



SATHYABAMA

INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)

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SCHOOL OF MECHANICAL ENGINEERING

DEPARTMENT OF MECHANICAL ENGINEERING

Syllabus

SME1615	FUEL CELL AND APPLICATIONS	L	T	P	Credits	Total Marks
		3	0	0	3	100

COURSE OBJECTIVES

- To understand the fundamentals of fuel cell technologies
- To understand the thermodynamics and kinetics of fuel cell To study the working of various types of fuel cell
- To analyze the cost effectiveness and eco-friendliness of Fuel Cells
-

UNIT 1 INTRODUCTION AND OVERVIEW OF FUEL CELLS 9 Hrs.

Overview of fuel cells – Need of fuel cell, History, Principle and overview of fuel cell, Basic electrochemistry for all the fuel cells, Low and high temperature fuel cells; Fuel cell thermodynamics - heat, work potentials, prediction of reversible voltage, Nernst equation; Effect of temperature, pressure, concentration on Nernst potential fuel cell efficiency, Concept of electrochemical potential.

UNIT 2 FUEL CELL TYPES 9 Hrs.

Types of fuel cells – Alkaline Fuel Cell, Phosphoric Acid Fuel Cell, Solid Oxide fuel cell, Molten Carbonate fuel cell, Direct Methanol Fuel Cell, Proton Exchange Membrane Fuel Cell – relative merits and demerits, comparison on battery Vs fuel cell.

UNIT 3 FUEL CELL COMPONENTS AND PERFORMANCE 9 Hrs.

Fuel cell performance characteristics – current/voltage, voltage efficiency and power density, ohmic resistance, Butler-Volmer equation; Tafel equation, kinetic performance, mass transfer effects – membrane electrode assembly components, fuel cell stack, bi-polar plate, humidifiers and cooling plates.

UNIT 4 FUELING 9 Hrs.

Hydrogen storage technology – pressure cylinders, liquid hydrogen, metal hydrides, carbon fibers – reformer technology – steam reforming, partial oxidation, auto thermal reforming – CO removal, fuel cell technology based on bio-mass.

UNIT 5 APPLICATION OF FUEL CELL AND ECONOMICS 9 Hrs.

Fuel cell usage for domestic power systems, large scale power generation, Automobile, Space, Economic and environmental analysis on usage of Hydrogen and Fuel cell. Future trends in fuel cells.

Max. 45 Hours

Course Outcomes: At the end of the course, students will able to

CO1: Identify the importance of fuel cells with applications

CO2: Classify the fuel cells according to electrolyte and temperature

CO3: Compare battery and fuel cell with needs

CO4: Demonstrate hydrogen storage technology

CO5; Apply the principle of fuel cell to power plants

TEXT / REFERENCE BOOKS

1. Larminie J. and Dicks A, Fuel Cell Systems Explained, 2nd Edition, Wiley, 2003
2. Xianguo Li, Principles of Fuel Cells, Taylor and Francis, 2005.
3. Srinivasan S, Fuel Cells: From Fundamentals to Applications, Springer, 2006.
4. Hayre, R. P, Cha S, Colella W.,Prinz F. B, Fuel Cell Fundamentals, Wiley, NY ,2006.
5. Basu, S. (Ed) Fuel Cell Science and Technology, Springer, N.Y, 2007.
6. Fuel Cells for automotive applications, Professional Engineering Publishing UK. ISBN 1-86058-4233, 2004.

END SEMESTER EXAM QUESTION PAPER PATTERN

Max. Marks : 80

Exam Duration : 3 Hrs.

PART A : 2 Questions from each unit, each carrying 2 marks

20 Marks

PART B : 2 Questions from each unit with internal choice, each carrying 12 marks

60 Marks

B.E. / B.Tech REGULAR

REGULATIONS 2015

UNIT – I – Fuel Cell and Applications – SME1615

I. Introduction and Overview of CFD Fuel Cells

Fuel cells are electrochemical devices that convert chemical energy in fuels into electrical energy directly, promising power generation with high efficiency and low environmental impact.

Because the intermediate steps of producing heat and mechanical work typical of most conventional power generation methods are avoided, fuel cells are not limited by thermodynamic limitations of heat engines such as the Carnot efficiency. In addition, because combustion is avoided, fuel cells produce power with minimal pollutant. However, unlike batteries the reductant and oxidant in fuel cells must be continuously replenished to allow continuous operation. Fuel cells bear significant resemblance to electrolyzers. In fact, some fuel cells operate in reverse as electrolyzers, yielding a reversible fuel cell that can be used for energy storage. Though fuel cells could, in principle, process a wide variety of fuels and oxidants, of most interest today are those fuel cells that use common fuels (or their derivatives) or hydrogen as a reductant, and ambient air as the oxidant.

Most fuel cell power systems comprise a number of components:

- Unit cells, in which the electrochemical reactions take place.
- Stacks, in which individual cells are modularly combined by electrically connecting the cells to form units with the desired output capacity.

Balance of plant which comprises components that provide feed stream conditioning (including a fuel processor if needed), thermal management, and electric power conditioning among other ancillary and interface functions.

In the following, an overview of fuel cell technology is given according to each of these categories, followed by a brief review of key potential applications of fuel cells.

- Unit Cells
- Basic Structure

Unit cells form the core of a fuel cell. These devices convert the chemical energy contained in a fuel electrochemically into electrical energy. The basic physical structure, or building block, of a fuel cell consists of an electrolyte layer in contact with an anode and a cathode on either side. A schematic representation of a unit cell with the reactant/product gases and the ion conduction flow directions through the cell is shown in Figure 1.1.

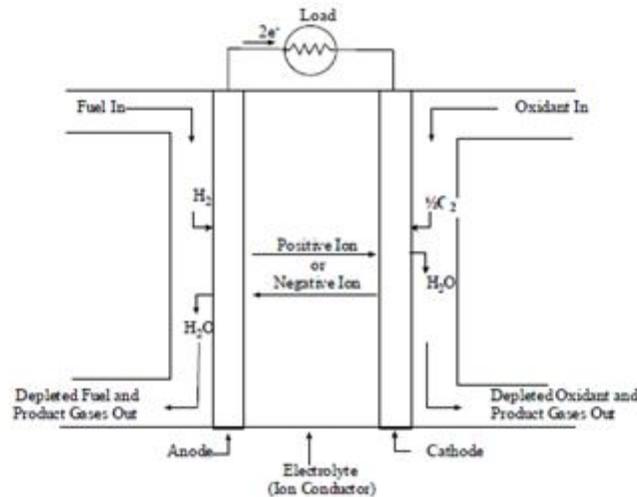


Figure 1.1 Schematic of Fuel Cell

In a typical fuel cell, fuel is fed continuously to the anode (negative electrode) and an oxidant (often oxygen from air) is fed continuously to the cathode (positive electrode). The electrochemical reactions take place at the electrodes to produce an electric current through the electrolyte, while driving a complementary electric current that performs work on the load.

Although a fuel cell is similar to a typical battery in many ways, it differs in several respects. The battery is an energy storage device in which all the energy available is stored within the battery itself (at least the reductant). The battery will cease to produce electrical energy when the chemical reactants are consumed (i.e., discharged). A fuel cell, on the other hand, is an energy conversion device to which fuel and oxidant are supplied continuously. In principle, the fuel cell produces power for as long as fuel is supplied.

Fuel cells are classified according to the choice of electrolyte and fuel, which in turn determine the electrode reactions and the type of ions that carry the current across the electrolyte. Appleby and Foulkes have noted that, in theory, any substance capable of chemical oxidation that can be supplied continuously (as a fluid) can be burned galvanically as fuel at the anode of a fuel cell. Similarly, the oxidant can be any fluid that can be reduced at a sufficient rate. Though the direct use of conventional fuels in fuel cells would be desirable, most fuel cells under development today use gaseous hydrogen, or a synthesis gas rich in hydrogen, as a fuel.

Hydrogen has a high reactivity for anode reactions, and can be produced chemically from a wide range of fossil and renewable fuels, as well as via electrolysis. For similar practical reasons, the most common oxidant is gaseous oxygen, which is readily available from air. For space applications, both hydrogen and oxygen can be stored compactly in cryogenic form, while the reaction product is only water.

1.1 Critical Functions of Cell Components

A critical portion of most unit cells is often referred to as the three-phase interface. These mostly microscopic regions, in which the actual electrochemical reactions take place, are found where either electrode meets the electrolyte. For a site or area to be active, it must be exposed to the reactant, be in electrical contact with the electrode, be in ionic contact with the electrolyte, and contain sufficient electro-catalyst for the reaction to proceed at the desired rate. The density of these regions and the nature of these interfaces play a critical role in the electrochemical performance of both liquid and solid electrolyte fuel cells:

In liquid electrolyte fuel cells, the reactant gases diffuse through a thin electrolyte film that wets portions of the porous electrode and react electrochemically on their respective electrode surface. If the porous electrode contains an excessive amount of electrolyte, the electrode may "flood" and restrict the transport of gaseous species in the electrolyte phase to the reaction sites. The consequence is a reduction in electrochemical performance of the porous electrode. Thus, a delicate

balance must be maintained among the electrode, electrolyte, and gaseous phases in the porous electrode structure.

In solid electrolyte fuel cells, the challenge is to engineer a large number of catalyst sites into the interface that are electrically and ionically connected to the electrode and the electrolyte, respectively, and that is efficiently exposed to the reactant gases. In most successful solid electrolyte fuel cells, a high-performance interface requires the use of an electrode which, in the zone near the catalyst, has mixed conductivity (i.e. it conducts both electrons and ions).

Over the past twenty years, the unit cell performance of at least some of the fuel cell technologies has been dramatically improved. These developments resulted from improvements in the three-phase boundary, reducing the thickness of the electrolyte, and developing improved electrode and electrolyte materials which broaden the temperature range over which the cells can be operated. In addition to facilitating electrochemical reactions, each of the unit cell components have other critical functions. The electrolyte not only transports dissolved reactants to the electrode, but also conducts ionic charge between the electrodes, and thereby completes the cell electric circuit. It also provides a physical barrier to prevent the fuel and oxidant gas streams from directly mixing.

The functions of porous electrodes in fuel cells, in addition to providing a surface for electrochemical reactions to take place, are to conduct electrons away from or into the three-phase interface once they are formed (so an electrode must be made of materials that have good electrical conductance) and provide current collection and connection with either other cells or the load ensure that reactant gases are equally distributed over the cell ensure that reaction products are efficiently led away to the bulk gas phase. As a consequence, the electrodes are typically porous and made of an electrically conductive material. At low temperatures, only a few relatively rare and expensive materials provide sufficient electro-catalytic activity, and so such catalysts are deposited in small quantities at the interface where they are needed. In high-temperature fuel cells, the electro-catalytic activity of the bulk electrode material is often sufficient. Though a wide range of fuel cell geometries has been considered, most fuel cells under development now are either planar

(rectangular or circular) or tubular (either single- or double-ended and cylindrical or flattened).

1.2 Fuel Cell Stacking

For most practical fuel cell applications, unit cells must be combined in a modular fashion into a cell stack to achieve the voltage and power output level required for the application. Generally, the stacking involves connecting multiple unit cells in series via electrically conductive interconnects. Different stacking arrangements have been developed, which are described below.

1.3 Planar-Bipolar Stacking

The most common fuel cell stack design is the so-called planar-bipolar arrangement (Figure 1-2 depicts a PAFC). Individual unit cells are electrically connected with interconnects. Because of the configuration of a flat plate cell, the interconnect becomes a separator plate with two functions:

- To provide an electrical series connection between adjacent cells, specifically for flat plate cells, and
- To provide a gas barrier that separates the fuel and oxidant of adjacent cells.

In many planar-bipolar designs, the interconnect also includes channels that distribute the gas flow over the cells. The planar-bipolar design is electrically simple and leads to short electronic current paths (which helps to minimize cell resistance).

