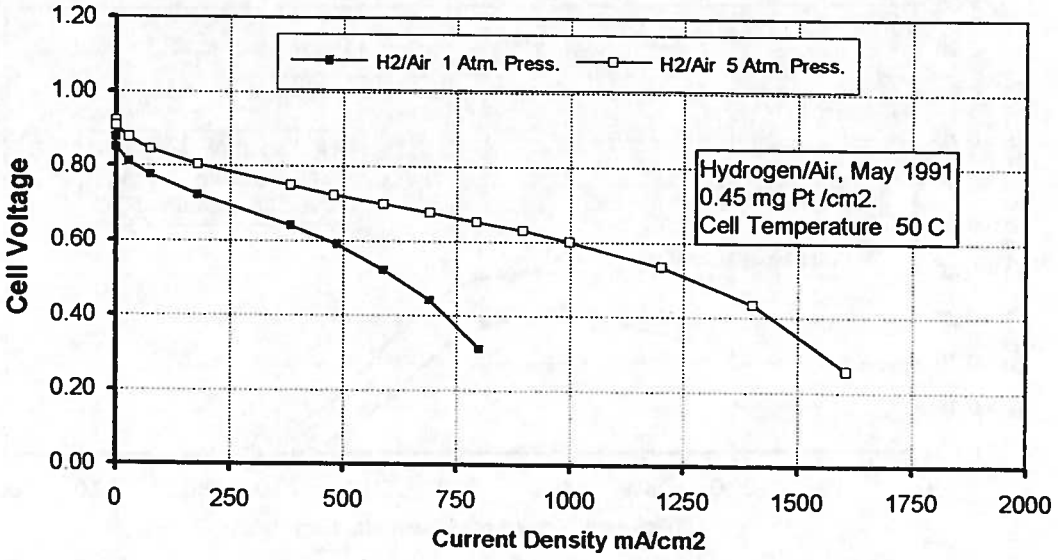

Figure 3. Polarity - Air Compression Comparison

Pressurization significantly increases the electrode performance. The 5 atmosphere air case achieves 0.6 volts at 1000 ma/cm² while the 1 atmosphere curve can only produce 475 mA/cm², greater than a factor of 2 decline in current density. It would seem logical that to achieve a high platinum utilization the reactant gases should always be compressed. For oxygen breathing fuel cells this is usually not a problem as the oxygen will be generally available in a compressed state. However, for an ambient air breathing electric vehicle fuel cell the pressurization will require energy. The following section analyzes this energy requirement and its effect on fuel cell performance.

3) Energy of Air Compression

By compressing the air going into a fuel cell stack the partial pressure of the oxygen is increased and the stack performance is improved. The stoichiometric mass fuel ratio of oxygen to hydrogen is 8 to 1. Air contains 23.18% oxygen by mass, 21.99 % by volume. Therefore the stoichiometric mass fuel ratio of air to hydrogen is 34.5 to 1. However due to nitrogen blanking of the electrode the fuel cell will probably be operated between 1.5 and 3.0 stoichiometric mixtures of air.

The energy for compression must be supplied by the fuel cell system, and the net fuel cell performance is therefore less than the gross stack performance. The air compression process can be adiabatic or isothermal and part of the compression energy may be recovered by an expander such as a turbine.

To simplify the analysis, it is assumed the compression to be performed by an ideal adiabatic compressor with no energy recovery upon expansion. The energy of air compression analysis is presented in Appendix A. In summary, if a constant number of stoichiometric mixtures is used throughout the operating region the energy of compression can be treated as an equivalent cell voltage loss. The voltage loss is a function of the number of stoichiometric mixtures, the initial air temperature T_1 and the pressure ratio P_2/P_1. Thus the effect of air compression can be simply presented on a polarization diagram as a constant reduction in voltage. The reduced voltage curve then may be used to determine the impact air compression has on power density and efficiency. Figure 4 presents the results of equation # 7 presented in Appendix A.

The curves in Figure 4 indicate that increasing the number of stoichiometric mixtures is proportionately to increase the compressor power and thus the effective voltage loss due to compression. The effect of pressure ratio effect is a power function that is less then 1. As a result the effect that compression has on effective voltage loss is

most pronounced at small pressure ratios. As the pressure ratio continues to increases the incremental impact on effective voltage loss is less.

