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HANDBOOK OF FUEL CELL PERFORMANCE

By
Thomas G. Benjamin
Elias H. Camara
Leonard G. Marianowski

May 1980
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Institute of Gas Technology
IIT Center
Chicago, Illinois

U. S. DEPARTMENT OF ENERGY

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TABLE OF CONTENTS

	<u>Page</u>
SCOPE	1
CHAPTER 1. INTRODUCTION TO FUEL CELLS	3
Definition	3
Advantages	3
Environmental Acceptability	3
Flexibility	4
Efficiency	5
Fuel Cell Efficiency	5
Fuel Cell System	8
Types of Fuel Cells	9
Solid Oxide Fuel Cells	9
Molten Carbonate Fuel Cells	10
Acid Fuel Cells	11
Alkaline Fuel Cells	11
Basic Principles of Operation	12
General	12
Phosphoric Acid	13
Molten Carbonate	13
References Cited	14
CHAPTER 2. ELEMENTARY ELECTROCHEMISTRY AND FUEL CELL OPERATING PARAMETERS	15
Introduction	15
Reversible (Equilibrium) Electrodes	15
The Nernst Equation	15
Exchange Current	17
Non-Equilibrium Electrodes — Polarization	17
Activation Polarization — Tafel Equation	17
Concentration Polarization — The Limiting Current	18
Total Electrode Polarization	19
Ohmic Polarization — iR Losses	19
Cell Performance	19
Fuel Cell Operating Variables	20
Temperature	20
Pressure	21
Utilization	21
Reactant Gas Composition	21
Impurities	21
References Cited	23

TABLE OF CONTENTS, Cont.

	<u>Page</u>
CHAPTER 3. PHOSPHORIC ACID FUEL CELLS	25
Introduction	25
Basic Concepts and Cell Components	30
Phosphoric Acid Fuel Cell Performance	31
General Considerations	31
Design Considerations	31
Effect of Temperature	33
Effect of Pressure	35
Effect of Reactant Concentration and Utilization	37
Oxidant	37
Fuel	37
Effect of Impurities	39
Carbon Compounds	39
Sulfur Compounds	40
Nitrogen Compounds	41
Summary, Other Compounds	42
Effect of Internal Resistance	45
Sample Calculations	45
Pressure	46
Temperature	46
Oxidant	47
Fuel	47
Design Considerations	48
References Cited	49
CHAPTER 4. MOLTEN CARBONATE FUEL CELLS	53
Introduction	53
Basic Concepts and Cell Components	55
Molten Carbonate Fuel Cell Performance	57
General Considerations	57
Design Considerations	58
Effect of Temperature	59
Effect of Pressure	61
Effect of Reactant Concentration and Utilization	63
Oxidant	63
Fuel	66
Effect of Impurities	67
Carbon	67
Sulfur	67
Nitrogen	68
Chlorine	68
Summary, Other Compounds	68
Effect of Internal Resistance	69

TABLE OF CONTENTS, Cont.

	<u>Page</u>
Sample Calculations	69
Temperature	69
Fuel	71
Oxidant	75
Pressure	76
Design Considerations	76
References Cited	77
CHAPTER 5. FUEL CELL EFFICIENCY AND HEAT BALANCE	79
Introduction	79
Fuel Cell Efficiency	79
Thermodynamic Efficiency	79
Voltage Efficiency	82
Current Efficiency	82
Electrochemical Efficiency	82
Heating Value Efficiency	83
Fuel Cell Efficiency	84
Sample Calculations	85
Phosphoric Acid Fuel Cell	85
Molten Carbonate Fuel Cell	
Experimental Fuel Cell Efficiencies	90
Phosphoric Acid	90
Molten Carbonate	90
Fuel Cell Heat Balance	93
References Cited	96
CHAPTER 6. FUEL CELL SYSTEM EFFICIENCY	97
Fuel Cell System Efficiency	97
System Examples	98
Air-Blown Coal Gasifier/Molten Carbonate Fuel Cell/ Bottoming Cycle	98
Oxygen-Blown Coal Gasifier/Molten Carbonate Fuel Cell/ Bottoming Cycle	101
Methanol Reformer/Phosphoric Acid Fuel Cell/Export Steam	104
No. 2 Fuel Oil Processing/Phosphoric Acid Fuel Cell/ Export Steam	106
Naphtha Reformer/Phosphoric Acid Fuel Cell	108
References Cited	110
APPENDIX A. HEATING VALUES OF POTENTIAL FUEL CELL SYSTEM FUELS	111
APPENDIX B. CONVERSION FACTORS AND FUEL CELL CONSTANTS	121
APPENDIX C. LIST OF SYMBOLS	125

