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4. ALKALINE FUEL CELL

The Alkaline Fuel Cell (AFC) was one of the first modern fuel cells to be developed, beginning in 1960. The application at that time was to provide on-board electric power for the Apollo space vehicle. Desirable attributes of the AFC include excellent performance compared to other candidate fuel cells due to its active O_2 electrode kinetics and flexibility to use a wide range of electro-catalysts. The AFC continues to be used: it now provides on-board power for the Space Shuttle Orbiter with cells manufactured by UTC Fuel Cells.

The AFC developed for space application was based, in large part, on work initiated by F.T. Bacon (1) in the 1930s. By 1952, construction and performance testing of a 5-kW alkaline fuel cell, operating on H₂ and O₂, was completed. The fuel cell developed by Bacon operated at 200 to 240 °C with 45 percent KOH electrolyte. Pressure was maintained at 40 to 55 atm to prevent the electrolyte from boiling. At this relatively high temperature and pressure, performance of the cell was quite good (0.78 volts at 800 mA/cm²). The anode consisted of a dual-porosity Ni electrolyte side and 30 μ m pore diameter on the gas side). The cathode consisted of a porous structure of lithiated NiO. The three-phase boundary in the porous electrodes was maintained by a differential gas pressure across the electrode, since a wetproofing agent was not available at that time, i.e., PTFE (polytetrafluoroethylene) as a wetproofing material did not exist, and it would not have been stable in the high temperature alkaline solution (2).

The kinetics of O_2 reduction in alkaline electrolytes are more favorable than in phosphoric acid electrolyte. Consider a Pt cathode (0.25 mg/cm²) in 30 percent KOH at 70 °C and in 96 percent phosphoric acid at 165 °C. The cathode potentials (vs. RHE - Reversible Hydrogen Electrode) at 100 mA/cm² in these two electrolytes are 0.868 and 0.730 V, respectively, according to data reported by Appleby (Figure 2.15-1 in Reference 3). Various explanations have been advanced for the higher O_2 reduction rates in alkaline electrolytes (4). The practical consequence of the higher performance of Pt cathodes in alkaline electrolytes is that AFCs are capable of higher efficiencies than PAFCs at a given current density, or higher power densities at the same efficiency. Bockris (2) estimates that the efficiency of AFCs fueled by pure H₂ is about 60 percent HHV, and that of PAFCs is about 50 percent HHV.

The high performance of the alkaline cell relative to phosphoric acid and other cells leads to the plausibility of developing the technology for terrestrial application. The leading developer of alkaline technology for space application, UTC Fuel Cells, investigated adaptating the

technology to terrestrial, stationary power applications using air as an oxidant in the early 1970s. The predominant drawback with terrestrial applications is that CO_2 in any hydrocarbon fuel or in the air reacts with the ion carrier in the electrolyte. During the 1970s, a high pressure drop platinum/palladium separator was used in the fuel processor to obtain a pure stream of H₂ from reformed hydrocarbon fuels (primarily natural gas for stationary power plants). Similarly, a soda-lime scrubber treated the inlet ambient air stream to minimize CO_2 entering the cell. The expense of the separator and scrubber was deemed uneconomical for commercial development of stationary power plants. Augmenting the issue was a slow build-up of K₂CO₃ due to the minuscule amount of CO_2 escaping the soda-lime scrubber. There was also an issue of component life for stationary power applications. Alkaline cell life (now 2,600 hours on H₂/O₂, but 5,000 hour R&D underway) is suitable for space missions, but too brief for terrestrial, stationary power plants. As a result of the CO₂ issue, UTC Fuel Cells, which uses an immobilized electrolyte, now focuses their alkaline program completely toward space applications with H₂/O₂ as fuel and oxidant.

Union Carbide Corp. (UCC) developed AFCs for terrestrial mobile applications starting in the late 1950s, lasting until the early 1970s. UCC systems used liquid caustic electrolytes; the electrodes were either pitch-bonded carbon plates or plastic-bonded carbon electrodes with a nickel current collector. UCC also built fuel cell systems for the U.S. Army and the U.S. Navy, an alkaline direct hydrazine powered motorcycle, and the "Electrovan" of General Motors. Finally, Professor Karl V. Kordesch built his Austin A-40 car, fitted with UCC fuel cells with lead acid batteries as hybrid. It was demonstrated on public roads for three years. The years of research and development are very well summarized in reference (5) *Brennstoffbatterien*.