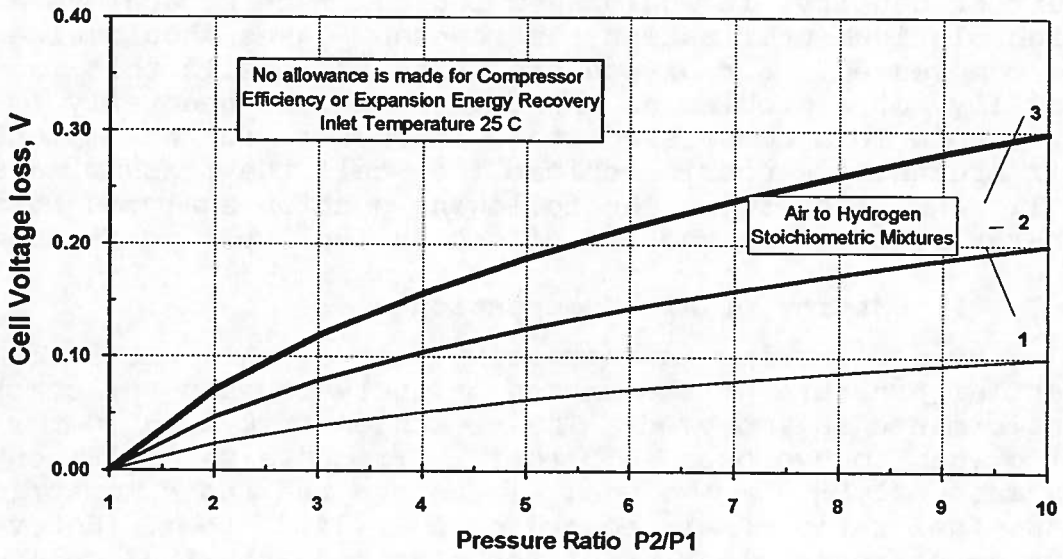

Figure 4. Effective Voltage Loss Due to Adiabatic Air Compression

Utilizing the energy of compression analysis, the data presented in Figure 3 is re drawn in Figure 5 and presented in the following section.

4) Net Effect of Operating Pressure

The net effect of ideal adiabatic air compression on the performance of fuel cell can be interpreted as a voltage reduction (See Appendix A). Data presented in Figure 3 is re drawn in Figure 5.