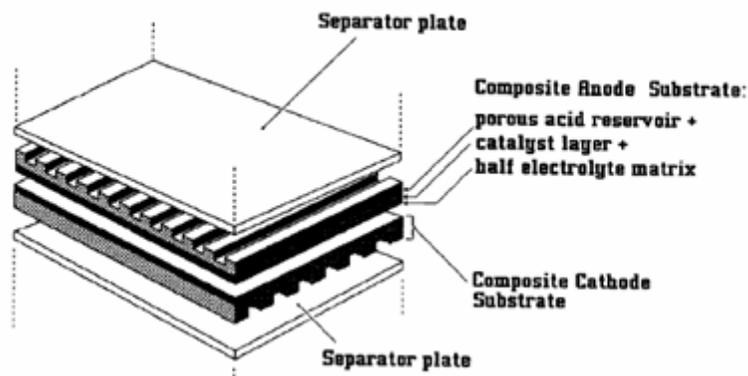


Figure 1.2 Expanded view of a Fuel cell unit and stack

Planar-bipolar stacks can be further characterized according to arrangement of the gas flow:

- Cross-flow. Air and fuel flow perpendicular to each other
- Co-flow. Air and fuel flow parallel and in the same direction. In the case of circular cells, this means the gases flow radially outward
- Counter-flow. Air and fuel flow parallel but in opposite directions. Again, in the case of circular cells this means radial flow
- Serpentine flow. Air or fuel follow a zig-zag path
- Spiral flow. Applies to circular cells

The choice of gas-flow arrangement depends on the type of fuel cell, the application, and other considerations. Finally, the manifolding of gas streams to the cells in bipolar stacks can be achieved in various ways:

- Internal: the manifolds run through the unit cells
- Integrated: the manifolds do not penetrate the unit cells but are integrated in the interconnects
- External: the manifold is completely external to the cell, much like a wind-box

1.3 Stacks with Tubular Cells

Especially for high-temperature fuel cells, stacks with tubular cells have been developed. Tubular cells have significant advantages in sealing and in the structural integrity of the cells. However, they represent a special geometric challenge to the stack designer when it comes to achieving high power density and short current paths. In one of the earliest tubular designs the current is conducted tangentially around the tube. Interconnects between the tubes are used to form rectangular arrays of tubes. Alternatively, the current can be conducted along the axis of the tube, in which case interconnection is done at the end of the tubes. To minimize the length of electronic conduction paths for individual cells, sequential series connected cells are being developed. The cell arrays can be connected in series or in parallel. For a more detailed description of the different stack types and pictorial descriptions, the reader is referred to Chapter 7 on SOFC (SOFC is the fuel cell type for which the widest range of cell and stack geometries is

pursued). To avoid the packing density limitations associated with cylindrical cells, some tubular stack designs use flattened tubes.

1.4 Fuel Cell Systems

In addition to the stack, practical fuel cell systems require several other sub-systems and components; the so-called balance of plant (BoP). Together with the stack, the BoP forms the fuel cell system. The precise arrangement of the BoP depends heavily on the fuel cell type, the fuel choice, and the application. In addition, specific operating conditions and requirements of individual cell and stack designs determine the characteristics of the BoP. Still, most fuel cell systems contain:

Fuel preparation. Except when pure fuels (such as pure hydrogen) are used, some fuel preparation is required, usually involving the removal of impurities and thermal conditioning. In addition, many fuel cells that use fuels other than pure hydrogen require some fuel processing, such as reforming, in which the fuel is reacted with some oxidant (usually steam or air) to form a hydrogen-rich anode feed mixture.

- Air supply. In most practical fuel cell systems, this includes air compressors or blowers as well as air filters.
- Thermal management. All fuel cell systems require careful management of the fuel cell stack temperature.
- Water management. Water is needed in some parts of the fuel cell, while overall water is a reaction product. To avoid having to feed water in addition to fuel, and to ensure smooth operation, water management systems are required in most fuel cell systems.
- Electric power conditioning equipment. Since fuel cell stacks provide a variable DC voltage output that is typically not directly usable for the load, electric power conditioning is typically required.

While perhaps not the focus of most development effort, the BoP represents a significant fraction of the weight, volume, and cost of most fuel cell systems.

Beginning with fuel processing, a conventional fuel (natural gas, other gaseous

hydrocarbons, methanol, naphtha, or coal) is cleaned, then converted into a gas containing hydrogen. Energy conversion occurs when dc electricity is generated by means of individual fuel cells combined in stacks or bundles. A varying number of cells or stacks can be matched to a particular power application. Finally, power conditioning converts the electric power from dc into regulated dc or ac for consumer use. Section 8.1 describes the processes of a fuel cell power plant system.

UNIT – II – Fuel Cell and Applications – SME1615

II. Fuel Cell Types

A variety of fuel cells are in different stages of development. The most common classification of fuel cells is by the type of electrolyte used in the cells and includes 1) polymer electrolyte fuel cell (PEFC), 2) alkaline fuel cell (AFC), 3) phosphoric acid fuel cell (PAFC), 4) molten carbonate fuel cell (MCFC), and 5) solid oxide fuel cell (SOFC). Broadly, the choice of electrolyte dictates the operating temperature range of the fuel cell. The operating temperature and useful life of a fuel cell dictate the physicochemical and thermo mechanical properties of materials used in the cell components (i.e., electrodes, electrolyte, interconnect, current collector, etc.). Aqueous electrolytes are limited to temperatures of about 200 °C or lower because of their high vapor pressure and rapid degradation at higher temperatures. The operating temperature also plays an important role in dictating the degree of fuel processing required. In low-temperature fuel cells, all the fuel must be converted to hydrogen prior to entering the fuel cell. In addition, the anode catalyst in low- temperature fuel cells (mainly platinum) is strongly poisoned by CO. In high-temperature fuel cells, CO and even CH₄ can be internally converted to hydrogen or even directly oxidized electrochemically. Table 2.1 provides an overview of the key characteristics of the main fuel cell types.

Table 2.1 Summary of Major Differences of the Fuel Cell Types

	PEFC	AFC	PAFC	MCFC	SOFC
Electrolyte	Hydrated Polymeric Ion Exchange Membranes	Mobilized or Immobilized Potassium Hydroxide in asbestos matrix	Immobilized Liquid Phosphoric Acid in SiC	Immobilized Liquid Molten Carbonate in LiAlO ₂	Perovskites (Ceramics)

Electrodes	Carbon	Transition metals	Carbon	Nickel and Nickel Oxide	Perovskite and perovskite / metal cermet
Catalyst	Platinum	Platinum	Platinum	Electrode material	Electrode material
Interconnect	Carbon or metal	Metal	Graphite	Stainless steel or Nickel	Nickel, ceramic, or steel
Operating Temperature	40 – 80 °C	65°C – 220 °C	205 °C	650 °C	600-1000 °C
Charge Carrier	H ⁺	OH ⁻	H ⁺	CO ₃ ⁼	O ⁼
External Reformer for hydrocarbon fuels	Yes	Yes	Yes	No, for some fuels	No, for some fuels and cell designs
External shift conversion of CO to hydrogen	Yes, plus purification to remove trace CO	Yes, plus purification to remove CO and CO ₂	Yes	No	No
Prime Cell	Carbon-	Carbon-based	Graphite-	Stainle	Ceramic

Components	based		based	ss-based	
Product Water Management	Evaporative	Evaporative	Evaporative	Gaseous Product	Gaseous Product
Product Heat Management	Process Gas + Liquid Cooling Medium	Process Gas + Electrolyte Circulation	Process Gas + Liquid cooling medium or steam generation	Internal Reforming + Process Gas	Internal Reforming + Process Gas

In parallel with the classification by electrolyte, some fuel cells are classified by the type of fuel used:

2.1 Direct Alcohol Fuel Cells (DAFC).

DAFC (or, more commonly, direct methanol fuel cells or DMFC) use alcohol without reforming. Mostly, this refers to a PEFC-type fuel cell in which methanol or another alcohol is used directly, mainly for portable applications. A more detailed description of the DMFC or DAFC. Direct Carbon Fuel Cells (DCFC). In direct carbon fuel cells, solid carbon (presumably a fuel derived from coal, petcoke or biomass) is used directly in the anode, without an intermediate gasification step. Concepts with solid oxide, molten carbonate, and alkaline electrolytes are all under development. The thermodynamics of the reactions in a DCFC allow very high efficiency conversion. Therefore, if the technology can be developed into practical systems, it could ultimately have a significant impact on coal-based power generation.

2.2 Polymer Electrolyte Fuel Cell (PEFC)

The electrolyte in this fuel cell is an ion exchange membrane (fluorinated sulfonic

acid polymer or other similar polymer) that is an excellent proton conductor. The only liquid in this fuel cell is water; thus, corrosion problems are minimal. Typically, carbon electrodes with platinum electro-catalyst are used for both anode and cathode, and with either carbon or metal interconnects.

Water management in the membrane is critical for efficient performance; the fuel cell must operate under conditions where the by-product water does not evaporate faster than it is produced because the membrane must be hydrated. Because of the limitation on the operating temperature imposed by the polymer, usually less than 100 °C, but more typically around 60 to 80 °C. , and because of problems with water balance, a H₂-rich gas with minimal or no CO (a poison at low temperature) is used. Higher catalyst loading (Pt in most cases) than that used in PAFCs is required for both the anode and cathode. Extensive fuel processing is required with other fuels, as the anode is easily poisoned by even trace levels of CO, sulfur species, and halogens. PEFCs are being pursued for a wide variety of applications, especially for prime power for fuel cell vehicles (FCVs). As a consequence of the high interest in FCVs and hydrogen, the investment in PEFC over the past decade easily surpasses all other types of fuel cells combined. Although significant development of PEFC for stationary applications has taken place, many developers now focus on automotive and portable applications.

Advantages: The PEFC has a solid electrolyte which provides excellent resistance to gas crossover. The PEFC's low operating temperature allows rapid start-up and, with the absence of corrosive cell constituents, the use of the exotic materials required in other fuel cell types, both in stack construction and in the BoP is not required. Test results have demonstrated that PEFCs are capable of high current densities of over 2 kW/l and 2 W/cm². The PEFC lends itself particularly to situations where pure hydrogen can be used as a fuel.

Disadvantages: The low and narrow operating temperature range makes thermal management difficult, especially at very high current densities, and makes it

difficult to use the rejected heat for cogeneration or in bottoming cycles. Water management is another significant challenge in PEFC design, as engineers must balance ensuring sufficient hydration of the electrolyte against flooding the electrolyte. In addition, PEFCs are quite sensitive to poisoning by trace levels of contaminants including CO, sulfur species, and ammonia. To some extent, some of these disadvantages can be counteracted by lowering operating current density and increasing electrode catalyst loading, but both increase cost of the system. If hydrocarbon fuels are used, the extensive fuel processing required negatively impacts system size, complexity, efficiency (typically in the mid thirties), and system cost. Finally, for hydrogen PEFC the need for a hydrogen infrastructure to be developed poses a barrier to commercialization.

2.3 Alkaline Fuel Cell (AFC)

The electrolyte in this fuel cell is concentrated (85 wt percent) KOH in fuel cells operated at high temperature ($\sim 250^\circ\text{C}$), or less concentrated (35 to 50 wt percent) KOH for lower temperature ($< 120^\circ\text{C}$) operation. 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). The fuel supply is limited to non-reactive constituents except for hydrogen. CO is a poison, and CO_2 will react with the KOH to form K_2CO_3 , thus altering the electrolyte. Even the small amount of CO_2 in air must be considered a potential poison for the alkaline cell. Generally, hydrogen is considered as the preferred fuel for AFC, although some direct carbon fuel cells use (different) alkaline electrolytes. The 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. The AFC has enjoyed considerable success in space applications, but its terrestrial application has been challenged by its sensitivity to CO_2 . Still, some developers in the U.S. and Europe pursue AFC for mobile and closed-system (reversible fuel cell) applications.

Advantages: Desirable attributes of the AFC include its excellent performance on

hydrogen (H₂) and oxygen (O₂) compared to other candidate fuel cells due to its active O₂ electrode kinetics and its flexibility to use a wide range of electro-catalysts.

Disadvantages: The sensitivity of the electrolyte to CO₂ requires the use of highly pure H₂ as a fuel. As a consequence, the use of a reformer would require a highly effective CO and CO₂ removal system. In addition, if ambient air is used as the oxidant, the CO₂ in the air must be removed. While this is technically not challenging, it has a significant impact on the size and cost of the system.

2.4 Phosphoric Acid Fuel Cell (PAFC)

Phosphoric acid, concentrated to 100 percent, is used as the electrolyte in this fuel cell, which typically operates at 150 to 220 °C. At lower temperatures, phosphoric acid is a poor ionic conductor, and CO poisoning of the Pt electro-catalyst in the anode becomes severe. The relative stability of concentrated phosphoric acid is high compared to other common acids; consequently the PAFC is capable of operating at the high end of the acid temperature range (100 to 220 °C). In addition, the use of concentrated acid (100 percent) minimizes the water vapor pressure so water management in the cell is not difficult. The matrix most commonly used to retain the acid is silicon carbide (SiC), and the electro-catalyst in both the anode and cathode is Pt. PAFCs are mostly developed for stationary applications. Both in the U.S. and Japan, hundreds of PAFC systems were produced, sold, and used in field tests and demonstrations. It is still one of the few fuel cell systems that are available for purchase. Development of PAFC had slowed down in the past ten years, in favor of PEMFCs that were thought to have better cost potential.

