3- PHOSPHORIC ACID FUEL CELLS (PAFCs)

The phosphoric acid fuel cell (PAFC) was the first fuel cell technology to be commercialized. The number of units built exceeds any other fuel cell technology, with over 85 MW of demonstrators that have been tested, are being tested, or are being fabricated worldwide. Most of the plants are in 50 to 200 kW capacity range, but large plants of 1 MW and 5 MW have been built. The largest plant operated to date achieved 11 MW of grid quality ac power. Figure 18 depicts the operating configuration of the phosphoric acid cell.

The electrochemical reactions occurring in PAFCs are:

\[ \text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^- \]

at the anode, and

\[ \frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O} \]

at the cathode. The overall cell reaction is

\[ \frac{1}{2}\text{O}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O} \]
The electrochemical reactions occur on highly dispersed electro-catalyst particles supported on carbon black. Platinum (Pt) or Pt alloys are used as the catalyst at both electrodes. The PAFC have a similar design with the PEMFC. The electrolyte used for PAFC is concentrated phosphoric acid (H₃PO₄), allowing operation at temperatures higher than the PEMFC (i.e., over 100°C). This electrolyte is contained in a silicon carbide matrix, and catalysts are typically made of Pt.

**Cell Components**

There have been only minor changes in cell design in recent years. The major U.S. manufacturer, UTC Fuel Cells, has concentrated on improving cell stability and life, and in improving the reliability of system components at reduced cost. Technological advances of the components of this type of fuel cells have been extensively documented over the last 40 years, and a brief summary is presented in Table 2.

**Table 2: PAFC Component Characteristics**

<table>
<thead>
<tr>
<th>Component</th>
<th>Ca.1965</th>
<th>Ca.1975</th>
<th>Current status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode</td>
<td>PTFE-bonded Pt black</td>
<td>PTFE-bonded Pt/C</td>
<td>PTFE-bonded Pt/C</td>
</tr>
<tr>
<td></td>
<td>Vulcan XC-72</td>
<td>Vulcan XC-72</td>
<td>Vulan XC-72</td>
</tr>
<tr>
<td></td>
<td>9 mg Pt/cm²</td>
<td>0.25 mg Pt/cm²</td>
<td>0.1 mg Pt/cm²</td>
</tr>
<tr>
<td>Cathode</td>
<td>PTFE-bonded Pt black</td>
<td>PTFE-bonded Pt/C</td>
<td>PTFE-bonded Pt/C</td>
</tr>
<tr>
<td></td>
<td>Vulcan XC-72</td>
<td>Vulcan XC-72</td>
<td>Vulan XC-72</td>
</tr>
<tr>
<td></td>
<td>9 mg Pt/cm²</td>
<td>0.5 mg Pt/cm²</td>
<td>0.5 mg Pt/cm²</td>
</tr>
<tr>
<td>Electrode Support</td>
<td>Ta mesh screen</td>
<td>Carbon paper</td>
<td>Carbon paper</td>
</tr>
<tr>
<td>Electrolyte Support</td>
<td>Glass fiber paper</td>
<td>PTFE-bonded SIC</td>
<td>PTFE-bonded SIC</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>85% H₃PO₄</td>
<td>95% H₃PO₄</td>
<td>100% H₃PO₄</td>
</tr>
</tbody>
</table>