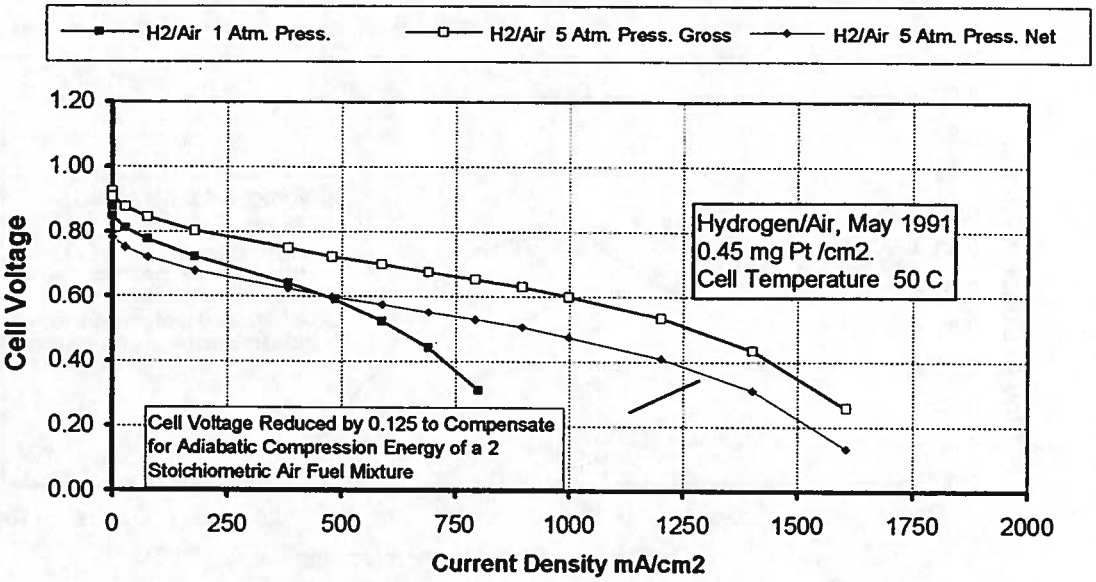

Figure 5. Polarity - Air Compression Comparison

The effect of energy of air compression on the 5 atmosphere case is determined by reducing the polarity curve by 0.125 volts. This reduction corresponds to an adiabatic compression of 2 stoichiometric air mixtures. Considering compression energy the figures shows that the 1 atmosphere condition actually out performs the 5 atmosphere condition down to 0.6 volts where the two curves cross.

Figure 6 presents the Figure 5 data as performance curves. The three curves represent the 1 atmosphere case and the 5 atmosphere gross and net power density cases. The curves show that when compressor energy is not considered, pressurization significantly increases efficiency at any given power density. For example at a power density of 0.2 W/cm^2 the 1 atmosphere case has an efficiency of 54%. Pressurized to 5 atmospheres the gross efficiency is 62%, however when the effect energy of air compression is considered the efficiency reduces to 52% (less then the 1 atmosphere case)

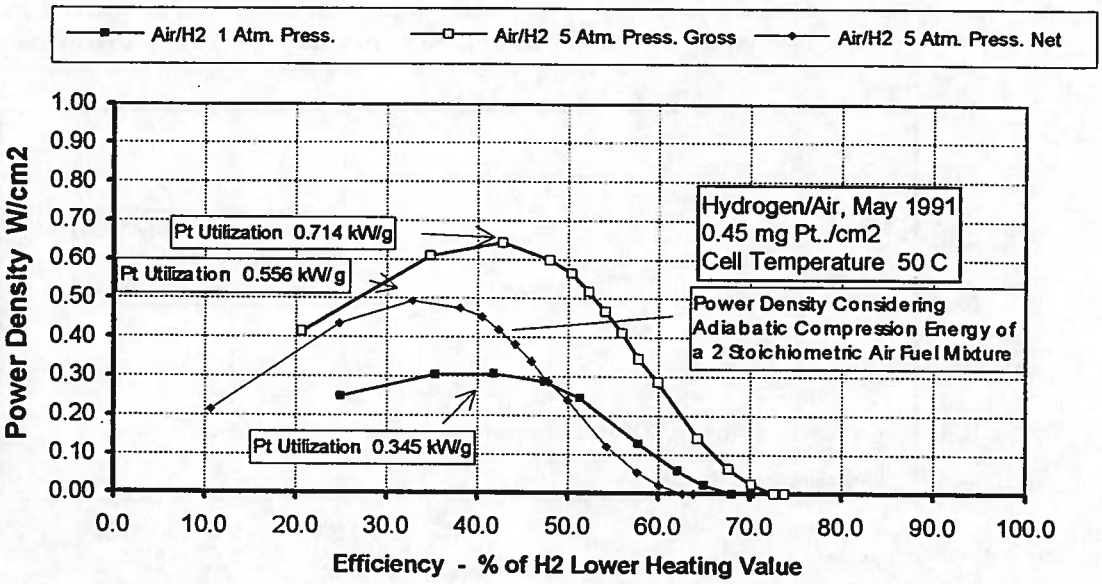

Figure 6. Performance - Air Compression Comparison

The curves in Figure 6 indicate that the air pressure effects the electrode power density/cell efficiency relationship.

The efficiency drop due to air compression may be most significant as it translates to a larger on-board hydrogen storage system. However air compression does improve platinum utilization, Comparing the 1 and 5 atmosphere cases, the platinum utilization increases from 0.345 kW per gram of platinum to 0.556 kW/g (factor of 1.6 increase in utilization). Considering a midsize hybrid vehicle (fuel cell battery combination) may require 30 kW of fuel cell power this translates to a total platinum usage of 87 and 54 grams respectively.