Advantages: PAFCs are much less sensitive to CO than PEMFCs and AFCs: PAFCs tolerate about one percent of CO as a diluent. The operating temperature is still low enough to allow the use of common construction materials, at least in the BoP components. The operating temperature also provides considerable design flexibility for thermal management. PAFCs have demonstrated system efficiencies of 37 to 42 percent (based on LHV of natural gas fuel), which is higher than most PEMFC systems could achieve (but

lower than many of the SOFC and MCFC systems). In addition, the waste heat from PAFC can be readily used in most commercial and industrial cogeneration applications, and would technically allow the use of a bottoming cycle.

Disadvantages: Cathode-side oxygen reduction is slower than in AFC, and requires the use of a Platinum catalyst. Although less complex than for PEFC, PAFCs still require extensive fuel processing, including typically a water gas shift reactor to achieve good performance. Finally, the highly corrosive nature of phosphoric acid requires the use of expensive materials in the stack (especially the graphite separator plates).

2.5 Molten Carbonate Fuel Cell (MCFC)

The electrolyte in this fuel cell is usually a combination of alkali carbonates, which is retained in a ceramic matrix of LiAlO_2 . The fuel cell operates at 600 to 700°C where the alkali carbonates form a highly conductive molten salt, with carbonate ions providing ionic conduction. At the high operating temperatures in MCFCs, Ni (anode) and nickel oxide (cathode) are adequate to promote reaction. Noble metals are not required for operation, and many common hydrocarbon fuels can be reformed internally.

The focus of MCFC development has been larger stationary and marine applications, where the relatively large size and weight of MCFC and slow start-up time are not an issue. MCFCs are under development for use with a wide range of conventional and renewable fuels. MCFC-like technology is also considered for DCFC. After the PAFC, MCFCs have been demonstrated most extensively in stationary applications, with dozens of demonstration projects either under way or completed. While the number of MCFC developers and the investment level are reduced compared to a decade ago, development and demonstrations continue.

Advantages: The relatively high operating temperature of the MCFC (650 °C) results in several benefits: no expensive electro-catalysts are needed as the nickel electrodes provide sufficient activity, and both CO and certain hydrocarbons are fuels for the MCFC, as they are converted to hydrogen within the stack (on special reformer plates) simplifying the BoP and improving system efficiency to the high forties to low fifties. In addition, the high temperature waste heat allows the use of a bottoming cycle to further boost the system efficiency to the high fifties to low sixties.

Disadvantages: The main challenge for MCFC developers stems from the very corrosive and mobile electrolyte, which requires use of nickel and high-grade stainless steel as the cell hardware (cheaper than graphite, but more expensive than ferritic steels). The higher temperatures promote material problems, impacting mechanical stability and stack life.

Also, a source of CO₂ is required at the cathode (usually recycled from anode exhaust) to form the carbonate ion, representing additional BoP components. High contact resistances and cathode resistance limit power densities to around 100 – 200 mW/cm₂ at practical operating voltages.

2.6 Solid Oxide Fuel Cell (SOFC)

The electrolyte in this fuel cell is a solid, nonporous metal oxide, usually Y₂O₃-stabilized ZrO₂. The cell operates at 600-1000 °C where ionic conduction by oxygen ions takes place. Typically, the anode is Co-ZrO₂ or Ni-ZrO₂ cermet, and the cathode is Sr-doped LaMnO₃.

Early on, the limited conductivity of solid electrolytes required cell operation at around 1000 °C, but more recently thin-electrolyte cells with improved cathodes have allowed a reduction in operating temperature to 650 – 850 °C. Some developers are attempting to push SOFC operating temperatures even lower. Over the past decade, this has allowed the development of compact and high-performance SOFC which utilized relatively low-cost construction materials.

Concerted stack development efforts, especially through the U.S. DOE's SECA program, have considerably advanced the knowledge and development of thin-electrolyte planar SOFC. As a consequence of the performance improvements, SOFCs are now considered for a wide range of applications, including stationary power generation, mobile power, auxiliary power for vehicles, and specialty applications.

Advantages: The SOFC is the fuel cell with the longest continuous development period, starting in the late 1950s, several years before the AFC. Because the electrolyte is solid, the cell can be cast into various shapes, such as tubular, planar, or monolithic. The solid ceramic construction of the unit cell alleviates any corrosion problems in the cell. The solid electrolyte also allows precise engineering of the three-phase boundary and avoids electrolyte movement or flooding in the electrodes. The kinetics of the cell are relatively fast, and CO is a directly useable fuel as it is in the MCFC. There is no requirement for

CO₂ at the cathode as with the MCFC. The materials used in SOFC are modest in cost. Thin-electrolyte planar SOFC unit cells have been demonstrated to be cable of power densities close to those achieved with PEFC. As with the MCFC, the high operating temperature allows use of most of the waste heat for cogeneration or in bottoming cycles. Efficiencies ranging from around 40 percent (simple cycle small systems) to over 50 percent (hybrid systems) have been demonstrated, and the potential for 60 percent+ efficiency exists as it does for MCFC.

Disadvantages: The high temperature of the SOFC has its drawbacks. There are thermal expansion mismatches among materials, and sealing between cells is difficult in the flat plate configurations. The high operating temperature places severe constraints on materials selection and results in difficult fabrication processes. Corrosion of metal stack components (such as the interconnects in some designs) is a challenge. These factors limit stack-level power density (though significantly higher than in PAFC and MCFC), and thermal cycling and stack life (though the latter is better than for MCFC and PEFC).

UNIT – III – Fuel Cell and Applications – SME1615

III. Fuel cell Components and Performance

3.1 Characteristics

The interest in terrestrial applications of fuel cells is driven primarily by their potential for high efficiency and very low environmental impact (virtually no acid gas or solid emissions).

Efficiencies of present fuel cell plants are in the range of 30 to 55 percent based on the lower heating value (LHV) of the fuel. Hybrid fuel cell/reheat gas turbine cycles that offer efficiencies greater than 70 percent LHV, using demonstrated cell performance, have been proposed. Tow emissions of installed PAFC units compared to the Los Angeles Basin (South Coast Air Quality Management District) requirements, the strictest requirements in the U.S. Measured emissions from the PAFC unit are < 1 ppm of NO_x, 4 ppm of CO, and <1 ppm of reactive organic gases (non-methane) (5). In addition, fuel cells operate at a constant temperature, and the heat from the electrochemical reaction is available for cogeneration applications. Table summarizes the impact of the major constituents within fuel gases on the various fuel cells. The reader is referred to Sections 3 through 7 for detail on trace contaminants. Another key feature of fuel cells is that their performance and cost are less dependent on scale than other power technologies. Small fuel cell plants operate nearly as efficiently as large ones, with equally low emissions, and comparable cost.¹ This opens up applications for fuel cells where conventional power technologies are not practical. In addition, fuel cell systems can be relatively quiet generators. To date, the major impediments to fuel cell commercialization have been insufficient longevity and reliability, unacceptably high cost, and lack of familiarity of markets with fuel cells. For fuel cells that require special fuels (such as hydrogen) the lack of a fuel infrastructure also limits commercialization.

Other characteristics that fuel cells and fuel cell plants offer are:

- Direct energy conversion (no combustion)
- No moving parts in the energy converter
- Quiet

- Demonstrated high availability of lower temperature units
 - Siting ability
 - Fuel flexibility
 - Demonstrated endurance/reliability of lower temperature units
 - Good performance at off-design load operation
 - Modular installations to match load and increase reliability
 - Remote/unattended operation
 - Size flexibility
 - Rapid load following capability
- General negative features of fuel cells include
- Market entry cost high; Nth cost goals not demonstrated.
 - Endurance/reliability of higher temperature units not demonstrated.

Table 3-1 Summary of Major Fuel Constituents Impact on PEFC, AFC, PAFC, MCFC, and SOFC

Gas Species	PEFC	AFC	PAFC	MCFC	SOFC
H ₂	Fuel	Fuel	Fuel	Fuel	Fuel
CO	Poison (reversible) (50 ppm per stack)	Poison	Poison (<0.5 %)	Fuel ^a	Fuel
CH ₄	Diluent	Poison	Diluent	Diluent	Fuel
CO ₂ & H ₂ O	Diluent	Poison	Diluent	Diluent	Diluent
S as (H ₂ S & COS)	No Studies to date (11)	Poison	Poison (<50 ppm)	Poison (<0.5 ppm)	Poison (<1.0 ppm)

In reality, CO, with H₂O, shifts to H₂ and CO₂, and CH₄, with H₂O, reforms to H₂ and CO faster than reacting as a fuel at the electrode.

Advantages/Disadvantages

The fuel cell types addressed in this handbook have significantly different operating regimes. As a result, their materials of construction, fabrication techniques, and system requirements differ.

These distinctions result in individual advantages and disadvantages that govern the potential of

the various cells to be used for different applications. Developers use the advantages of fuel cells to identify early applications and address research and development issues to expand applications

The characteristics, advantages, and disadvantages summarized in the previous section form the basis for selection of the candidate fuel cell types to respond to a variety of application needs.

The major applications for fuel cells are as stationary electric power plants, including cogeneration units; as motive power for vehicles, and as on-board electric power for space vehicles or other closed environments.

3.2 Stationary Electric Power

One characteristic of fuel cell systems is that their efficiency is nearly unaffected by size. This means that small, relatively high efficient power plants can be developed, thus avoiding the higher cost exposure associated with large plant development. As a result, initial stationary plant development has been focused on several hundred kW to low MW capacity plants. Smaller plants (several hundred kW to 1 to 2 MW) can be sited at the user's facility and are suited for cogeneration operation, that is, the plants produce electricity and thermal energy. Larger, dispersed plants (1 to 10 MW) are likely to be used for distributed generation. The plants are fueled primarily with natural gas. Once these plants are commercialized and price improvements materialize, fuel cells will be considered for large base-load plants because of their high efficiency.

The base-load plants could be fueled by natural gas or coal. The fuel product from a coal gasifier, once cleaned, is compatible for use with fuel cells. Systems integration studies show that high temperature fuel cells closely match coal gasifier operation. Operation of complete, self-contained, stationary plants continues to be demonstrated using PEFC, AFC, PAFC, MCFC, and SOFC technology. Demonstrations of these technologies that occurred before 2000 were addressed in previous editions of the Fuel Cell Handbook and in the literature of the period. A case in point is the 200 kW PAFC on-site plant, the PC-25, that was the first to enter the commercial market.

3.3 Thermodynamic System Models

Fuel cell system models have been developed to help understand the interactions between various unit operations within a fuel cell system. Most fuel cell system models are based on thermodynamic process flow simulators used by the process industry (power industry, petroleum industry, or chemical industry) such as Aspen Plus, HYSIS, and Chem CAD. Most of these codes are commercially distributed, and over the past years they have offered specific unit operations to assist modeling fuel cell stacks (or at least a guide for putting together existing unit operations to represent a fuel cell stack) and reformers. Others (16) have developed more sophisticated 2-D models to help with dynamic or quasi-dynamic simulations. The balance of plant components usually can be readily modeled using existing unit operations included in the packages. These types of models are used routinely by fuel cell developers, and have become an indispensable tool for system engineers. The accuracy of the basic thermodynamic models is quite good, but because the fuel cell sub-models are typically lumped parameter models or simply look-up tables, their accuracy depends heavily on model parameters that have been developed and validated for relevant situations. Aspen Plus is described below as an example, followed by a description of GCTools, an Argonne National Laboratory modeling set that offers an alternative to codes from the commercial software industry.