Based on the UCC technology, other developers are now pursuing terrestrial applications of alkaline technology due to its high performance, particularly for motive power. The majority of these developers use circulating electrolytes with an external, commercial type soda-lime absorber that promises to resolve the problem of CO_2 in the air stream. The quantity of CO_2 can be limited to a small amount with a circulating electrolyte, versus a continual build-up with an immobilized electrolyte. Life expectancy increases (~5,000 hour life is ample for personal automobile engine life) because the cell is nearly inactive when switched off. Hence, only the true operating hours count for the total lifetime. During normal operation, the electrolyte circulates continuously, which has several advantages over an immobilized system: 1) no drying-out of the cell occurs because the water content of the caustic electrolyte remains quite constant everywhere inside the stack; 2) heat management by dedicated heat exchanger compartments in the stack becomes unnecessary - the electrolyte itself works as a cooling liquid inside each cell; 3) accumulated impurities, such as carbonates, are concentrated in the circulating stream and can easily be removed (comparable to a function of oil in today's gasoline engines); 4) the OH⁻ concentration gradient is highly diminished, and 5) the electrolyte prevents the build-up of gas bubbles between electrodes and electrolyte as they are washed away.

Other attributes are that the alkaline cell could have high reactivity without the need for noble metal catalysts on the cell electrodes; this represents a cost savings (6). Additionally, the radiator of the alkaline cell system should be smaller than the radiator in the competitive PEFC system because of higher alkaline cell temperature and its higher performance.

In stacks using circulating electrolytes, parasitic currents might occur. All cells are connected via the electrolyte stream to all other cells, producing high voltages between the electrodes. Parasitic current not only lowers the stack performance, but can also harm the electrodes. Fortunately, this issue can be resolved easily by using a special electrode frame design with long, narrow electrolyte channels.

Some developers have investigated a direct methanol alkaline cell to circumnavigate hydrocarbon fuel separator issues. These cells exhibit a reduced performance, and have not been as thoroughly investigated as the hydrogen-fueled cells.

The unusual economics for remote power applications (i.e., space, undersea, and military applications) result in the cell itself not being strongly constrained by cost. The consumer and industrial markets, however, require the development of low-cost components if the AFC is to successfully compete with alternative technologies. Much of the recent interest in AFCs for mobile and stationary terrestrial applications has addressed the development of low-cost cell components. In this regard, carbon-based porous electrodes play a prominent role (6). It remains to be demonstrated whether alkaline cells will prove commercially viable for the transportation sector. Reference (7) provides an in-depth view of the development history and the potential of alkaline technology for terrestrial application.

Figures 4-1 and 4-2 depict the operating configuration of the H_2/O_2 alkaline fuel cell (8) and a H_2/air cell (9). In both, the half-cell reactions are:

$$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$$
 (Anode) (4-1)

$$\frac{1}{2}O_2 + H_2O + 2e \rightarrow 2OH^-$$
 (Cathode) (4-2)

Hydroxyl ions, OH⁻, are the conducting species in the electrolyte. The equivalent overall cell reaction is:

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O + \text{electric energy} + \text{heat}$$
 (4-3)

Since KOH has the highest conductance among the alkaline hydroxides, it is the preferred electrolyte.



Figure 4-1 Principles of Operation of H₂/O₂ Alkaline Fuel Cell, Immobilized Electrolyte (8)



Figure 4-2 Principles of Operation of H₂/Air Alkaline Fuel Cell, Circulating Electrolyte (9)

4.1 Cell Components

4.1.1 State-of-the-Art Components

The concentration of KOH in an immobilized electrolyte typically used in the space program varies from 35 to 50 wt percent KOH for low temperature (<120 °C) operation to 85 wt percent KOH in cells designed for operation at high temperature (~260 °C). The electrolyte is retained in a matrix (usually asbestos), and a wide range of electro-catalysts can be used (e.g., Ni, Ag, metal oxides, spinels, and noble metals) to promote reaction.