The operating temperatures and acid concentrations of PAFCs have increased to achieve higher cell performance; temperatures of about 200 °C and acid concentrations of 100 % H₃PO₄ are commonly used today. Although the present practice is to operate at atmospheric pressure, the operating pressure of PAFCs surpassed 8 atm in the 11 MW electric utility demonstration plant, confirming an increase in power plant efficiency. However, a number of issues remain whether to design and operate PAFC units at atmospheric vs. pressurized conditions. Primarily, small, multi-kW PAFC power units that were the focus of initial commercial applications led to atmospheric pressure operation. Although pressurization increased efficiency (lower fuel cost), it complicated the power unit - resulting in higher capital cost. The economic trade-off favored simpler, atmospheric operation for early commercial units. Another important issue, independent of power unit size, is that pressure promotes corrosion. Phosphoric acid electrolyte (H₃PO₄) produces a vapor. This vapor, which forms over the electrolyte, is corrosive to cell locations other than the active cell area. These cell locations are at a mixed voltage (open circuit and cell voltage), that can be over ~0.8V/cell. That is the limit above which corrosion occurs (active area limited to operation under ~0.8 V/cell). An increase in cell total pressure causes the partial pressure of the H₃PO₄ vapor to increase, causing increased corrosion in the cell. Cell temperature must also be increased with pressurized conditions to produce steam for the steam reformer.
Carbon black and graphite were sufficiently stable to replace the more expensive gold-plated tantalum cell hardware used at the time. The use of high-surface area graphite to support Pt permitted a dramatic reduction in Pt loading without sacrificing electrode performance. It was reported that "without graphite, a reasonably inexpensive acid fuel cell would be impossible, since no other material combines the necessary properties of electronic conductivity, good corrosion resistance, low density, surface properties (especially in high area form) and, above all, low cost". However, carbon corrosion and Pt dissolution become an issue at cell voltages above ~0.8 V. Consequently, low current densities at cell voltage above 0.8 V and hot idle at open circuit potential should be avoided.

The porous electrodes contain a mixture of electro-catalyst supported on carbon black and a polymeric binder, usually PTFE (30 to 50 wt %). The PTFE binds the carbon black particles together to form an integral, but porous, structure that is supported on a porous graphite substrate. The graphite structure serves as a support for the electro-catalyst layer, as well as the current collector. A typical graphite structure used in PAFCs has an initial porosity of about 90 %, which is reduced to about 60 % by impregnation with 40 wt % PTFE. This wet-proof graphite structure contains macro pores of 3 to 50 µm diameter (median pore diameter of about 12.5 µm) and micropores with a median pore diameter of about 34 Å for gas permeability. The composite structure, consisting of a carbon black/PTFE layer on the graphite substrate, forms a stable, three-phase interface in the fuel cell, with H₃PO₄ electrolyte on one side (electro-catalyst side) and the reactant gas environment on the other.

A bipolar plate separates the individual cells and electrically connects them in series in a fuel cell stack. In some designs, the bipolar plate also contains gas channels that feed the reactant gases to the porous electrodes and remove the reaction products and inerts. Bipolar plates made from graphite resin mixtures that are carbonized at low temperature (~900 °C) are not suitable because of their rapid degradation in PAFC operating environments. However, corrosion stability is improved by heat treatment to 2,700 °C, i.e., the corrosion current is reduced by two orders of magnitude at 0.8 V in 97 % H₃PO₄ at 190°C and 4.8 atm. The all-graphite bipolar plates are sufficiently corrosion-resistant for a projected life of 40,000 hours in PAFCs, but they are still relatively costly to produce.

A typical PAFC stack contains cells connected in series to obtain the practical voltage level desired for the load. In such an arrangement, individual cells are stacked with bipolar plates between the cells. The bipolar plates used in early PAFCs consisted of a single piece of graphite with gas channels machined on either side to direct the flow of fuel and oxidant. Currently, both bipolar plates of the previous design and new designs consisting of several components are being considered. In the multi-component bipolar plates, a thin impervious plate separates the reactant gases in adjacent cells in the stack, and separate porous plates with ribbed channels are used to direct gas flow. In a cell stack, the impervious plate is subdivided into two parts, and each joins one of the porous plates. The electrolyte vaporizes so that a portion of H₃PO₄ escapes from the cell in the air stream over time. An electrolyte reservoir plate (ERP), made of porous graphite, provides enough electrolyte to achieve a 40,000-hour cell life goal (there is no electrolyte replacement). The ERP also accommodates increases in electrolyte volume due to an increase in H₂O, so the porous graphite electrodes don’t flood. These fluctuations in electrolyte volume occur during start-up and during transient operation. The porous structure, which allows rapid
gas transport, is also used to store additional acid to replenish the supply lost by evaporation during the cell operating life.

In PAFC stacks, provisions must be included to remove heat generated during cell operation. In practice, heat has been removed by either liquid (two-phase water or a dielectric fluid) or gas (air) coolants that are routed through cooling channels located (usually about every fifth cell) in the cell stack. Liquid cooling requires complex manifolds and connections, but better heat removal is achieved than with air-cooling. The advantage of gas cooling is its simplicity, reliability, and relatively low cost. However, the size of the cell is limited, and the air-cooling passages must be much larger than the liquid-cooling passages.