3.4 Unit Operations Models for Process Analysis using ASPEN

DOE's National Energy Technology Laboratory has been engaged in the development of systems models for fuel cells for over 15 years. The models were originally intended for use in applications of stationary power generation designs to optimize process performance and to evaluate process alternatives. Hence, the models were designed to work within DOE's ASPEN process simulator and later ported to the commercial version of this product, ASPEN Plus. ASPEN is a sophisticated software application developed to model a wide variety of chemical processes. It contains a library of unit operations models that simulate process equipment and processing steps, and it has a chemical component data bank that contains physical property parameters that are used to compute thermodynamic properties, including phase and chemical equilibrium. The first general purpose fuel cell model was a Nernst-limited model designed to compute the maximum attainable fuel cell voltage as a function of the cell operating conditions, inlet stream compositions, and desired fuel utilization. Subsequently, customized unit operations models were developed to simulate the operation of solid oxide (internal reforming), molten carbonate (both external and internal reforming), phosphoric acid, and polymer electrolyte fuel cells (PEFC). These fuel cell models are lumped parameter models based on empirical performance equations. As operation deviates from the setpoint conditions at a "reference" state, a voltage adjustment is applied to account for perturbations. Separate voltage adjustments are applied for current density, temperature, pressure, fuel utilization, fuel composition, oxidant utilization, oxidant composition, cell lifetime, and production year. These models were developed in a collaborative effort by DOE's National Energy Technology Laboratory and the National Renewable Energy Laboratory. In recent years, participants in the SECA core program have developed a stack sub-model for ASPEN that adequately represents intermediate temperature SOFC. Stand-alone fuel cell power systems have been investigated, as well as hybrid systems using a wide variety of fuels and process configurations. Some of the systems analyses studies that have been conducted using these fuel cell models

3.5 Argonne's GCTool

Argonne National Laboratory developed the General Computational Toolkit (GCTool) specifically for designing, analyzing, and comparing fuel cell systems and other power plant configurations, including automotive, space-based, and stationary power systems. A library of models for subcomponents and physical property tables is available, and users can add empirical models of subcomponents as needed. Four different types of fuel cell models are included: polymer electrolyte, molten carbonate, phosphoric acid, and solid oxide. Other process equipment models include heat exchangers, reactors (including reformers), and vehicle systems. The physical property models include multiphase chemical equilibrium. Mathematical utilities include a nonlinear equation solver, a constrained nonlinear optimizer, an integrator, and an ordinary differential equation solver. GCTool has been used to analyze a variety of PEFC systems using different fuels, fuel storage methods, and fuel processing techniques. Examples include compressed hydrogen, metal hydride, glass microsphere, and sponge-iron hydrogen storage systems. Fuel processing alternatives have included reformers for methanol, natural gas, and gasoline using either partial oxidation or steam reforming. Researchers have examined atmospheric and pressurized PEFC automotive systems. These analyses included the identification of key constraints and operational analysis for off-design operation, system dynamic and transient performance, and the effects of operation at extreme temperatures.

3.6 3-D Cell / Stack Models

Fuel cell stack models are used to evaluate different cell and stack geometries and to help understand the impact of stack operating conditions on fuel cell stack performance. Given the wide range of possible stack geometries and the wide range of operating parameters that influence stack operation, optimization of stack design under specific application requirements is difficult without the help of a model that represents the key physico-chemical characteristics of stacks. A number of three-dimensional stack models has been developed for this purpose. In all of these models, the stack geometry is discretized into finite elements, or

volumes, that can be assigned the properties of the various stack components and sub-components. At a minimum, the models must represent electrochemical reactions, ionic and electronic conduction, and heat and mass transfer within the cell. As with system models, most of these models rely on existing modeling platforms although in the case of stack models, an advanced 3-D modeling platform is generally required.

- Computational Fluid Dynamics (CFD) – based Fuel Cell Codes. These are based on commercial CFD codes (e.g. StarCD, Fluent, AEA Technologies' CFX) that have been augmented to represent electrochemical reactions and electronic and ionic conduction. In many cases, refinements in the treatment of catalytic chemical reactions and flow through porous media are also incorporated to represent various electrode processes. In addition to evaluating basic fuel cell performance (current density, temperature and species concentration profiles) these models can help understand the impact of different manifolding arrangements.
- Computational Structural Analysis – based codes. These are based on publicly or commercially available 3-dimensional structural analysis codes (e.g. ANSYS, Nastran, Abacus). Typically, these must be augmented to represent ionic conduction, fluid flow, and electrochemical and chemical reactions. While these codes do not provide as much insight into the impact of complex flows as the CFD-based codes, they are usually more efficient (run faster) than CFD-based codes and can be used to assess mechanical stresses in the stack; a key issue in some of the high-temperature fuel cell technologies.
- Because many of the basic elements describing the core cell performance in all of these approaches is similar, approaches developed for one type of stack model can be ported to another. Below the approach taken by NETL and Fluent is described, which is similar to the approach taken for PEFC cells developed by Arthur D. Little (17), which also applied that approach to SOFC using a structural code (ABACUS (18, 19)). Pacific Northwest

National Laboratory (PNNL) has developed several 3-D stack models based on a CFD code (StarCD) and structural codes (MARC). In Europe, Forschungs-Zentrum Julich has developed its own 3-D codes. These models have been applied to a range of cell geometries, though in recent years the focus has been on planar cells.

- NETL's 3-D Analysis
- The National Energy Technology Laboratory (NETL) developed a 3-dimensional computational fluid dynamics (CFD) model to allow stack developers to reduce time-consuming build-and-test efforts. As opposed to systems models, 3-dimensional CFD models can address critical issues such as temperature profiles and fuel utilization; important considerations in fuel cell development.
- CFD analysis computes local fluid velocity, pressure, and temperature throughout the region of interest for problems with complex geometries and boundary conditions. By coupling the CFD- predicted fluid flow behavior with the electrochemistry and accompanying thermodynamics, detailed predictions are possible. Improved knowledge of temperature and flow conditions at all points in the fuel cell lead to improved design and performance of the unit.
- In this code, a 1-dimensional electrochemical element is defined, which represents a finite volume of active unit cell. This 1-D sub-model can be validated with appropriate single-cell data and established 1-D codes. This 1-D element is then used in FLUENT, a commercially available product, to carry out 3-D simulations of realistic fuel cell geometries. One configuration studied was a single tubular solid oxide fuel cell (TSOFC) including a support tube on the cathode side of the cell. Six chemical species were tracked in the simulation: H₂, CO₂, CO, O₂, H₂O, and N₂. Fluid dynamics, heat transfer, electrochemistry, and the potential field in electrode and interconnect regions were all simulated. Voltage losses due to chemical kinetics, ohmic conduction, and diffusion were accounted for in the model. Because of a lack of accurate and detailed in situ characterization of the

SOFC modeled, a direct validation of the model results was not possible. However, the results are consistent with input-output observations on experimental cells of this type.

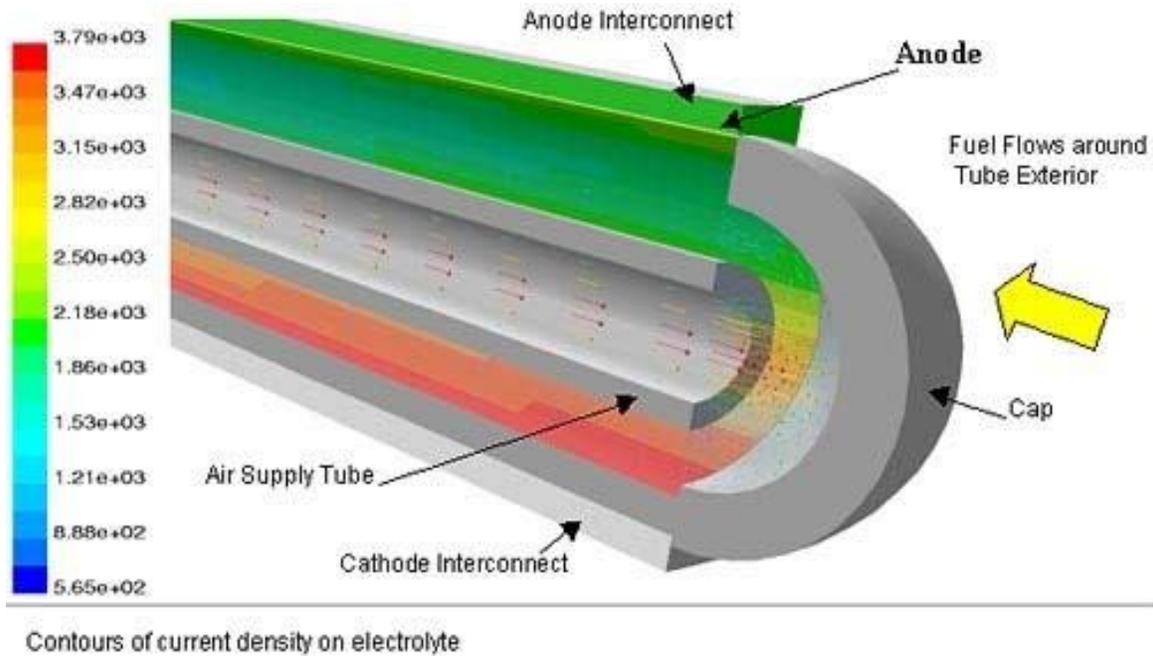


Figure 3.1 Conours of Current Density on Electrolyte

Current density is shown on the electrolyte and air-flow velocity vectors are shown for the cap- end of the tubular fuel cell. Cathode and support tube layers have been removed for clarity.

Results indicate that current density and fuel consumption vary significantly along the electrolyte surface as hydrogen fuel is consumed and current flows around the electrodes between interconnect regions. Peak temperature occurs about one-third of the axial distance along the tube from the cap end. NETL’s CFD research has demonstrated that CFD-based codes can provide detailed temperature and chemical species information needed to develop improved fuel cell designs. The output of the FLUENT-based fuel cell model has been ported to finite element-based stress analysis software to model thermal stresses in the porous and solid regions of the cell. In principle, this approach can be used for other types of fuel cells as well, as demonstrated by Arthur D. Little and NETL. Further

enhancement of the design tool is continuing. The next steps are to validate the model with experimental data and then extend the model to stack module and stack analysis. NETL now operates SOFC test facilities to generate detailed model validation data using well- characterized SOFC test specimens. These steps should make it possible to create a model that accurately predicts the performance of cells and stacks so that critical design information, such as the distribution of cell and stack stresses, can be provided to the fuel cell design engineer.

3.7 1-D Cell Models

1-D cell models are critical for constructing 3-D models, but they are also highly useful in interpreting and planning button cell experiments. In 1-D models, all of the critical phenomena in a cell are considered in a 1-D fashion. Generally they incorporate the following elements:

- Transport phenomena:
 - Convective mass transport of reactants and products to/from the surface of the electrodes
 - Mass transport of reactants and products through the porous electrodes
 - Conduction of electronic current through the electrodes and current collectors
 - Conduction of ions through the electrolyte and electrodes (where applicable)
 - Conduction, convection, and radiation of heat throughout the cell
 - Chemical reactions:
 - Electrochemical reactions at or near the triple phase boundary (TPB)
 - Internal reforming and shift reactions taking place inside the anode
- Figure 3.2 shows an example for a PEFC cell.

A large number of 1-D models have been developed. Some are based on numerical discretization methods (e.g. finite element or finite difference methods), while others are analytical in nature. An example of the former was given in the description of the NETL 3-D model. An example of an analytical approach is provided by Chick and Stevenson .

3.8 Electrode Models

Given the importance of electrode polarization in overall cell performance, electrode sub-models are critical in the development of all other fuel cell models. As described in an excellent review by Fleig ((9), Figure 2-12), one can distinguish four levels of electrode models: Continuum electrode approach. In this approach the electrode is represented as a homogeneous zone for diffusion, electrochemical reaction, and ion- and electron-conduction. Because this approach ignores the specific processes occurring at the TPB and the impact of the microstructure of the electrode, this approach yields models that must be calibrated for each specific electrode design and for each set of operating conditions. With this approach it is impossible to distinguish between rate-determining steps in the electrochemically active zone, though the relative importance of mass transfer versus kinetic processes can be expressed crudely.

Multi-particle approach. This approach recognizes that electrodes are typically made up of many particles that have different (at least two) phases with different characteristics. Issues of connectivity, percolation, and other mass-transfer-related factors can be addressed with this approach, but the details of the electrochemical reaction steps at the TPB are lumped together. From a numerical perspective, one or more resistor networks are added to the continuum model.

- *Local current density distribution approach.* A refinement on the multi-particle approach, this approach considers that current-densities are not necessarily homogeneous within the particles, which can strongly impact electrode resistances. Often this approach is executed using a finite element method.
- *Micro-kinetics approach.* In this approach, the individual reaction steps at or near the TPB are considered. Although analytical solutions (in Butler-Volmer form) can be found if a single rate-determining step is considered, generally a numerical solution is necessary for multi-step reactions. This approach can be embedded in the multi-particle or local-current density approaches, or directly used in a 1-D model with simpler assumptions for

the transport phenomena. This is the only approach that can give insight into the rate- determining electrochemical processes that take place in the cell. When optimizing electro- catalysts or studying direct oxidation of hydrocarbons, this type of model can be very enlightening.