The cylindrical AFC modules used in the U.S. Apollo Space Program had a 57 cm diameter, a 112 cm height, weighed about 110 kg, produced a peak power of 1.42 kW at 27 to 31 V, and operated at an average power of 0.6 kW. These cells operated on pure H₂ and O₂ and concentrated electrolyte (85 percent KOH) at a moderate pressure (4 atmospheres reactant gas pressure) without electrolyte boiling. With this concentrated electrolyte, cell performance was not as high as in the less-concentrated electrolyte; consequently, the operating temperature was increased to 260 °C. The typical performance of this AFC cell was 0.85 V at 150 mA/cm², comparing favorably to the performance of the Bacon cell operating at about 10 times higher pressure.

The state-of-the-art alkaline fuel cell stacks in the Space Shuttle Orbiter are rectangular with a width of 38 cm, a length of 114 cm, and a height of 35 cm. They weigh 118 kg, produce a peak power of 12 kW at a minimum of 27.5 V (end of life), and operate at an average power of 7 kW. They operate in the same pressure range as the Apollo cells (4 atmospheres), but at a lower temperature (85 to 95 °C) and higher current density (0.88 V at 470 mA/cm²; UTC Fuel Cells has demonstrated 3.4 W/cm² at 0.8 V and 4,300 mA/cm², Reference (8)). The electrodes contain high loadings of noble metals: 80 percent Pt – 20 percent Pd anodes are loaded at 10 mg/cm² on Ag-plated Ni screen; 90 percent Au – 10 percent Pt cathodes are loaded at 20 mg/cm² on Ag-plated Ni screen. Both are bonded with PTFE to achieve high performance at the lower temperature of 85 ot 95 °C. A wide variety of materials (e.g., potassium titanate, ceria, asbestos, zirconium phosphate gel) have been used in the micro-porous separators for AFCs. The electrolyte is 35 percent KOH and is replenished via a reservoir on the anode side. Gold-plated magnesium is used for the bipolar plates. Sheibley and Martin (10) provide a brief survey of the advanced technology components in AFCs for space applications.

An advanced cell configuration for underwater application was developed using high surface area Raney nickel anodes loaded at 120 mg/cm^2 (1 to 2 percent Ti) and Raney silver cathodes loaded at 60 mg/cm^2 containing small amounts of Ni, Bi, and Ti (11).

The efforts of Union Carbide Corporation have formed the basis for most of today's terrestrial applications of AFCs with circulating liquid electrolytes. Companies like Da Capo Fuel Cell Ltd. (which bought ZeTek Power (formerly Zevco and Elenco)), Astris Energy, and Apollo Energy System Inc. are developing circulating electrolyte cells for motive and backup power primarily based on that technology. A typical configuration (Apollo, Figure 4-2) uses carbon-based plastic-bonded gas diffusion electrodes with a current collector (nickel) inside. Due to the ease of preparation, the electrodes in present stacks use noble metals loaded to less than 0.5mg/cm². The 0.3 cm thick cells are stacked in a monopolar order and are commonly

connected in series via edge connectors. Neither membranes nor bipolar plates are needed. The stacks operate at 75 °C, using a 9N KOH electrolyte. The gases are fed at ambient pressure; either pure hydrogen or cracked ammonia is used. Lifetime testing (12) has not been finished, but is >1,000 hours at intermittent operation (a few hours per day).

Several types of catalysts are used or are being considered for the electrodes: 1) noble metals (expensive but simple, and acceptable for low volume stack preparation); 2) "classic" non-noble metals (silver for the cathode and Raney nickel for the anode), and 3) spinels and perovskites (often referred to as alternative catalysts, these are being developed because they cost less than the noble metal catalysts).

4.1.2 Development Components

Immobilized electrolyte AFCs, used mostly in space or closed environments, and circulating electrolyte AFCs, used for terrestrial application, face separate and unique development challenges.

 H_2/O_2 alkaline technology using immobilized electrolytes is considered to be fully developed. Confidence in the present cell technology is best represented by the fact that there is no back-up electric power on the Space Shuttle Orbiter. Further improvement of the present H_2/O_2 design is not considered to be cost effective with one exception: maintenance cost can be decreased directly by increasing the cell stack life of the Orbiter power plant.