**Development Components**

Phosphoric acid electrode/electrolyte technology has reached a level of maturity at which developers commit resources for commercial capacity, multi-unit demonstrations and preprototype installations. UTC Fuel Cells has 25 (200 kW) atmospheric pressure power plants that have operated between 30,000 to 40,000 hours. Most cell parts are graphite, and there has been no electrolyte replacement over the cell life of 40,000 hours. Grid-independent units undergo extensive cycling. Cell components are manufactured at scale and in large quantities, demonstrating confidence that predicted performance will be met. However, further increases in power density and reduced cost are needed to achieve economic competitiveness with other energy technologies, as expressed in the early 1990s. Fuel cell developers continue to address these issues.

In 1992, UTC Fuel Cells' predecessor, International Fuel Cells, completed a government sponsored, advanced water-cooled PAFC development project to improve the performance and reduce the cost of both its atmospheric and pressurized technology for both on-site and utility applications. The project focused on five major activities:

1. produce a conceptual design of a large stack with a goal of 0.188 W/cm², 40,000 hour useful life, and a stack cost of less than $400/kW
2. test pressurized Configuration "B" single cells developed in a previous program, but improved with proprietary design advances in substrates, electrolyte reservoir plates, catalysts, seals, and electrolyte matrix to demonstrate the 0.188 W/cm² power density goal
3. test a pressurized short stack with subscale size, improved component cells, and additional improvements in the integral separators and coolers to confirm the stack design
4. test a pressurized short stack of improved full-size cell components, nominal 1 m² size, to demonstrate the 0.188 W/cm² power density goal
5. test an advanced atmospheric "on-site" power unit stack with the improved components.

Several important technology development efforts for which details have been published include catalyst improvements, advanced gas diffusion electrode development, and tests on materials that offer better carbon corrosion protection. Transition metal (e.g., iron, cobalt) organic macrocycles from the families of tetramethoxyphenylporphyrins (TMPP), phthalocyanines (PC), tetraazannulenes (TAA) and tetraphenylporphyrins (TPP) have been evaluated as O₂-reduction electro-catalysts in PAFCs. One major problem with these organic macrocycles is their limited chemical stability in hot concentrated phosphoric acid. However, after heat treatment of the
organic macrocycle (i.e., CoTAA, CoPC, CoTMPP, FePC, FeTMPP) on carbon at about 500 to 800 °C, the pyrolyzed residue exhibits electro-catalytic activity that, in some instances, is comparable to that of Pt and has promising stability, at least up to about 100 °C. Another successful approach for enhancing the electro-catalysis of O₂-reduction is to alloy Pt with transition metals such as Ti, Cr, V, Zr, and Ta. The enhancement in electro-catalytic activity has been explained by a correlation between the optimum nearest-neighbor distance of the elements in the alloy and the bond length in O₂. Conventional cathode catalysts comprise either platinum or platinum alloys supported on conducting carbon black at 10 wt % platinum. Present platinum loadings on the anode and cathode are 0.1 mg/cm² and 0.5 mg/cm², respectively. It has been suggested by Ito, et al., that the amount of platinum may have been reduced to the extent that it might be cost effective to increase the amount of platinum loading on the cathode. However, a problem exists in that fuel cell stack developers have not experienced satisfactory performance improvements when increasing the platinum loading. Johnson Matthey Technology Centre (J-M) presented data that resulted in improved performance nearly in direct proportion to that expected based on the increase in platinum. Initial tests by J-M confirmed previous results - that using platinum alloy catalyst with a 10 wt % net platinum loading improves performance. Platinum/nickel alloy catalysts yielded a 49 wt % increase in specific activity over pure platinum. This translated into a 39 mV improvement in the air electrode performance at 200 mA/cm². Johnson Matthey then determined that the platinum loading in the alloyed catalyst could be increased up to 30 wt % while retaining the same amount of platinum without any decrease in specific activity or performance; the amount of nickel, hence the total amount of alloyed catalyst, decreased. Next, J-M researchers increased the amount of platinum from 10 to 30 wt % while keeping the same nickel catalyst loading. The total amount of alloyed catalyst increased in this case. Results showed an additional 36 wt % increase in specific activity, which provided another 41 mV increase at 200 mA/cm². The ideal voltage increase would have been 46 mV for this increase in platinum. Thus, the performance increase obtained experimentally was nearly in direct proportion to the theoretical amount expected. The type of carbon support did not seem to be a major factor, based on using several typical supports during the tests.