3.9 Cell Components

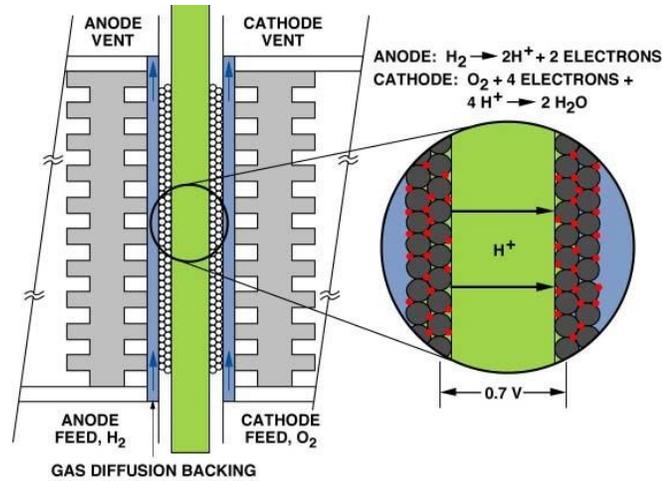
Typical cell components within a PEFC stack include:

- the ion exchange membrane
- an electrically conductive porous backing layer
- an electro-catalyst (the electrodes) at the interface between the backing layer and the membrane
- cell interconnects and flowplates that deliver the fuel and oxidant to reactive sites via flowchannels and electrically connect the cells

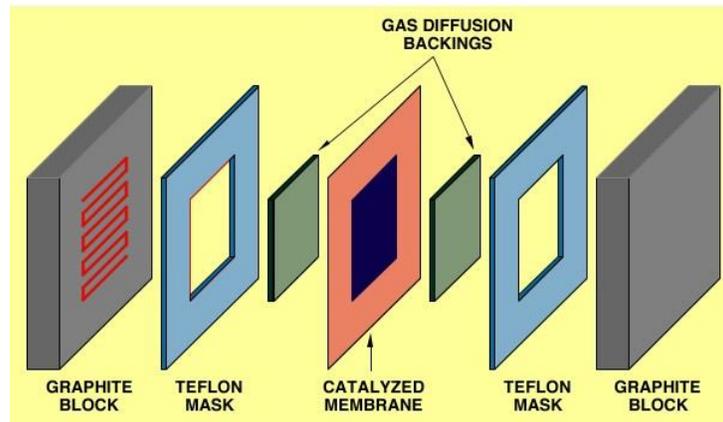
PEFC stacks are almost universally of the planar bipolar type. Typically, the electrodes are cast as thin films that are either transferred to the membrane or applied directly to the membrane.

Alternatively, the catalyst-electrode layer may be deposited onto the backing layer, then bonded to the membrane.

Polymer electrolyte membrane fuel cells are referred to by several acronyms; a common one is PEM, which stands for Proton Exchange Membrane.



(a)



(b)

Figure 3.2 (a) Schematic of Representative PEFC (b) Single Cell Structure of Representative PEFC

Organic-based cation exchange membranes in fuel cells were originally conceived by William T. Grubb (2) in 1959. That initial effort eventually led to development of the perfluorosulfonic acid polymer used in today's systems. The function of the ion exchange membrane is to provide a conductive path, while at the same time separating the reactant gases. The material is an electrical insulator. As a result, ion conduction takes place via ionic groups within the polymer structure. Ion transport at such sites is highly dependent on the bound and free water associated with those

sites. An accelerated interest in polymer electrolyte fuel cells has led to improvements in both cost and performance. Development has reached the point where both motive and stationary power applications are nearing an acceptable cost for commercial markets. Operation of PEFC membrane electrode assemblies (MEAs) and single cells under laboratory conditions similar to transportation or stationary applications have operated for over 20,000 hrs continuously with degradation rates of 4 to 6 $\mu\text{V/hr}$ (or about 0.67 to 1.0 percent per 1000 hrs), which approaches the degradation rates needed for stationary applications (about 0.1 percent per 1000 hrs is used as a rule of thumb). Complete fuel cell systems have been demonstrated for a number of transportation applications including public transit buses and passenger automobiles. For stationary applications, a number of demonstration systems have been developed and numerous systems have been installed, mostly in the 2 to 10 kW range. However, although these systems have collectively logged millions of kWhrs (3), developers have not yet demonstrated system or stack life of more than 8,000 hours with realistic catalyst loadings and realistic operating conditions, and then with degradation rates of several percent per 1000 hrs. Consequently, PEFC developers and researchers are focused on achieving critical improvements in extending stack life, simpler system integration, and reduction of system cost. This is true both for stationary and mobile applications. Manufacturing details of Plug Power's cell and stack design are proprietary, but the literature provides some information on the cell and stack design. Example schematics for the cross-section and a current collecting plate are shown in Figure 3-2 (4, 5). An approach for sealing the cell with flat gaskets is shown (Label 402) but there are many alternatives with gaskets and plates having different shapes and grooves, respectively. The plate shows the flow path for one of the reactants from the inlet to the outlet manifold. The other side of the plate (not shown) would have channels either for coolant flow or the other reactant. The standard electrolyte material in PEFCs belongs to the fully fluorinated Teflon[®]-based family similar to that produced by E.I. DuPont de Nemours for space application in the mid-1960s. The membrane is characterized by its equivalent weight (inversely proportional to the ion exchange capacity). A

typical equivalent weight range is 800 to 1100 milliequivalents per dry gram of polymer. The type used most often in the past was a melt-extruded membrane manufactured by DuPont and sold under the label.

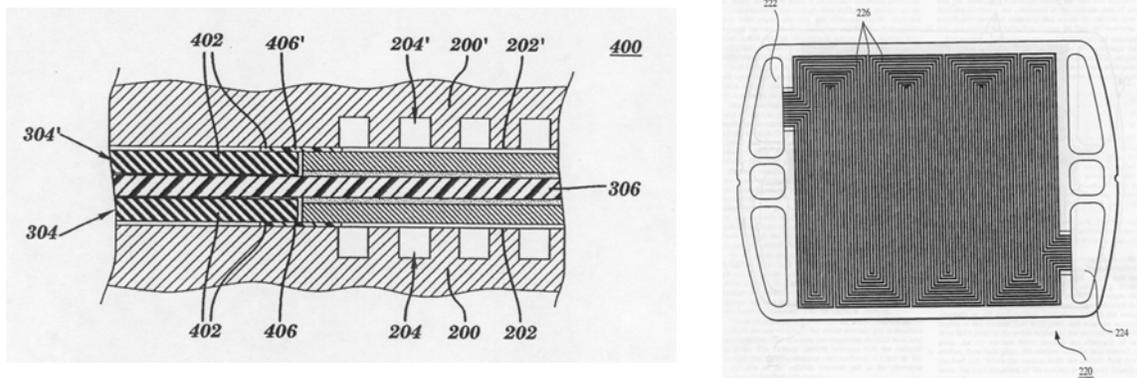


Figure 3-3 PEFC Schematic (4, 5)

. The perfluorosulfonic acid family of membranes exhibits exceptionally high chemical and thermal stability, and is stable against chemical attack in strong bases, strong oxidizing and reducing acids, Cl_2 , H_2 , and O_2 at temperatures up to 125°C . Nafion consists of a fluoropolymer backbone, similar to Teflon®, upon which sulfonic acid groups are chemically bonded (7,29). Nafion membranes have exhibited long life in selected applications, operating conditions, and electrochemical applications. In selected fuel cell tests and water electrolysis systems, lifetimes of over 50,000 hours have been demonstrated. The Dow Chemical Company produced an electrolyte membrane, the XUS 13204.10, that contained a polymeric structure similar to that of Nafion, except that the side chain length was shortened (8). As a result, the membrane properties were significantly impacted, including a higher degree of water interactions within the membrane. This translated to lower electrical resistance and permitted higher current densities than the Nafion membrane, particularly when used in thinner form (9). These short side-chain membranes exhibited good performance and stability, but are no longer supplied by Dow. Furthermore, due to Nafion's

expense and other engineering issues, new alternative membranes are being developed by a number of different companies.

Progress in manufacturing techniques has been made. Although melt-extruded films were the norm, the industry is moving to a solution-cast film process to reduce costs and improve manufacturing throughput efficiency. In this process, the ionic form of the polymer is solubilized in alcoholic solution, such as propanol, and then fabricated into a film of desired thickness. The conversion of the non-ionic polymer to an ionic phase, ready for use in a fuel cell, is carried out prior to the solubilization step. Another advancement in membrane technology is that of using an internal support layer to enhance the mechanical strength of the membrane film, especially as the membrane thickness is decreased. The Primea 55 and 56 series membranes manufactured by W.L. Gore are examples of such internally-supported membranes.

3.10 Porous Backing Layer

The polymer membrane is sandwiched between two sheets of porous backing media (also referred to as gas diffusion layers or current collectors). The functions of the backing layer⁸ are to: (1) act as a gas diffuser; (2) provide mechanical support, (3) provide an electrical pathway for electrons, and (4) channel product water away from the electrodes. The backing layer is typically carbon-based, and may be in cloth form, a non-woven pressed carbon fiber configuration, or simply a felt-like material. The layer incorporates a hydrophobic material, such as polytetrafluoroethylene. The function of polytetrafluoroethylene is to prevent water from “pooling” within the pore volume of the backing layer so that gases freely contact the catalyst sites. Furthermore, it facilitates product water removal on the cathode as it creates a non-wetting surface within the passages of the backing material. One PEFC developer (10) devised an alternative plate structure that provides passive water control. Product water is removed by two mechanisms: (1) transport of liquid water through the porous bipolar plate into the coolant, and (2) evaporation into the reactant gas streams. The cell is similar in

basic design to other PEFCs with membrane, catalysts, substrates, and bipolar plate components. However, there is a difference in construction and composition of the bipolar plate: Commonly referred to as the gas diffusion layer (GDL) even though it has additional functions. It is made of porous graphite. During operation, the pores are filled with liquid water that communicates directly with the coolant stream. Product water flows from the cathode through the pores into the coolant stream (a small pressure gradient between reactant and the coolant stream is needed). The water in the coolant stream is then routed to a reservoir. Removal of water by the porous membrane results in the reactant flow stream being free of any obstructions (liquid water). The flooded pores serve a second purpose of supplying water to the incoming reactant gases and humidifying those gases. This prevents drying of the membrane, a common failure mode, particularly at the anode. Control of the amount of area used to humidify the inlet gases has eliminated the need to pre-humidify the reactant gases.

Reasons for removing the water through the porous plate are: (1) there is less water in the spent reactant streams; (2) this approach reduces parasitic power needs of the oxidant exhaust condenser; (3) the cell can operate at high utilizations that further reduce water in the reactant streams; (4) higher temperatures can be used with higher utilizations so that the radiator can be smaller,⁹ and (5) the control system is simplified. In fact, in-stack water conservation is even more important in arid climates, where there may exist a significant challenge to achieve water balance at the system level without supplying water or refrigerating the exhaust stream. Hand-in-hand with water management goes the thermal management of the stack. Temperatures within the stack must be kept within a narrow range in order to avoid local dehydration and hot-spots as well as local dead zones. This is particularly challenging when one recognizes the narrow temperature zone and the relatively small temperature difference between the cell operating temperature and the ambient temperature.

3.11 Electrode-Catalyst Layer

In intimate contact with the membrane and the backing layer is the catalyst layer. This catalyst layer, integral with its binder, forms the electrode. The catalyst and binder electrode structure is applied either to the membrane or to the backing layer. In either case, the degree of intimacy of the catalyst particles and the membrane is critical for optimal proton mobility. The binder performs multiple functions. In one case, it “fixes” the catalyst particles within a layered structure, while a second function is to contribute to the overall architecture of the electrode. This architecture has a direct bearing on performance. There are two schools of thought on the electrode composition, in particular, the binder. In the original hydrophobic, porous, gaseous electrodes developed by Union Carbide and later advanced by General Electric, the Dow Chemical Company, and others, the binder was polytetrafluoroethylene: a non-wetting component within the electrode itself. The second school of electrode science developed a hydrophillic electrode in which the binder was perfluorosulfonic acid. The driver for this development was to enhance the membrane/catalyst contact to minimize the platinum loading requirements (11). In most state-of-the-art PEFC membrane electrode assemblies (MEAs), the catalyst is largely embedded in a solution of electrolyte monomer, which provides high solubility for protons as well as oxygen, and thus effective use of the platinum catalyst surface.

Higher average temperature operation is possible because of the reduction of hot spots within the cell. Water will evaporate through the porous plate in the vicinity of a hot spot. Conversely, a local cool spot can produce a concentration of water. This water is quickly removed through the porous plate. The catalyst is platinum-based for both the anode and cathode. To promote hydrogen oxidation, the anode uses either pure platinum metal catalyst or, as is common in most modern PEFC catalysts, a supported platinum catalyst, typically on carbon or graphite for pure hydrogen feed streams. For other fuels, such as reformat (containing H_2 , CO_2 , CO , and N_2), the desired catalyst is an alloy of platinum containing ruthenium. Oxygen reduction at the cathode may use either the platinum metal or the supported catalyst.