LIST OF FIGURES

<u>Figure No.</u>		<u>Page</u>
1.1	Complete Fuel Cell Power Plant	4
1.2	Comparison of Power System Emissions	4
1.3	Power System Efficiency Comparison as a Function of Size	5
1.4	Comparison of Power System Efficiencies	6
1.5	Preliminary Fuel Utilization Characteristics for a Fuel Cell Power Plant	9
1.6	Fuel Cell Types	10
1.7a	Conceptual Diagram of a Phosphoric Acid Fuel Cell	12
1.7b	Illustrative Cell Configurations	12
2.1	Schematic Fuel Cell Polarization Curve	16
3.1	Phosphoric Acid Fuel Cell Polarization Curves	25
3.2	1.5-kW Indirect Methanol-Air Phosphoric Acid Fuel Cell Power Plant Mock-Up	26
3.3	Energy Research Corporation's Phosphoric Acid Fuel Cell Components and Stack	27
3.4	United Technologies' 40-kW Phosphoric Acid Fuel Cell Power Plant	28
3.5	United Technologies' 1.0-MW Phosphoric Acid Fuel Cell Pilot Power Plant	28
3.6a	United Technologies' 4.8-MW Phosphoric Acid Fuel Cell Power Plant Demonstrator (Fuel Cell d-c Module)	28
3.6b	United Technologies' 4.8-MW Phosphoric Acid Fuel Cell Power Plant Demonstrator (Power Plant: Artist's Conception)	29
3.7	Elemental Phosphoric Acid Fuel Cell Schematic	30
3.8	Phosphoric Acid Fuel Cell at 190°C, 3 atm, Air, Platinum Loading: 0.75 mg/cm ² , H ₂ Fuel	32

LIST OF FIGURES, Cont.

<u>Figure No.</u>		<u>Page</u>
3.9	Baseline Phosphoric Acid Fuel Cell Performance at 175°C, 1 atm, H ₂ Fuel, O ₂ Oxidant, Low Utilization	32
3.10	Effects of Temperature on Phosphoric Acid Fuel Cell Performance at 50 psia, 300 ASF, 190°F Anode Dewpoint	34
3.11	Effects of Temperature on Phosphoric Acid Fuel Cell Anode CO Tolerance	34
3.12	Cell Voltage Gain at a Fixed Current Density as a Function of Cell Operating Pressure	36
3.13	Effect of Pressure on Cell Voltage at 375°F, 300 ASF, 190°F Anode Dewpoint	36
3.14	Effects of Oxygen Partial Pressure on Cathode Performance, 192°C, 100% H ₃ PO ₄	38
3.15	Effect of CO Content and Temperature on Anode Performance, 0.35 mg Pt/cm ² , 269 mA/cm ²	39
3.16	Effect of Temperature on Slope of Performance Loss vs. CO Concentration	40
3.17	Effect of H ₂ S on Phosphoric Acid Fuel Cell Performance	41
3.18	Performance Loss Due to Ammoniation of H ₃ PO ₄	42
3.19	Relative Cathode Catalyst Activity as a Function of Percent H ₃ PO ₄ Conversion to (NH ₄) H ₂ PO ₄	43
3.20	Cell Endurance in the Presence of Ammonia	43
3.21	Potential vs. Ammonium Phosphate Oxidation Content	44
4.1	Molten Carbonate Performance History at Design Voltage Required to Achieve 7500 Btu/kWhr Heat Rate	53
4.2	Molten Carbonate Fuel Cell Schematic	56

LIST OF FIGURES, Cont.