The life-limiting event in the present Orbiter cell is KOH corrosion of the cell frame (cell support). Present stack life is 2,600 hours. The cell stacks have demonstrated capability to reach this life in 110 flights and a total of ~87,000 hours in the Orbiter (July 2002). Present practice is to refurbish the power unit at 2,600 hours by installing a new stack, and cleaning and inspecting the balance of equipment. The stack life is being improved to 5,000 hours by elongating the path length associated with KOH-induced corrosion of the cell frame. A 10 cell short stack has demonstrated the new 5,000 hours concept. The concept is now being qualified in a complete power plant, presently being tested (13).

Electrode development in circulating electrolyte AFCs has concentrated on 1) multi-layered structures with porosity characteristics optimized for flow of liquid electrolytes and gases (H_2 and air), and 2) catalyst development. Another area for concern is the instability of PTFE, which causes weeping of the electrodes. Most developers use noble metal catalysts; some use non-noble catalysts. Spinels and perovskites are being developed in an attempt to lower the cost of the electrodes. Development of low-cost manufacturing processes includes powder mixing and pressing of carbon-based electrodes, sedimentation and spraying, and high-temperature sintering.

AFC electrolyte development has been restricted to KOH water solutions with concentrations ranging from 6 to12N. Still, use of less expensive NaOH has been considered. Minimal cost advantages appear to be far outweighed by performance reductions due to wetting angle and lower conductivity. However, NaOH as an electrolyte increases the lifetime of electrodes when CO_2 is present, because sodium carbonate, although less soluble than potassium carbonate, forms much smaller crystals, which do not harm the carbon pores.

Other approaches to increasing life and reducing weight and cost include investigating epoxy resins, polysulfone and ABS (acrylonitrile-butadiene-styrene). Framing techniques under development include injection molding, filter pressing, and welding (14, 15).

Immobilized electrolyte AFCs are highly sensitive to carbon dioxide (CO₂). Non-hydrocarbon hydrogen fuel or pure H₂ can be fed directly to the anode. For example, a carbon-free fuel gas such as cracked ammonia (25 percent N₂, 75 percent H₂, and residual NH₃) can be fed directly to the cell. Due to the high diffusion rate of hydrogen compared to nitrogen, only a very small decrease in potential is observed with hydrogen content greater than 25 percent (at medium current densities). Gas purification is necessary when H₂ is produced from carbon-containing fuel sources (e.g., methanol, gasoline, propane and others). There are many approaches to separate CO₂ from gaseous or liquid streams. Physical separation and chemical separation are the most common methods used. However, CO₂ removal by these methods requires more than one process step to reduce the CO_2 to the limits required by the fuel cell. Two additional methods include cryogenic separation and biological fixation. If liquid hydrogen is used as the fuel for the alkaline fuel cell, a system of heat exchangers can be used to condense the CO₂ out of the air for the oxidant stream. This technique has a potential weight advantage over the sodalime scrubber. Low-temperature distillation is commonly used for the liquefaction of CO₂ from high purity sources. A new, potentially efficient technique that is being investigated uses capillary condensation to separate gases by selective wicking. Biological separation is promising, but must overcome the challenge of reactivation after shutdown periods.

Another promising CO_2 separation method is membrane separation. This has the advantages of being compact, no moving parts, and the potential for high energy efficiency. Polymer membranes transport gases by solution diffusion, and typically have a low gas flux and are subject to degradation. These membranes are relatively expensive. The main drawbacks of membrane separation are the significant pressure differential that may be required across the membrane and its high cost. The need for a high pressure gradient can be eliminated by using a membrane in which a potential is applied over the membrane. This approach is sometimes referred to as the "sacrificial cell" technique. Another approach is to use a membrane with steam reforming of liquid fuels. Little additional energy is needed to pressurize the liquid fuel and water to the pressure required for separation.

Alkaline cell developers continue to investigate CO_2 separation methods that show economic promise. However, circulating electrolyte is the technology of choice for terrestrial applications.

4.2 Performance

Performance of AFCs since 1960 has undergone many changes, as evident in the performance data in Figure 4-3. H₂/air performance is shown as solid lines, and H₂/O₂ performance is shown as dashed lines. The early AFCs operated at relatively high temperature and pressure to meet the requirements for space applications. More recently, a major focus of the technology is for terrestrial applications in which low-cost components operating at near-ambient temperature and pressure with air as the oxidant are desirable. This shift in fuel cell operating conditions resulted in the lower performance shown in Figure 4-3. The figure shows, using dotted lines, H₂/O₂ performance for: 1) the Orbiter with immobilized electrolyte (8), and 2) a circulating electrolyte cell (12).