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IV. Hydrogen Storage Technology

Typically, electrodes can be cast as thin films and transferred to the membrane or applied directly to the membrane. Alternatively, the catalyst-electrode layer may be deposited onto the gas diffusion layer (GDL), then bonded to the membrane. Low platinum loading electrodes (

1.0 mg Pt/cm² total on the anode and the cathode) are regularly used, and have performed as well as earlier, higher platinum loading electrodes (2.0 to 4.0 mg Pt/cm²). These electrodes, which have been produced using a high-volume manufacturing process, have achieved nearly

600 mA/cm² at 0.7 V on reformat. A number of companies globally are developing such electrodes. An example of electrode performance is shown in Figure 3-3. The figure depicts the performance of a standard 100 cm² 7-layer membrane electrode assembly (MEA) manufactured by the 3M Corporation operating on hydrogen and reformat at 70 °C . Recent advances in MEA performance and durability have led to tests with reformat in excess of 10,000 hours with the 3M 7-layer MEA. This MEA is produced using high-speed, continuous, automated assembly equipment.

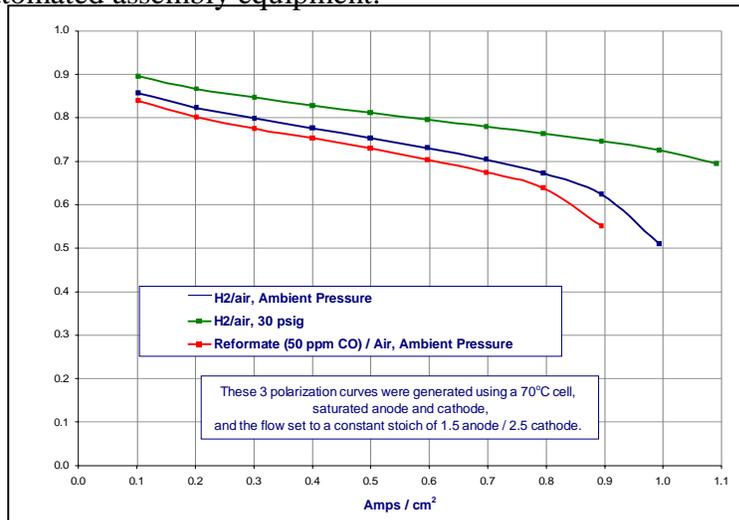


Figure 4.1 Polarization Curves for 3M 7 Layer MEA

The electrochemical reactions of the PEFC are similar to those of the PAFC¹⁰: molecular hydrogen at the anode is oxidized to provide protons, while at the same

time freeing two electrons that pass through an external “electrical” circuit to reach the cathode. The voltages at each electrode, due to the hydrogen oxidation potential and the oxygen reduction potential, form a voltage gradient of approximately 1 volt (depending on conditions) at open circuit, i.e., zero current draw. It is this potential that drives the proton through the membrane. As the proton is “pulled” through the membrane, it drags with it a certain number of water molecules. The proton reacts with oxygen to form water at the catalyst sites on the cathode. Because of the intrinsic nature of the materials used, the PEFC operates at temperatures between 0 °C to 90 °C, typically in the 60 °C to 80 °C range. When compared to other fuel cells, PEFC technology has been capable of very high current densities: while most technologies can operate up to approximately 1 amp/cm², polymer electrolyte membrane fuel cells have operated at up to 4 amps/cm². Stack level power densities under practical operating conditions (cathode stoichiometry less than 3, anode utilization more than 85%, pressure less than 3 bar, and catalyst loadings less than 1 mg/cm²) with reformat of around 50 mW/cm² at 0.7 V and of around 400 – 600 mW/cm² when operating with hydrogen are feasible (14, 15, 16, 17). This performance is due primarily to the impressive ionic conductivity of PEFC membranes and the high electrical conductivity of the materials used in the gas diffusion layers and bipolar plates (mostly carbon or metals). Other desirable attributes include fast start capability and rapid response to load changes. Because of the high power density capability, smaller, lighter-weight stacks are possible (18). Other beneficial attributes of the cell include no corrosive fluid hazard and lower sensitivity to orientation. As a result, the PEFC is thought to be best suited for vehicular power applications.

The low operating temperature of a PEFC has both advantages and disadvantages. Low temperature operation is advantageous because the cell can start from ambient conditions quickly, especially when pure hydrogen fuel is available. It is a disadvantage in carbon monoxide-containing fuel streams, because carbon will attack the platinum catalyst sites, masking the catalytic activity and reducing cell performance.¹¹ The effect is reversible by flowing a CO-free gas over the

electrode. To minimize CO poisoning, operating temperatures must be greater than 120 °C, at which point there is a reduction in chemisorption and electro-oxidation. Due to CO affecting the anode, only a few ppm of CO can be tolerated at 80 °C. Because reformed and shifted hydrocarbons contain about one percent CO, a mechanism to eliminate CO in the fuel gas is needed. This can be accomplished with preferential oxidation (PROX) that selectively oxidizes CO over H₂ using a precious metal catalyst. The low operating temperature also means that little, if any, heat is available from the fuel cell for endothermic reforming. As this discussion suggests, there is a considerable advantage at the stack level to the use of pure hydrogen rather than reformat, but in most PEFC applications this must be traded off against the challenges in storing hydrogen and the limited availability of hydrogen. Although considerable effort has been expended to develop liquid-fueled PEFC for transportation applications, most believe that on-board storage of hydrogen will be necessary for practical vehicles. To overcome the challenges of operating on reformat, attempts have been made to develop so-called high-temperature PEFC, which would operate in the 120 °C to 160°C range. New or modified ion exchange membranes would be needed to allow this, because Nafion dehydrates rapidly at such temperatures unless high (greater than 10 bar) pressures are applied. One candidate material is polybenzimidazole (PBI). The higher operating temperature eliminates CO poisoning by eliminating CO occlusion of the platinum sites. Also, this operating regime provides higher quality heat for possible use in stationary combined heat/power (CHP) applications. Because PBI requires significantly lower water content to facilitate proton transport, an additional benefit is that water management is dramatically simplified. However, to achieve acceptable ionic conductivity, the membrane must be impregnated with phosphoric acid, which is apparently not very tightly bound to the polymer backbone. As a result, similar precautions are necessary as in a PAFC (avoiding liquid water, corrosion protection). The conductivity of PBI can approach the target of 10 S/cm set for high temperature membranes. Other approaches to high-temperature membranes are based on the modification of Nafion. Reports indicate that some of the

modified materials achieve conductivities close to that of Nafion 112, while allowing operation up to 120 °C at low hydration levels (25,14 ,16 ,17)

Both temperature and pressure significantly influence cell performance. Present cells operate at 80 °C over a range of 0.0010 to 1.0 MPa (~0.1 to 150 psig). Nominally, 0.285 MPa (25 psig)

(18) is used for some transportation applications although some developers (26) pursue ambient- pressure technology. Using appropriate current collectors and supporting structure, polymer electrolyte fuel cells and electrolysis cells should be capable of operating at pressures up to 3000 psi and differential pressures up to 500 psi .

4.1 Water and Thermal Management

Due to operation at less than 100 °C and atmospheric pressure, water is produced as a liquid. A critical requirement is to maintain high water content in the electrolyte to ensure high ionic conductivity. Maintaining high water content is particularly critical when operating at high current densities (approximately 1 A/cm²) because mass transport issues associated with water formation and distribution limit cell output. The ionic conductivity of the electrolyte is higher when the membrane is fully saturated: this impacts the overall efficiency of the fuel cell. Without adequate water management, an imbalance will occur between water production and water removal from the cell.

Water content is determined by balance of water¹² during operation. Contributing factors to water transport are the water drag through the cell, back-diffusion from the cathode, and the diffusion of water in the fuel stream through the anode. Water transport is not only a function of the operating conditions but also the characteristics of the membrane and the electrodes. Water drag refers to the amount of water that is pulled by osmotic action along with the proton . One estimate is that between 1 to 2.5 molecules are dragged with each proton. As a result, transported water can be envisioned as a hydrated proton, H(H₂O)_n. During operation, a concentration gradient may form whereby the anode is drier than the cathode. Under these conditions, there is back-diffusion of water from the cathode

to the anode. Membrane thickness is also a factor in that the thinner the membrane, the greater the transport of water back to the anode. The objective of the stack engineer is to ensure that all parts of the cell are sufficiently hydrated, and that no excessive flooding occurs. Adherence of the membrane to the electrode will be adversely affected if dehydration occurs. Intimate contact between the electrodes and the electrolyte membrane is important because there is no free liquid electrolyte to form a conducting bridge. Because this type of degradation is largely irreversible, operation under dry conditions will severely impact membrane lifetime.

Reliable forms of water management have been developed based on continuous flow field design and appropriate operating adjustments. For this reason, flow field designs often feature serpentine channels or unstructured flow passages. The flow-plates (which also serve as bipolar plates) are typically made of graphite, an injection-molded and cured carbon material, or a metal. If more water is exhausted than produced, then humidification of the incoming anode gas becomes important (31). If there is too much humidification, however, the electrode floods, which causes problems with gas diffusion to the electrode. A temperature rise between the inlet and outlet of the flow field increases evaporation to maintain water content in the cell. There also have been attempts to control the water in the cell using external wicking connected to the membrane to either drain or supply water by capillary action. Much progress has been made towards PEFC commercialization. Figure 3-4, from Gore Fuel Cell Technologies, demonstrates the company's newest commercial offering, PRIMEA® Series 56 MEA that has demonstrated over 15,000 hours of cell operation .

A smaller current, larger reactant flow, lower humidity, higher temperature, or lower pressure will result in a water deficit. A higher current, smaller reactant flow, higher humidity, lower temperature, or higher pressure will lead to a water surplus.

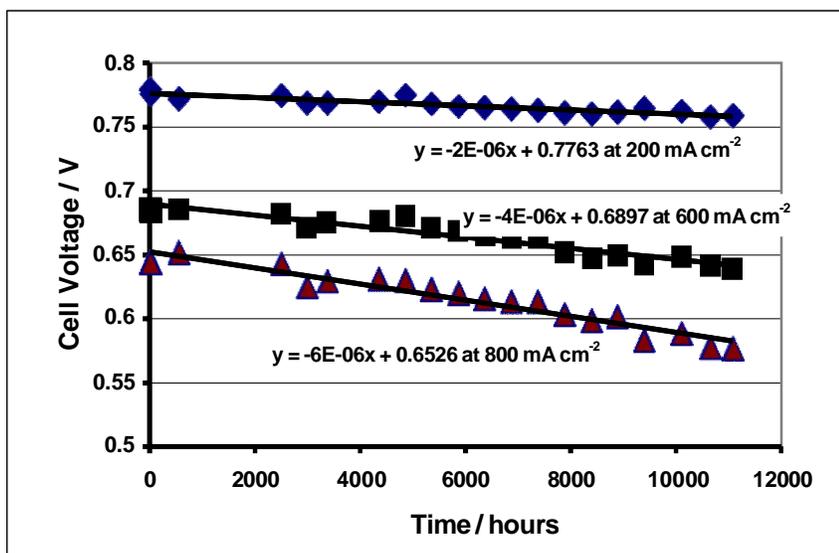


Figure 4.2 Endurance Test Results for Gore Primea 56 MEA at Three Current Densities

To improve effectiveness of the platinum catalyst, a soluble form of the polymer is incorporated into the pores of the carbon support structure. This increases the interface between the electrocatalyst and the solid polymer electrolyte. Two methods are used to incorporate the polymer solution within the catalyst. In Type A, the polymer is introduced after fabrication of the electrode; in Type B, it is introduced before fabrication. Most PEFCs presently use cast carbon composite plates for current collection and distribution, gas distribution, and thermal management. Cooling is accomplished using a circulating fluid, usually water that is pumped through integrated coolers within the stack. The temperature rise across the cell is kept to less than 10 °C. In one configuration, water-cooling and humidification are in series, which results in the need for high quality water. The cooling unit of a cell can be integrated to supply reactants to the MEA, remove reaction products from the cell, and seal off the various media against each other and the outside. Metal (usually coated) plates are used as an alternative by some developers. The primary contaminants of a PEFC are carbon monoxide (CO) and sulfur (S). Carbon dioxide (CO₂) and unreacted hydrocarbon fuel act as diluents. Reformed hydrocarbon fuels typically contain at least 1 percent CO. Even small

amounts of CO in the gas stream, however, will preferentially adsorb on the platinum catalyst and block hydrogen from the catalyst sites. Tests indicate that as little as 10 ppm of CO in the gas stream impacts cell performance (35, 36). Fuel processing can reduce CO content to several ppm, but there are system costs associated with increased fuel purification. Platinum/ruthenium catalysts with intrinsic tolerance to CO have been developed. These electrodes have been shown to tolerate CO up to 200 ppm. Although much less significant than the catalyst poisoning by CO, anode performance is adversely affected by the reaction of CO₂ with adsorbed hydrides on platinum. This reaction is the electrochemical equivalent of the water gas shift reaction.