<u>Figure No.</u>		<u>Page</u>
4.3	Baseline Molten Carbonate Fuel Cell Performance at 1 atm, 650°C, 67 mol % CO ₂ /33 mol % O ₂ Oxidant at 15% Utilization, 60 mol % H ₂ /10 mol % CO/7.4 mol % CO ₂ /22.6 mol % H ₂ O Fuel at 25% Utilization	58
4.4	Effect of Temperature on Cell, Anode, and Cathode Performance at 1 atm, 650°C, 200 mA/cm ² , and Low Utilizations	60
4.5	Effect of Temperature on Molten Carbonate Fuel Cell Performance at 1 atm, 200 mA/cm ² , 70 mol % Air 30/mol % CO ₂ Oxidant at 50% Utilization, 75% Fuel Utilization	61
4.6	Effect of Pressure on Molten Carbonate Fuel Cell Performance at 650°C, 160 mA/cm ² , 70 mol % Air 30/mol % CO ₂ Oxidant at 50% Utilization, 75% Fuel Utilization	62
4.7	Effect of Reactant Utilization on Molten Carbonate Fuel Cell Performance at 1 atm, 650°C, 160 mA/cm ² , 70 mol % Air/ 30 mol % CO ₂ Oxidant, Simulated Reformed Methane Fuel	64
4.8	Effect of Oxidant Partial Pressure on Molten Carbonate Fuel Cell Performance at 1 atm Total Pressure, 650°C, 160 mA/cm ²	64
4.9	Effect of Fuel Partial Pressure on Molten Carbonate Fuel Cell Performance at 1 atm Total Pressure, 650°C, 160 mA/cm ²	66
5.1	Fuel Cell Heat Balance	93
6.1	Complete Fuel Cell Power Plant	97
6.2a	Air-Blown Coal Gasifier/Molten Carbonate Fuel Cell/Bottoming Cycle - Flow Schematic	99
6.2b	Air-Blown Coal Gasifier/Molten Carbonate Fuel Cell/Bottoming Cycle - Energy Balance	99
6.3	Oxygen-Blown Coal Gasifier/Molten Carbonate Fuel Cell System With Partially Cascaded Steam Bottoming Cycle	101

LIST OF FIGURES, Cont.

<u>Figure No.</u>		<u>Page</u>
6.4	Methanol Reformer/Phosphoric Acid Fuel Cell System With Export Steam	104
6.5	No. 2 Fuel Oil Processing/Phosphoric Acid Fuel Cell/Export Steam	106
6.6	Naptha Steam Reformer/Phosphoric Acid Fuel Cell — Flow Schematic	107
A-1	Mean Heat Capacities of Gases in the Ideal-Gas State (Base Temperature, 77°F)	118

LIST OF TABLES

<u>Table No.</u>		<u>Page</u>
3.1	Estimated Maximum Allowable Impurity Levels — Phosphoric Acid Fuel Cells	44
3.2	Summary of Parametric Design Equations for Phosphoric Acid Fuel Cell	45
3.3	Comparison of Baseline and Projected 4.8-MW Performance and Effect of Contributing Factors	46
3.4	Composition Profile of Oxidant at 70% Utilization	47
3.5	Composition Profile of Fuel at 85% Utilization	48
4.1	Simulated Fuel Processor Product Gas Compositions	60
4.2	Fuel Gas Dew Point for Data in Figure 4.6	62
4.3	Summary of Data in Figure 4.8	65
4.4	Applicable Range of Data for Equation 4.20	67
4.5	Estimated Maximum Allowable Impurity Levels — Molten Carbonate Fuel Cell	69
4.6	Summary of Parametric Design Equations for Molten Carbonate Fuel Cell	70
4.7	Comparison of Baseline and Candidate Molten Carbonate Fuel Cell Performance and Effect of Contributing Factors	71
4.8	Composition Profile — Reformed Methane at 25% Utilization	73
4.9	Composition Profile — Air-Blown Coal Gas at 75% Utilization	73
4.10	Composition Profile of Oxidant at 50% Utilization	75
5.1	Summary of Efficiency Equations	85
5.2	Fuel Gas Composition and Thermodynamic Values for Phosphoric Acid Fuel Cell Sample Efficiency Calculation, 1 atm, 190°C	86

LIST OF TABLES, Cont.

<u>Table No.</u>		<u>Page</u>
5.3	Fuel Gas Composition and Thermodynamic Values for Molten Carbonate Fuel Cell Sample Efficiency Calculation, 1 atm, 650°C	89
5.4	Summary of Phosphoric Acid Fuel Cell Efficiency Calculations	91
5.5	Cell Operating Conditions for Table 5.4	91
5.6	Summary of Molten Carbonate Fuel Cell Efficiency Calculations	92
5.7	Cell Operating Conditions for Table 5.6	93
6.1	Design System Efficiencies for Fuel Cell Power Plants	98
6.2	Mass Balance for the System in Figure 6.2	100
6.3	Efficiency Summary of the System in Figure 6.2	101
6.4	Mass Balance for the System in Figure 6.3	102
6.5	Efficiency Summary of the System in Figure 6.3	103
6.6	Mass Balance for the System in Figure 6.4	105
6.7	Mass and Energy Balance for the System in Figure 6.5	108
6.8	Mass and Energy Balance for the System in Figure 6.6	109
A-1	Fuel Oil Higher Heating Values	114
A-2	Higher Heating Value of Benzene and Alcohols	114
A-3	Composition and Higher Heating Value of Natural Gas	114
A-4	Higher Heating Value of Coal	115
A-5	Ideal Gas Heating Values	116
A-6	Thermodynamic Values for $H_2 + 1/2 O_2 \rightarrow H_2O(g)$	117

LIST OF TABLES, Cont.