The average conventional vehicle contains 3 g of platinum and thus these values are still an order of magnitude greater. However future research will probably remove this barrier by incremental improvements in platinum utilization or its outright replacement as a catalyst. Unpublished results measured in January 1992 at CESHR have found that the electrode loading can be further reduced by a factor of 4 while maintaining performance. This translates to a 30 kW fuel cell requiring 10 to 20 grams of platinum.

Conclusions

Mandates for zero emission vehicle are stimulating the development of fuel cells as a power systems for electric vehicles. The PEMFC is a favored technology due to its use of a solid electrolyte, cold start capability, high power density, and efficiency characteristics. This paper

presented performance data on electrode platinum utilization and reactant gas operating pressure.

High electrode platinum loading was found to increases performance (W/cm^2) but reduce platinum utilization (kW/gram). The trend is to lower electrode platinum loading (g/cm^2) while maintaining electrode performance. At some point the reduction in platinum will probably reduce utilization however, that limit has not yet been experimentally reached.

Air compression increases the electrode power density and thus the platinum utilization is improved. However the energy for compression must be supplied by the fuel cell system, and the net fuel cell performance is therefore less than the gross performance. Through analysis it was found that the theoretical effect of adiabatic air compression can be simply related to a constant reduction in cell voltage. The reduced voltage curve then may be used to determine the impact air compression has on electrode power density and efficiency. For the specific experimental data presented it was found that at high efficiencies (>50%) the 1 atmosphere operating pressure case gave a higher net power density then did the 5 atmosphere case.

The trade off between platinum utilization, electrode power density, and efficiency is complex. The optimum combination will depend on the vehicles performance requirement, the cost of hydrogen the on-board storage system, and finally the market cost and availability of platinum. From a systems point of view a variable capacity, high efficiency air compression system may be necessary to balance the conflicting goals of platinum utilization, fuel cell power density and overall system efficiency.

Acknoledgements

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References

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[2] S. Srinivasan, D. Manko, H. Koch, M.A. Enayetullah, A.J. Appleby, J. Power Sources 29, 367 (1990)

[3] S. Srinivasan, O. Velev, A. Partasarathy, D. Manko, A.J. Appleby, J. Power Sources 36, 299 (1991).

Appendix A*

The specific power needed to operate the compressor (w_c/cm^2 of electrode area) is proportional to the reaction rate, (the amount of air needed, $\dot{m}_{air}$, g/hr) and the pressure ratio (P_2/P_1). The stoichiometric mass fuel ratio of oxygen to hydrogen is 8 to 1. Air contains 23.18% oxygen by mass, 21.99 % by volume. Therefore the stoichiometric mass fuel ratio of air to hydrogen is 34.5 to 1. However due to nitrogen blanking of the electrode the fuel cell will probably be operated between 1.5 and 3.0 stoichiometric mixtures of air.

The specific amount of air mass needed for the electrode ($g/hr/cm^2$) is dependent on the current density (i, $amps/cm^2$). The mass needed can be determined by Faradays' Law - 96487 coulombs per gram equivalent of consumed hydrogen. Faradays' Law translates to 26.8 amp hours/g of H_2, or 26.8 amp hours/34.5 g of air assuming a 1 stoichiometric mass fuel ratio. Inverting this value results in 1.287 g of Air/hr/i per stoichiometric mass fuel ratio. The specific rate of air use as a ratio of current density is as follows:

(1) $$\frac{\dot{m}_{air}}{i} = \frac{1.287}{3600} \times \#\ \text{of Stoich. Mixtures} \qquad \frac{g/second}{amp/cm^2}$$

The specific energy to adiabatically compress Air is as follows:

(2) $$E_{1\rightarrow 2} = C_p T_1 \left(\frac{P_2}{P_1}^{\frac{k-1}{k}} - 1 \right) \qquad \frac{Joules}{gram}$$

Where
- $E_{1\rightarrow 2}$ Energy of Adiabatic Compression
- C_p Specific Heat (Air 1.004 J/(g K))
- T_1 Inlet Air Temperature
- P_1 Inlet Air Pressure
- P_2 Fuel Cell Air Pressure
- k Specific Heat Ratio (Air 1.4)

Multiplying the specific rate of air use, $\frac{\dot{m}_{air}}{i}$ and the specific energy of compression results in specific power of compression for the electrode (w_c/i):