Other contaminants of concern include ammonia (membrane deterioration), alkali metals (catalyst poisoning, membrane degradation), particles, and heavy hydrocarbons (catalyst poisoning and plugging). Both the anode and cathode flows must be carefully filtered for these contaminants, as even ppb-level concentration can lead to premature cell and stack failure.

A number of technical and cost issues face polymer electrolyte fuel cells at the present stage of development (35, 38, 39, 40, 41). These concern the cell membrane, cathode performance, and cell heating limits. The membranes used in present cells are expensive, and available only in limited ranges of thickness and specific ionic conductivity. Lower-cost membranes that exhibit low resistivity are needed. This is particularly important for transportation applications characterized by high current density operation. Less expensive membranes promote lower-cost PEFCs, and thinner membranes with lower resistivities could contribute to power density improvement (41). It is estimated that the present cost of membranes could fall (by a factor of 5) if market demand increased significantly (to millions of square meters per year). The DOE has set platinum loading targets at 0.4 mg/cm² total, a maximum to allow achieving the automotive cost targets. This will require a significantly higher catalyst effectiveness (present loadings are on the order of 1 mg/cm² total) while achieving the other improvements in performance required. Improved cathode performance, when operating on air at high current densities, is needed. At high current densities, there is a limiting gas permeability and ionic

conductivity within the catalyst layer. A nitrogen blanket forming on the gas side of the cathode is suspected of creating additional limitations (1). There is a need to develop a cathode that lessens the impact of the nitrogen blanket, allows an increase in cell pressure, and increases ionic conductivity. Local heat dissipation limits stack operation with air at a current density of approximately 2 A/cm². Single cells have shown the capability to operate at higher current densities on pure oxygen. It may be possible to increase current density and power density through better cooling schemes.

4.2 Component Development

The primary focus of ongoing research has been to improve performance and reduce cost. The principal areas of development are improved cell membranes, CO removal from the fuel stream, and improved electrode design. There has been a move toward operation with zero humidification at ambient pressure, increased cell temperature, and direct fuel use. DuPont now produces a membrane of 2 mils or less thickness that performs (at lower current densities) similar to the Dow Chemical Company membrane, the XUS 13204.10 depicted in the top curve of Figure 4.3. There is ongoing work to investigate alternative membranes and MEAs that not only exhibit durability and high performance, but also can be manufactured inexpensively in high volume.

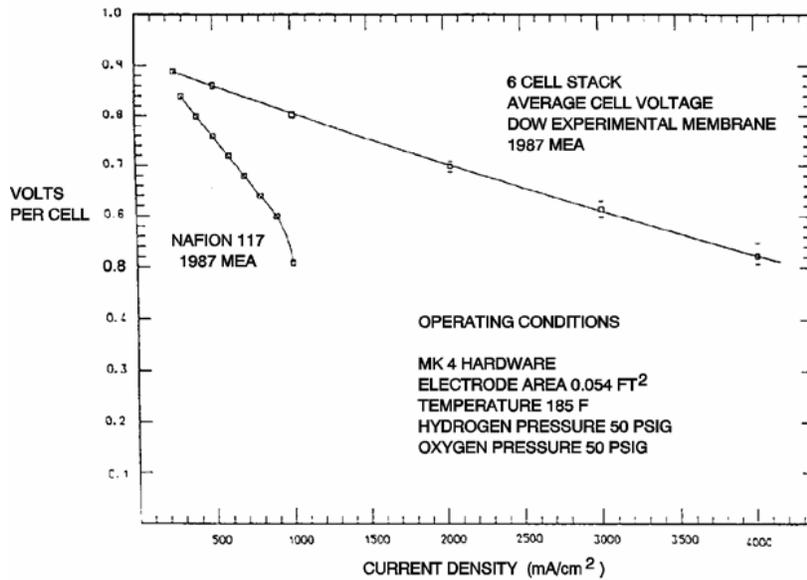


Figure 4.3 Multi-Cell Stack Performance on Dow Membrane

PEFCs were originally made with an unimpregnated electrode/Nafion electrolyte interface. This was later replaced by a proton conductor that was impregnated into the active layer of the electrode. This allowed reduced catalyst loading to 0.4 mg/cm² while obtaining high power density (27). The standard "Prototech" electrodes contained 10 percent Pt on carbon supports.

Using higher surface area carbon-supported catalysts, researchers have tested electrodes with even lower platinum loading, but having performance comparable to conventional electrodes. Los Alamos National Laboratory has tested a cathode with 0.12 mg Pt/cm² loading, and Texas A&M University has tested a cathode with 0.05 mg Pt/cm² loading. Another example of low catalyst loadings is the work carried out at DLR (43) in which loadings as low as 0.07 mg/cm² were applied to the membrane using a dry process. Another approach has been developed to fabricate electrodes with loading as low as 0.1 mg Pt/cm². The electrode structure was improved by increasing the contact area between the electrolyte and the platinum clusters. The advantages of this approach were that a thinner catalyst layer of 2 to 3 microns and a uniform mix of catalyst and polymer were produced. For example, a cell with a Pt loading of

0.07 to 0.13 mg/cm² was fabricated. The cell generated 3 A/cm² at > 0.4V on pressurized O₂, and 0.65 V at 1 A/cm² on pressurized air. Stable performance was demonstrated over 4,000 hours with Nafion membrane cells having 0.13 mg Pt/cm² catalyst loading and cell conditions of 2.4 atmospheres H₂, 5.1 atmospheres air, and 80 °C (4,000 hour performance was 0.5 V at 600 mA/cm²). Water management was stable, particularly after thinner membranes of somewhat lower equivalent weight became available. Some performance losses may have been caused by slow anode catalyst deactivation, but the platinum catalyst "ripening" phenomenon was not considered to contribute significantly to the long-term performance losses observed in PEFCs. Other research has focused on developing low-cost, lightweight, graphite carbon-based materials that can be used in place of expensive, high-purity graphite bipolar plates. Plated metals, such as aluminum and stainless steel, are also under consideration for this application, despite contact resistance and durability concerns. Conductive plastic and composite bipolar plates have met with significant success in the laboratory, and have even reached commercial production. The time line for development of a vinyl ester configuration is shown in Reference (46) for a material that has reached almost 100 S/cm. Selective oxidation is able to decrease CO in a methanol reformed gas (anode fuel supply stream) from 1% to approximately 10 ppm using a platinum/alumina catalyst. The resulting performance of the anode catalyst, though satisfactory, is impacted even by this low amount of CO. Research at Los Alamos National Laboratory has demonstrated an approach to remedy this problem by bleeding a small amount of air or oxygen into the anode compartment.

Figure 4.4 shows that performance equivalent to that obtained on pure hydrogen can be achieved using this approach. It is assumed that this approach would also apply to reformed natural gas that incorporate water gas shift to obtain CO levels of 1% entering the fuel cell. This approach results in a loss of fuel, that should not exceed 4 percent provided the reformed fuel gas can be limited to 1 percent CO.

Another approach is to develop a CO-tolerant anode catalyst such as the platinum/ruthenium electrodes currently under consideration. Platinum/ruthenium anodes have allowed cells to operate, with a low-level air bleed, for over 3,000 continuous hours on reformat fuel containing 10 ppm CO. There is considerable interest in extending PEFC technology to direct methanol and formaldehyde electro-oxidation (47, 48) using Pt-based bi-metallic catalyst. Tests have been conducted with gas diffusion-type Vulcan XC-72/Toray support electrodes with Pt/Sn (0.5 mg/cm², 8 percent Sn) and Pt/Ru (0.5 mg/cm², 50 percent Ru). The electrodes have Teflon content of 20 percent in the catalyst layer.

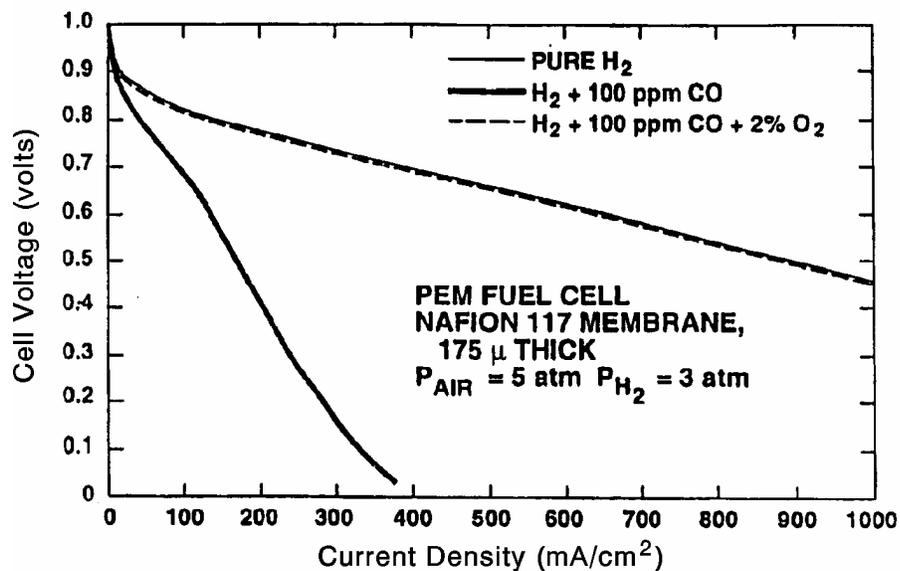


Figure 4.4 Effect on PEFC Performance of Bleeding Oxygen into the AnodeCompartment

4.3 Performance

A summary of the performance levels achieved with PEFCs since the mid-1960s is presented in Figure 3-7. Because of changes in operating conditions involving pressure, temperature, reactant gases, and other parameters, a wide range of performance levels can be obtained. The performance of the PEFC in the U.S. Gemini Space Program was 37 mA/cm² at 0.78 V in a 32- cell stack that typically operated at 50 °C and 2 atmospheres (49). Current technology yields performance levels that are vastly superior. Results from Los Alamos National Laboratory

show that 0.78 V at about 200 mA/cm² (3 atmospheres H₂ and 5 atmospheres air) can be obtained at 80 °C in PEFCs containing a Nafion membrane and electrodes with a platinum loading of 0.4 mg/cm². Further details on PEFC performance with Nafion membranes are presented by Watkins, et al. (50). In recent years, the development effort has been focused on maintaining power density while reducing platinum loading, broadening temperature and humidity operating envelopes, and other improvements that will reduce cost.

UNIT –V – Fuel Cell and Applications – SME1615

V. Fuel Cell Application and Economics

Immobilized electrolyte AFCs, used mostly in space or closed environments, and circulating electrolyte AFCs, used for terrestrial application, face separate and unique development challenges. H₂/O₂ 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 H₂/O₂ 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 pathlength 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. Electrode development in circulating electrolyte AFCs has concentrated on 1) multi-layered structures with porosity characteristics optimized for flow of liquid electrolytes and gases (H₂ 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 to 12N. 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 CO₂ 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. 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 CO₂ 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 soda-lime 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 CO₂ 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 CO₂ separation methods that show economic promise. However, circulating electrolyte is the technology of choice for terrestrial applications.

5.1 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.

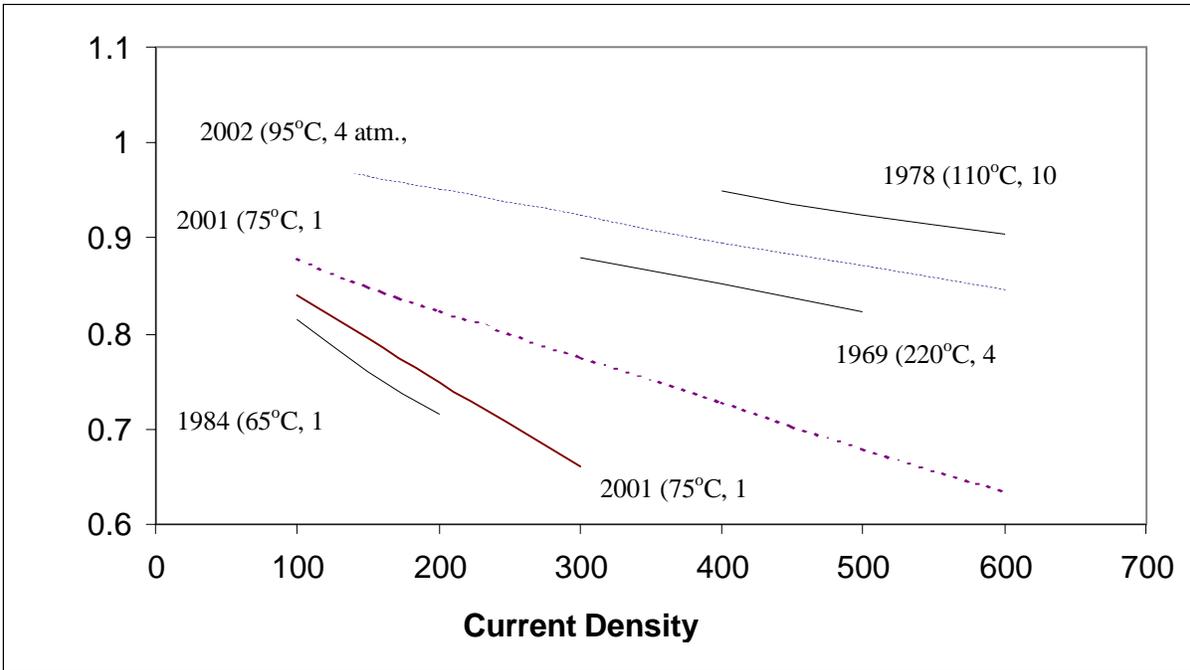


Figure 5.1 Evolutionary Changes in the Performance of AFCs

The data described in the following paragraphs pertains to the H₂/air cell. Unfortunately, H₂/air performance data is rather dated; there has been a noticeable lack of recent H₂/air data.