The anode of a phosphoric acid fuel cell is subject to a reduction in performance when even low amounts of contaminants are preferentially absorbed on the noble catalysts. Yet, hydrogen-rich fuel gases, other than pure hydrogen, are produced with contaminant levels well in excess of the anode's tolerance limit. Of particular concern are CO, COS, and H₂S in the fuel gas. The fuel stream in a state-of-the-art PAFC anode, operating at approximately 200 °C, must contain 1 vol % or less of CO, less than 50 ppmv of COS plus H₂S, and less than 20 ppmv of H₂S. Current practice is to place COS and H₂S cleanup systems and CO shift converters prior to the cell (normally in the fuel processor before reforming) to reduce the fuel stream contaminant levels to the required amounts. Giner, Inc. performed experiments to develop a contaminant tolerant node catalyst in order to reduce or eliminate the cleanup equipment. An anode catalyst, G87A-17-2, was identified that resulted in only a 24 mV loss from reference when exposed to a 75 % H₂, 1 % CO, 24 % CO₂, 80 ppm H₂S gas mixture at 190 °C, 85 % fuel utilization, and 200 mA/cm². A baseline anode experienced a 36 mV loss from the reference at the same conditions. At 9.2 atm pressure, the anode loss was only 19 mV at 190 °C and 17 mV at 210 °C (compared with pure H₂) with a gas of 71 % H₂, 5 % CO, 24 % CO₂, and 200 ppm H₂S. Economic studies comparing
the tradeoff between decreased cell performance with increased savings in plant cost showed no advantage when the new anode catalyst was used with gas containing 1 % CO/200 ppm H₂S. A $7/kW increase resulted with the 5 % CO gas (compared to a 1 % CO gas) at a 50 MW size. Some savings would result by eliminating the low temperature shift converter. The real value of the catalyst may be its ability to tolerate excessive CO and H₂S concentrations during fuel processor upsets, and to simplify the system by eliminating equipment.

As previously mentioned, state-of-the-art gas diffusion electrodes are configured to provide an electrolyte network and a gas network formed with the mixture of carbon black and PTFE. In the electrodes, carbon black agglomerates, consisting of small primary particles 0.02 to 0.04 µm, are mixed with much larger PTFE particles of ~0.3 µm. The carbon black surface may not be covered completely by the PTFE because of the large size of conventional PTFE particles. The space in the agglomerates or the space between the agglomerates and PTFE may act as gas networks at the initial stage of operation, but fill with electrolyte eventually because of the small contact angle of carbon black, uncovered with PTFE, to electrolyte (<90°), resulting in the degradation of cell performance. Attempts to solve this flooding problem by increasing the PTFE content have not been successful because of the offset in performance resulting from the reduction of catalyst utilization. Higher performance and longer lifetime of electrodes are intrinsically at odds, and there is a limit to the improvement in performance over life by optimizing PTFE content in the state-of-the-art electrode structures. Watanabe, et al. proposed preparing an electrode utilizing 100 % of catalyst clusters, where the functions of gas diffusion electrodes were allotted completely to a hydrophilic, catalyzed carbon black and a wet-proofed carbon black. The former worked as a fine electrolyte network, and the latter worked as a gas-supplying network in a reaction layer. Higher utilization of catalyst clusters and longer life at the reaction layer were expected, compared to state-of-the-art electrodes consisting of the uniform mixture of catalyzed carbon black and PTFE particles. The iR-free electrode potentials for the reduction of oxygen and air at 200 mA/cm² on the advanced electrode were 10 mV higher than those of the conventional electrode.

There is a trade-off between high power density and cell life performance. One of the major causes of declining cell performance over its life is that electrode flooding and drying, caused by migration of phosphoric acid between the matrix and the electrodes, occurs during cell load cycling. Researchers at Fuji Electric addressed two approaches to improve cell life performance while keeping power density high. In one, the wettability of the cathode and anode were optimized, and in the other a heat treatment was applied to the carbon support for the cathode catalyst. During tests, it was observed that a cell with low cathode wettability and high anode wettability was more than 50 mV higher than a cell with the reverse wetting conditions after 40 start/stop cycles.