Figure 4-3 Evolutionary Changes in the Performance of AFCs (8, 12, & 16)

The data described in the following paragraphs pertains to the H_2/air cell. Unfortunately, H_2/air performance data is rather dated; there has been a noticeable lack of recent H_2/air data.

4.2.1 Effect of Pressure

AFCs experience the typical enhanced performance with an increase in cell operating pressure. Figure 4-4 plots the increase in reversible e.m.f. (electromotive force) of alkaline cells with pressure over a wide range of temperatures (17). The actual increase in cell open circuit voltage is somewhat less than shown because of the greater gas solubility with increasing pressure that produces higher parasitic current.

At an operating temperature (T), the change in voltage (ΔV_P) as a function of pressure (P) can be expressed fairly accurately using the expression:

$$\Delta V_{\rm P} \,({\rm mV}) = 0.15 \,{\rm T} \,(^{\circ}{\rm K}) \,\log({\rm P_2}/{\rm P_1}) \tag{4-4}$$

over the entire range of pressures and temperatures shown in Fig. 4-4. In this expression, P_2 is the desired performance pressure and P_1 is the reference pressure at which performance is known.



Figure 4-4 Reversible Voltage of the Hydrogen-Oxygen Cell (14)

To achieve faster kinetics, operating temperatures greater than 100 °C, accompanied by higher pressures, are used. Spacecraft fuel cells have operated for over 5,000 hours at 200 °C at 5 atm achieving HHV efficiencies exceeding 60 percent (18, 19). It should be noted that a pressure increase beyond about 5 atm produces improvements that are usually outweighed by a significant weight increase required to sustain the higher operating pressure. For space applications, weight is critical. Also, this increase in performance can only be realized in applications where compressed gases are available (such as in space vehicles or submarines). In all other cases, compressors are needed. Compressors are not only noisy, but incur parasitic power that lowers the system efficiency (20). An increase of overall efficiency when using compressors in simple cycles is very unlikely.

4.2.2 Effect of Temperature

Section 2.1 describes that the reversible cell potential for a fuel cell consuming H_2 and O_2 decreases by 49 mV under standard conditions in which the reaction product is water vapor. However, as is the case in PAFCs, an increase in temperature improves cell performance because activation polarization, mass transfer polarization, and ohmic losses are reduced.

The improvement in performance with cell temperature of catalyzed carbon-based (0.5 mg Pt/cm^2) porous cathodes is illustrated in Figure 4-5 (21). As expected, the electrode potential at a given current density decreases at lower temperatures, and the decrease is more significant at higher current densities. In the temperature range of 60 to 90 °C, the cathode performance increases by about 0.5 mV/°C at 50 to 150 mA/cm².



Figure 4-5 Influence of Temperature on O₂, (air) Reduction in 12 N KOH. Source: Fig. 10, p. 324, Reference (21).

Early data by Clark, et al. (22) indicated a temperature coefficient for AFCs operating between 50 to 70 °C of about 3 mV/°C at 50 mA/cm², and cells with higher polarization had higher temperature coefficients under load. Later measurements by McBreen, et al. (23) on H₂/air single cells (289 cm² active area, carbon-based Pd anode and Pt cathode) with 50 percent KOH showed that the temperature coefficient above 60 °C was considerably lower than that obtained at lower temperatures, as shown in Figure 4-6. The McBreen data suggest the following expressions for evaluating the change in voltage (ΔV_T) as a function of temperature (T) at 100 mA/cm²:

$$\Delta V_t (mV) = 4.0 (T_2 - T_1) \qquad \text{for } T < 63 \ ^{\circ}\text{C}$$
(4-5)

or

$$\Delta V_t (mV) = 0.7 (T_2 - T_1) \qquad \text{for } T > 63 \ ^{\circ}\text{C}$$
(4-6)

Alkaline cells exhibit reasonable performance when operating at low temperatures (room temperature up to about 70 °C). This is because the conductivity of KOH solutions is relatively high at low temperatures. For instance, an alkaline fuel cell designed to operate at 70 °C will reduce to only half power level when its operating temperature is reduced to room temperature (24).