5.2 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. 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:

$$\Delta V_P \text{ (mV)} = 0.15T \text{ (°K)} \log(P_2/P_1) \quad (5.1)$$

over the entire range of pressures and temperatures shown in Fig. 4-4. In this expression, P₂ is the desired performance pressure and P₁ is the reference pressure

at which performance is known.

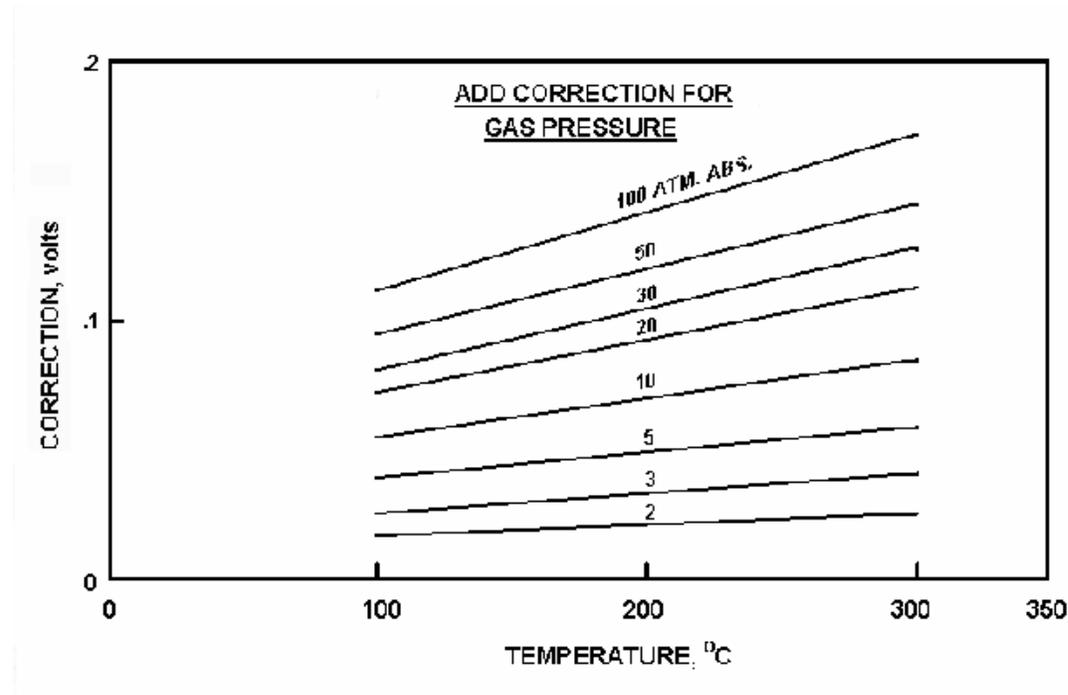


Figure 5.2 Reversible Voltage of the Hydrogen-Oxygen Cell

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.

5.3 Effect of Temperature

A fuel cell consuming H₂ and O₂ 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. 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 $0.5 \text{ mV/}^\circ\text{C}$ at 50 to 150 mA/cm^2 .

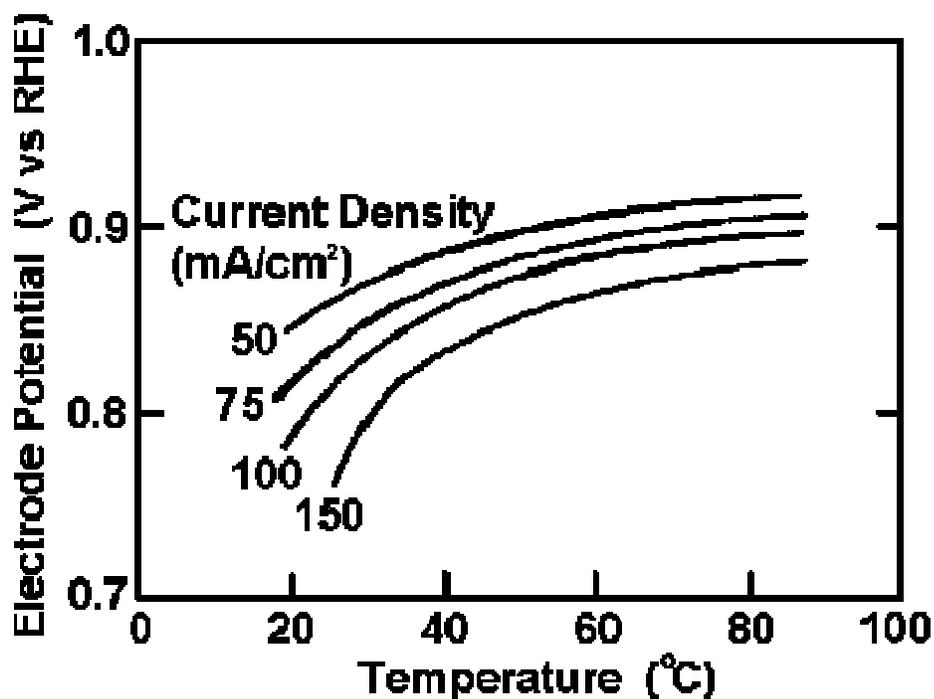


Figure 5.3 Influence of Temperature on O_2 , (air) Reduction in 12 N KOH.

Early data by Clark, et al. (22) indicated a temperature coefficient for AFCs operating between 50 to 70 °C of about $3 \text{ mV/}^\circ\text{C}$ at 50 mA/cm^2 , and cells with higher polarization had higher temperature coefficients under load. Later measurements by McBreen, et al. (23) on H_2 /air single cells (289 cm^2 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:

$$\Delta V_t \text{ (mV)} = 4.0 (T_2 - T_1) \quad \text{for } T < 63 \text{ }^\circ\text{C} \quad (5.2)$$

or

$$\Delta V_t \text{ (mV)} = 0.7 (T_2 - T_1) \quad \text{for } T > 63 \text{ }^\circ\text{C} \quad (5.3)$$

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.

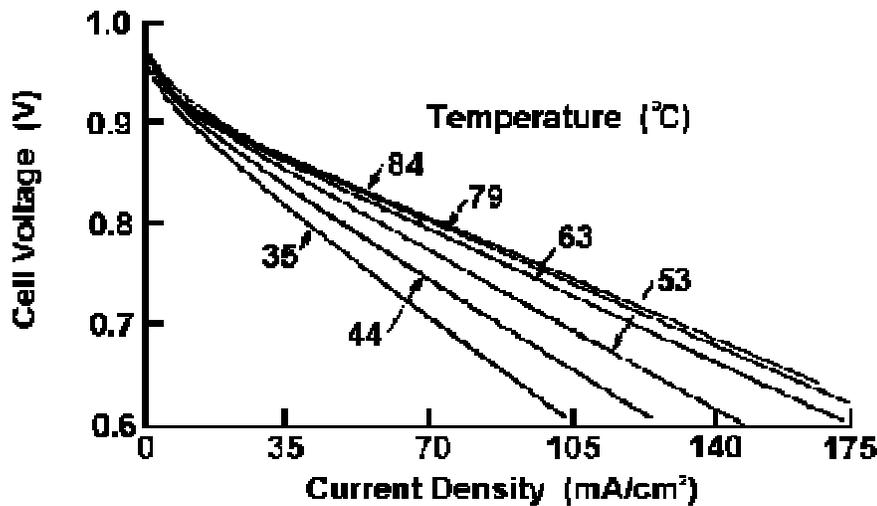


Figure 5.4 Influence of Temperature on the AFC Cell Voltage

5.4 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 CO₂ and from the presence of CO₂ in air (typically ~350 ppm CO₂ in ambient air). The negative impact of CO₂ arises from its reaction with OH⁻ producing the following effects:

- reduced OH⁻ concentration, interfering with kinetics;
- electrolyte viscosity increase, resulting in lower diffusion rate and lower limiting currents;
- precipitation of carbonate salts in the porous electrode, reducing mass transport;
-) 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 CO₂ 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 CO₂-free air and CO₂-containing air showed evidence of degradation with time. However, with CO₂-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 CO₂ (5 percent) over many thousands of hours, as proven recently by DLR (Deutsches Zentrum fuer Luft- und Raumfahrt). High concentrations of KOH are also detrimental to the life of O₂ electrodes operating with CO₂-containing air, but operating the electrode at higher temperature is beneficial because it increases the solubility of CO₂ 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 CO₂-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 CO₂-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.

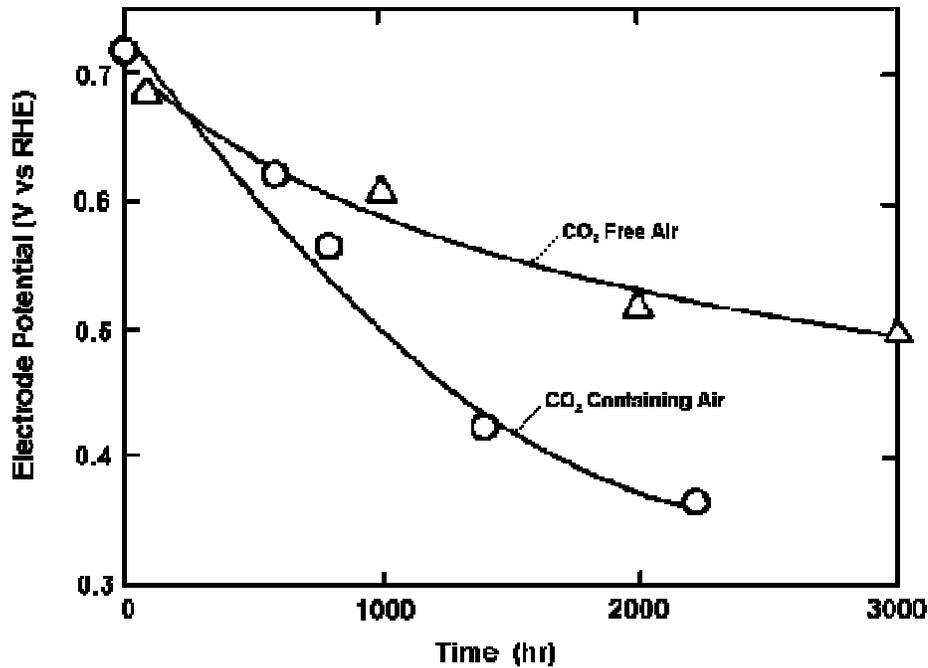


Figure 5.5 Degradation in AFC Electrode Potential with CO₂ Containing and CO₂Free Air

5.5 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.

TEXT / REFERENCE BOOKS

1. Larminie J. and Dicks A, Fuel Cell Systems Explained, 2nd Edition, Wiley, 2003
2. Xianguo Li, Principles of Fuel Cells, Taylor and Francis, 2005.
3. Srinivasan S, Fuel Cells: From Fundamentals to Applications, Springer, 2006.
4. Hayre, R. P, Cha S, Colella W.,Prinz F. B, Fuel Cell Fundamentals, Wiley, NY ,2006.
5. Basu, S. (Ed) Fuel Cell Science and Technology, Springer, N.Y, 2007.
6. Fuel Cells for automotive applications, Professional Engineering Publishing UK. ISBN 1-86058-4233, 2004.
7. Fuel Cell Technology Handbook SAE International GregorHoogers CRC Press ISBN 0-8493-0877-1-2003.