The use of carbon black with large surface area to improve platinum dispersion on supports was investigated as a method to increase the power density of a cell. However, some large surface area carbon blacks are fairly corrosive in hot potassium acid, resulting in a loss of catalytic activity. The corrosivity of the carbon support affects both the rate of catalyst loss and electrode flooding and, in turn, the life performance of a cell. Furnace black has been heat treated at high temperature by Fuji Electric to increase its resistance to corrosion. It was found that corrosion could be reduced and cell life performance improved by heat treating carbon supports at high temperature, at least to around 3,000 °C.
More recently, UTC Fuel Cells cites improvements to achieve 40,000 hour cell life through better cell temperature control, increasing H₃PO₄ inventory, and incorporating electrolyte reservoir plates in the cell stack.

**Cell Performance**

Cell performance for any fuel cell is a function of pressure, temperature, reactant gas composition, and fuel utilization. In addition, performance can be adversely affected by impurities in both the fuel and oxidant gases. The major polarization occurs at the cathode, and furthermore, the polarization is greater with air than with pure oxygen because of dilution of the reactant. The anode exhibits very low polarization on pure H₂, and increases when CO is present in the fuel gas. The ohmic (iR) loss in PAFCs is also relatively small, amounting to about 12 mV at 100 mA/cm². Typical PAFCs will generally operate in the range of 100 to 400 mA/cm² at 600 to 800 mV/cell. Voltage and power constraints arise from increased corrosion of platinum and carbon components at cell potentials above approximately 800 mV.

1- **Effect of Pressure**

Even though pressure operation is not being pursued, it is still of interest for possible future development. It is well known that an increase in the cell operating pressure enhances the performance of PAFCs. The theoretical change in voltage ($\Delta V_p$) as a function of pressure (P) is expressed as:

$$\Delta V_p (mV) = \frac{3(2.3 RT)}{2F} \log \frac{P_2}{P_1}$$

where $\frac{3(2.3 RT)}{2F} = 138 \ mV$ at 190°C (374 °F),

where $P_1$ and $P_2$ are different cell pressures.

Experimental data reported that the effect of pressure on cell performance at 190°C and 323 mA/cm² is correlated by the equation:

$$\Delta V_p (mV) = 146 \log \frac{P_2}{P_1}$$

for a temperature range of 177 °C < T < 218 °C and a pressure range of 1 atm < P < 10 atm.

The improvement in cell performance at higher pressure and high current density can be attributed to a lower diffusion polarization at the cathode and an increase in the reversible cell potential. In addition, pressurization decreases activation polarization at the cathode because of the increased oxygen and water partial pressures. If the partial pressure of water is allowed to increase, a lower acid concentration will result. This will increase ionic conductivity and bring about a higher exchange current density. The net outcome is a reduction in ohmic losses.

2- **Effect of Temperature**

An increase in temperature has a beneficial effect on cell performance because activation polarization, mass transfer polarization, and ohmic losses are reduced.
The kinetics for the reduction of oxygen on Pt improves as the cell temperature increases. At a mid-range operating load (~250 mA/cm²), the voltage gain (ΔVT) with increasing temperature of pure H₂ and air is correlated by:

\[ ΔV_T \text{ (mV)} = 1.15 \left( T_2 - T_1 \right) \text{ (°C)} \]

for a temperature range of 180 °C < T < 250 °C.

Although temperature has only a minimal effect on the H₂ oxidation reaction at the anode, it is important in terms of the amount of CO that can be absorbed by the anode. Figure 19 shows that increasing the cell temperature results in increased anode tolerance to CO absorption. A strong temperature effect was also observed using simulated coal gas. Below 200 °C, the cell voltage drop was significant. Experimental data suggest that the effect of contaminants is not additive, indicating that there is an interaction between CO and H₂S. Increasing temperature increases performance, but elevated temperature also increases catalyst sintering, component corrosion, electrolyte degradation, and evaporation. UTC Fuel Cells operates its phosphoric acid cells at 207 °C, which is a compromise that allows reasonable performance at a life of 40,000 hours.

![Figure 19: Effect of Temperature: Ultra-High Surface Area Pt Catalyst.](image)

3- **Effect of Reactant Gas Composition and Utilization**

Increasing reactant gas utilization or decreasing inlet concentration results in decreased cell performance due to increased concentration polarization and Nernst losses. These effects are related to the partial pressures of reactant gases and are discussed below.