(3) $$\frac{w_c}{i} = \frac{1.287}{3600} \times \#\text{ of Stoich. Mixtures} \times C_p T_1 \left(\frac{P_2}{P_1}^{\frac{k-1}{k}} - 1 \right) \quad \frac{\text{Watts}}{\text{amp}/\text{cm}^2}$$

The electric power to operate the compressor (w_c) comes from the fuel cell. Thus the gross specific fuel cell power (w_{FC}) is the summation of the specific electric load power (w_{FCL}) and specific compressor power (w_c)

(4) $$w_{FC} = w_{FCL} + w_C = v_{cell} \times i \quad \text{Watts}$$

Consider that the compressor is in series with the electrical load as in the following Figure.

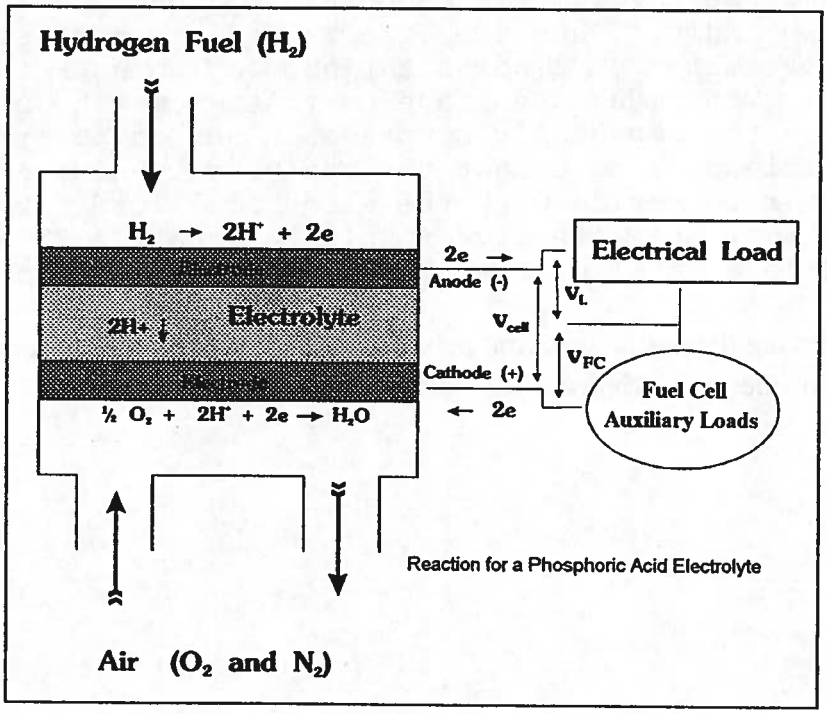

Figure A-1 Fuel Cell Schematic

Both the electrical load and compressor received the same specific current (i) with the respective voltage drops for the compressor (v_c) and the electrical load (v_L) being in proportion to the specific powers w_{FCL} and w_c:

(5) $$w_{FC} = w_{FCL} + w_C = i \times (v_L + v_C) \quad \text{Watts}$$

The specific work of compression is simply the product of the specific amps and the voltage drop due to the compressor:

(6) $$w_c = i \times v_c \quad \text{Watts}$$

Rearranging and applying the specific energy of compression equation results in the following:

(7) $$v_c = \frac{w_c}{i} = \frac{1.287}{3600} \times \#\ \text{of Stoich. Mixtures} \times C_p T_1 \left(\frac{P_2}{P_1}^{\frac{k-1}{k}} - 1 \right) \quad \text{Volts}$$

It is important to note that the effective compressor voltage v_c is a function of the number of stoichiometric mixtures, the initial air temperature T_1 and the pressure ratio P_2/P_1 only. Thus the effect of air compression can be simply presented on a polarization diagram as a reduction in voltage. The reduced voltage curve then may be used to determine the impact air compression has on power density and efficiency. Note that the analysis considered the compressor in series with the electrical load for ease of explanation, the effective result in equation #7 also applies to a parallel placement of the compressor.

* The following derivation was first published in the International Association for Hydrogen Energy, Technical Proceedings - D.H. Swan et al. 1991.