Figure 4-6 Influence of Temperature on the AFC Cell Voltage Source: Figure 6, p. 889, reference (23).

4.2.3 Effect of Impurities

Carbon dioxide was the only impurity of concern in the data surveyed. AFCs with immobilized electrolytes suffer a considerable performance loss with reformed fuels containing CO_2 and from the presence of CO_2 in air (typically ~350 ppm CO_2 in ambient air). The negative impact of CO_2 arises from its reaction with OH⁻

$$\mathrm{CO}_2 + 2\mathrm{OH}^- \to \mathrm{CO}_3^- + \mathrm{H}_2\mathrm{O} \tag{4-7}$$

producing the following effects: 1) reduced OH⁻ concentration, interfering with kinetics; 2) electrolyte viscosity increase, resulting in lower diffusion rate and lower limiting currents; 3) precipitation of carbonate salts in the porous electrode, reducing mass transport; 4) reduced oxygen solubility, and 5) reduced electrolyte conductivity.

In the case of circulating liquid electrolytes, the situation is not as critical, but is still significant. The influence of CO_2 on air cathodes (0.2 mg Pt/cm² supported on carbon black) in 6N KOH at 50 °C can be ascertained by analysis of the performance data presented in Figure 4-7 (25). To obtain these data, the electrodes were operated continuously at 32 mA/cm², and current-voltage performance curves were periodically measured. Performance in both CO_2 -free air and CO_2 -containing air showed evidence of degradation with time. However, with CO_2 -free air the performance remained much more constant after 2,000 to 3,000 hours of operation. Later tests, however, showed that this drop in performance was caused purely by mechanical destruction of

the carbon pores by carbonate crystals. Improved electrodes can withstand even high amounts of CO_2 (5 percent) over many thousands of hours, as proven recently by DLR (Deutsches Zentrum fuer Luft- und Raumfahrt) (26).



Figure 4-7 Degradation in AFC Electrode Potential with CO₂ Containing and CO₂ Free Air Source: Figure 2, p. 381, Reference (25)

High concentrations of KOH are also detrimental to the life of O_2 electrodes operating with CO_2 containing air, but operating the electrode at higher temperature is beneficial because it increases the solubility of CO_2 in the electrolyte. Hence, modifying the operating conditions can prolong electrode life. Extensive studies by Kordesch, et al. (25) indicate that the operational life of air electrodes (PTFE-bonded carbon electrodes on porous nickel substrates) with CO_2 -containing air in 9N KOH at 65 °C ranges from 1,600 to 3,400 hours at a current density of 65 mA/cm². The life of these electrodes with CO_2 -free air tested under similar conditions ranged from 4,000 to 5,500 hours. It was reported (2) that a lifetime of 15,000 hours was achieved with AFCs, with failure caused at that time by corrosion of the cell frames.

4.2.4 Effects of Current Density

As in the case with PAFCs, voltage obtained from an AFC is affected by ohmic, activation, and concentration losses. Figure 4-8 presents data obtained in the 1960s (22) that summarizes these effects, excluding electrolyte ohmic (iR) losses, for a catalyzed reaction (0.5 to 2.0 mg noble metal/cm²) with carbon-based porous electrodes for H₂ oxidation and O₂ reduction in 9N KOH at 55 to 60 °C. The electrode technology was similar to that employed in the fabrication of PAFC electrodes.



Figure 4-8 iR-Free Electrode Performance with O₂ and Air in 9 N KOH at 55 to 60°C. Catalyzed (0.5 mg Pt/cm² Cathode, 0.5 mg Pt-Rh/cm² Anode) Carbon-based Porous Electrodes (22)

The results in Figure 4-8 yield the following current density equations for cells operating in 9N KOH at 55 to 60 $^{\circ}$ C:

 $\Delta V_{J} (mV) = -0.18\Delta J \qquad \text{for } J = 40 \text{ to } 100 \text{ mA/cm}^{2} \text{ operating in } O_{2} \qquad (4-8)$ $\Delta V_{I} (mV) = -0.31\Delta J \qquad \text{for } J = 40 \text{ to } 100 \text{ mA/cm}^{2} \text{ operating in air} \qquad (4-9)$

where J is in mA/cm². The performance of a single cell with supported noble metal electrocatalyst (0.5 mg Pt-Rh/cm² anode, 0.5 mg Pt/cm² cathode) in 12N KOH at 65 °C is shown in Figure 4-9 (21). These results, reported in 1986, are comparable to those obtained in 1965. The iR-free electrode potentials (vs. RHE) at 100 mA/cm² in Figure 4-9 are 0.9 V with O₂ and 0.85 V with air. One major difference between the early cathodes and the cathodes in current use is that the limiting current for O₂ reduction from air has been improved (i.e., 100 to 200 mA/cm² improved to >250 mA/cm²).

These results yield the following equations for cells operating in 12N KOH at 65 °C:

$$\Delta V_{J} (mV) = -0.25\Delta J \qquad \text{for } J = 50 \text{ to } 200 \text{ mA/cm}^{2} \text{ operating in } O_{2} \quad (4-10)$$

or

or

$$\Delta V_{J} (mV) = -0.47 \Delta J \qquad \text{for } J = 50 \text{ to } 200 \text{ mA/cm}^{2} \text{ operating in air.} \quad (4-11)$$



Figure 4-9 iR Free Electrode Performance with O₂ and Air in 12N KOH at 65 °C. Catalyzed (0.5 mg Pt/cm² Cathode, 0.5 mg Pt-Rh/cm² Anode), Carbon-based Porous Electrodes (21).

4.2.5 Effects of Cell Life

The UTC Fuel Cells H_2/O_2 alkaline technology exhibits a degradation of ~25 mV/1,000 hours (13). AFC cell stacks have demonstrated sufficiently stable operation for at least 5,000 hours, with degradation rates of 20 mV per 1,000 hours or less (24). Siemens reported a total of >8,000 operating hours with approximately 20 units (27). For large scale utility applications, economics demand operating times exceeding 40,000 hours, which presents perhaps the most significant obstacle to commercialization of AFC devices for stationary electric power generation.

4.3 Summary of Equations for AFC

The preceding sections described parametric performance based on various referenced data at different cell conditions. The following set of equations can be used to predict performance only if no better data or basis for estimate is available. Unfortunately, a noticeable lack of recent, published H₂/air data is available to predict performance trends. The equations presented below can be used in conjunction with the measured H₂/air performance shown in Figure 4-10 (12) as a basis for predicting performance at various operating conditions. The Space Shuttle Orbiter performance is included in Figure 4-10 as a reference point for H₂/O₂ performance (8); however, the trend equations should not be used for H₂/O₂ cells to predict operation at other conditions.

<u>Parameter</u>	Equation	<u>Comments</u>	
Pressure	$\Delta V_{P} (mV) = 0.15 \text{ T} (^{\circ}\text{K}) \log (P_{2}/P_{1})$	1 atm < P < 100 atm 100 °C < T < 300 °C	(4-4)
Temperature	$\Delta V_{\rm T} ({\rm mV}) = 4.0 ({\rm T_2-T_1})$	for T < 63 °C, at 100 mA/cm ²	(4-5)
	$\Delta V_{T} (mV) = 0.7 (T_2 - T_1)$	for T > 63 °C, at 100 mA/cm ²	(4-6)
Current Density	$\Delta V_{J} (mV) = -0.18 \Delta J$	for J = 40 to 100 mA/cm ² operating in O_2 with 9N KOH at 55-60 °C.	(4-8)
	$\Delta V_{J} (mV) = -0.31 \Delta J$	for J = 40 ti 100 mA/cm ² operating in air with 9N KOH at 55-60 °C.	(4-9)
	$\Delta V_{J} (mV) = -0.25 \Delta J$	for J = 50 to 200 mA/cm ² operating in O_2 with 12N KOH at 65 °C.	(4-10)
	$\Delta V_{J} (mV) = -0.047 \Delta J$	for $J = 50$ to 200 mA/cm ² operating in air with 12N KOH at 65 °C.	(4-11)
Life Effects	$\Delta V_{\text{Lifetime}} (mV) = 20 \ \mu V \ \text{per} \ 1,000$) hours or less	(4-12)



Figure 4-10 Reference for Alkaline Cell Performance