**Oxidant:** The oxidant composition and utilization are parameters that affect the cathode performance, air, which contains ~21 % O₂, is the obvious oxidant for terrestrial application PAFCs. The use of air with ~21 % O₂ instead of pure O₂ results in a decrease in the current...
density of about a factor of three at constant electrode potential. The polarization at the cathode increases with an increase in O$_2$ utilization. Based on experimental data, the voltage loss due to a change in oxidant utilization can be described by:

$$\Delta V_{\text{Cathode}} (\text{mV}) = 148 \log \frac{\overline{P_{O_2}}}{\overline{P_{O_2}}_1} \quad 0.04 \leq \frac{\overline{P_{O_2}}}{\overline{P_{Total}}} \leq 0.20$$

$$\Delta V_{\text{Cathode}} (\text{mV}) = 96 \log \frac{\overline{P_{O_2}}}{\overline{P_{O_2}}_1} \quad 0.20 < \frac{\overline{P_{O_2}}}{\overline{P_{Total}}} < 1.00$$

where $\overline{P_{O_2}}$ is the average partial pressure of O$_2$.

The first equation will generally apply to fuel cells using air as the oxidant and the second equation for fuel cells using an O$_2$-enriched oxidant.

**Fuel:** Hydrogen for PAFC power plants will typically be produced from conversion of a wide variety of primary fuels such as CH$_4$ (e.g., natural gas), petroleum products (e.g., naphtha), coal liquids (e.g., CH$_3$OH), or coal gases. Besides H$_2$, CO and CO$_2$ are also produced during conversion of these fuels (unreacted hydrocarbons are also present). These reformed fuels contain low levels of CO (after steam reforming and shift conversion reactions in the fuel processor) that cause anode CO absorption in PAFCs. The CO$_2$ and unreacted hydrocarbons (e.g., CH$_4$) are electrochemically inert and act as diluents. Because the anode reaction is nearly reversible, the fuel composition and hydrogen utilization generally do not strongly influence cell performance. The voltage change due to a change in the partial pressure of hydrogen (which can result from a change in either the fuel composition or utilization) can be described by:

$$\Delta V_{\text{Anode}} (\text{mV}) = 55 \log \frac{\overline{P_{H_2}}}{\overline{P_{H_2}}_1}$$

where $\overline{P_{H_2}}$ is the average partial pressure of H$_2$.

At 190 °C, the presence of 10 % CO$_2$ in H$_2$ should cause a voltage loss of about 2 mV. Thus, diluents in low concentrations are not expected to have a major effect on electrode performance; however, relative to the total anode polarization (i.e., 3 mV/100 mA/cm$^2$), the effects are large. It has been reported that with pure H$_2$, the cell voltage at 215 mA/cm$^2$ remains nearly constant at H$_2$ utilizations up to 90 %, and then it decreases sharply at H$_2$ utilizations above this value. Low utilizations, particularly oxygen utilization, yield high performance. Low utilizations, however, result in poor fuel use. Optimization of this parameter is required. State-of-the-art utilizations are on the order of 85 % and 50 % for the fuel and oxidant, respectively.
4- Effect of Impurities

The concentrations of impurities entering the PAFC are very low relative to diluents and reactant gases, but their impact on performance is significant. Some impurities (e.g., sulfur compounds) originate from fuel gas entering the fuel processor and are carried into the fuel cell with the reformed fuel, whereas others (e.g., CO) are produced in the fuel processor.

**Carbon Monoxide:** The presence of CO in a H₂-rich fuel has a significant effect on anode performance because CO affects Pt electrode catalysts. CO absorption is reported to arise from the dual site replacement of one H₂ molecule by two CO molecules on the Pt surface. According to this model, the anodic oxidation current at a fixed overpotential, with (i₀) and without (i₁) CO present, is given as a function of CO coverage (θᵦ) by:

\[
\frac{i₀}{i₁} = (1 - θₐ)²
\]

For \([\text{CO}]/[\text{H}_2] = 0.025\), \(θₐ = 0.31\) at 190°C, therefore, \(i₀\) is about 50% of \(i₁\).

Both temperature and CO concentration have a major influence on the oxidation of H₂ on Pt in CO containing fuel gases. Benjamin, et al. derived the following equation for the voltage loss resulting from CO absorption as a function of temperature:

\[
ΔV_{CO} = k(T) ([\text{CO}]_2 - [\text{CO}]_1)
\]

where \(k(T)\) is a function of temperature, and \([\text{CO}]_1\) and \([\text{CO}]_2\) are the mole fractions CO in the fuel gas.

**Sulfur Containing Compounds:** Hydrogen sulfide and carbonyl sulfide (COS) impurities in fuel gases from fuel processors and coal gasifiers can reduce the effectiveness of fuel cell catalysts. Concentrations of these compounds must also be limited in a power plant's fuel processing section, because the fuel reformer too has catalysts. As a result, sulfur must be removed prior to fuel reforming with the non-sulfur tolerant catalysts now in use in PAFC power plants. It is prudent to be concerned about sulfur effects in the cell, however, because the fuel processor catalyst's tolerance limits may be less than the fuel cell catalyst's or there could be an upset of the fuel processor sulfur guard with sulfur passing through to the cell. The concentration levels of H₂S in an operating PAFC (190 to 210 °C, 9.2 atm, 80 % H₂ utilization, <325 mA/cm²) that can be tolerated by Pt anodes without suffering a destructive loss in performance are <50 ppm (H₂S + COS) or <20 ppm (H₂S). Rapid cell failure occurs with fuel gas containing more than 50 ppm H₂S. Sulfur does not affect the cathode, and the impact of sulfur on the anodes can be re-activated by polarization at high potentials (i.e., operating cathode potentials). A synergistic effect between H₂S and CO negatively impacts cell performance.

Experimental studies by Chin and Howard indicate that H₂S adsorbs on Pt and blocks the active sites for H₂ oxidation. The following electrochemical reactions:
Elemental sulfur (in the last equation) is expected on Pt electrodes only at high anodic potentials; at sufficiently high potentials, sulfur is oxidized to SO2. The extent of catalyst masking by H2S increases with increasing H2S concentration, electrode potential, and exposure time. The effect of H2S, however, decreases with increasing cell temperature.

**Other Compounds:** The effects of other compounds (such as those containing nitrogen) on PAFC performance has been adequately reviewed by Benjamin, et al.. Molecular nitrogen acts as a diluent but other nitrogen compounds (e.g., NH3, HCN, NOX) may not be as innocuous. NH3 in the fuel or oxidant gases reacts with H3PO4 to form a phosphate salt, (NH4)H2PO4, which decreases the rate of O2 reduction. A concentration of less than 0.2 mol % (NH4)H2PO4 must be maintained to avoid unacceptable performance losses. Consequently, the amount of molecular nitrogen must be limited to 4 % because it will react with hydrogen to form NH3. The effects of HCN and NOX on fuel cell performance have not been clearly established.

### 5- Effects of Current Density

The voltage that can be obtained from a PAFC is reduced by ohmic, activation, and concentration losses that increase with increasing current density. The magnitude of this loss can be approximated by the following equations:

\[ \Delta V_J (mV) = -0.53 \Delta J \quad \text{for } J = 100 \text{ to } 200 \text{ mA/cm}^2 \]

\[ \Delta V_J (mV) = -0.39 \Delta J \quad \text{for } J = 200 \text{ to } 650 \text{ mA/cm}^2 \]

Similarly, at atmospheric conditions, the magnitude of this loss can be approximated by:

\[ \Delta V_J (mV) = -0.74 \Delta J \quad \text{for } J = 50 \text{ to } 120 \text{ mA/cm}^2 \]

\[ \Delta V_J (mV) = -0.45 \Delta J \quad \text{for } J = 120 \text{ to } 215 \text{ mA/cm}^2 \]

### 6- Effects of Cell Life

One of the primary areas of research is in extending cell life. The goal is to maintain the performance of the cell stack during a standard utility application (~40,000 hours). Previous state-of-the-art PAFCs showed the following degradation over time:

\[ \Delta V_{\text{lifetime}} (mV) = -3 \text{ mV/1,000 hours} \]

Assuming that the loss in efficiency is due solely to cell voltage loss, the maximum degradation rate can be determined as:

\[ \Delta V_{\text{lifetime}} (mV) = -2 \text{ mV/1,000 hours} \]