<u>Table No.</u>		<u>Page</u>
B-1	Value of Universal Gas Constant R in Various Units	123
B-2	Value of Faraday's Constant F in Various Units	123
B-3	Miscellaneous Conversion Factors	123
B-4	Energy Unit Conversion Chart	124

SCOPE

A fuel cell power plant system consists of a fuel processor that produces H_2 -rich fuel cell feeds from raw and primary fuels, a power section that converts the chemical energy in the gaseous feeds to d-c power, and a power conditioner that converts d-c to a-c power. The relationships between the d-c power provided by the cell and the power conditioner are well defined. But the interrelationships between the fuel processor and the power section are complex and have not been well documented. This is especially important in light of the growing number of fuel processing engineers entering the fuel cell power plant field and the growing interest in advanced fuel processing concepts such as coal conversion and autothermal reforming. The intent of this document is to provide a description of fuel cells, their performances and operating conditions, and the relationship between fuel processors and fuel cells. This information will enable fuel cell engineers to know which fuel processing schemes are most compatible with which fuel cells and to predict the performance of a fuel cell integrated with any fuel processor.

The data and estimates presented here are for the phosphoric acid and molten carbonate fuel cells because they are closer to commercialization than other types of fuel cells. Performance of the cells is shown as a function of operating temperature, pressure, fuel conversion (utilization), and oxidant utilization. The effect of oxidant composition (for example, air versus O_2) as well as fuel composition is examined because fuels provided by some of the more advanced fuel processing schemes such as coal conversion will contain varying amounts of H_2 , CO, CO_2 , CH_4 , H_2O , and sulfur and nitrogen compounds.

Chapter 1 includes a brief description of fuel cells and their application to industrial, commercial, and residential power generation. Chapter 2 includes development of the background necessary to understand the electrochemical aspects of fuel cells. The phosphoric acid fuel cell is discussed in Chapter 3, including how it is affected by operating conditions. Chapter 4 covers the molten carbonate fuel cell. The equations developed in Chapters 3 and 4 will help systems engineers to evaluate the application of the phosphoric acid and molten carbonate fuel cells to commercial, utility, and industrial power generation and waste heat utilization. The document concludes with Chapter 5, a detailed discussion of fuel cell efficiency, with examples, and Chapter 6, a sampling of fuel cell systems.

A comprehensive listing of fuel cell related publications since the mid-1960's is contained in "Fuel Cells: A Bibliography," Technical Information Center Report TID-3359, June 1977.

CHAPTER 1. INTRODUCTION TO FUEL CELLS

Definition

Fuel cells are electrochemical energy conversion devices, defined as electrochemical cells that can continuously transform the chemical energy of a fuel and oxidant to electrical energy by an isothermal process involving an essentially invariant electrode-electrolyte system. Unlike a battery, a fuel cell does not run down or require recharging; it will operate as long as both fuel (H_2 from a hydrocarbon fuel such as coal, oil, or gas) and an oxidant (O_2 from air) are supplied to the electrodes. The electrodes act as reaction sites or catalysts where the electrochemical transformation of the fuel and oxidant occurs, producing d-c power. This electrochemical transformation is isothermal; that is, the fuel cell directly uses the available free energy in the fuel at its operating temperature. Thus, it is not Carnot-cycle limited and can yield a high fuel to d-c power conversion efficiency.

For a fuel cell power plant to be a useful contributor to an energy generation scheme, it must be able to use commercially available fuels and be able to produce a-c electrical power. Thus, a fuel cell generator system has three components, which are shown schematically in Figure 1.1. The fuel processor converts a hydrocarbon fuel to a hydrogen-rich gas that is fed to the fuel cell stacks to produce d-c power. The power conditioner or inverter transforms the d-c power to a-c power compatible with user requirements. The concept of the fuel cell system will be further developed in a later section.

Advantages

Environmental Acceptability. The fuel cell is quiet because it has no moving parts. Because the fuel cell is not a combustion device, emissions such as NO_x , CO, and unburned hydrocarbons are not a serious problem. SO_x emissions are not a problem because the sulfur content of the fuel stream to the power plant must be reduced to attain long fuel cell life. Such low levels of emissions (Figure 1.2), coupled with the fuel cell's quiet, water-conserving operation, result in environmental acceptability and siting flexibility.

Figure 1.1. COMPLETE FUEL CELL POWER PLANT¹

Figure 1.2. COMPARISON OF POWER SYSTEM EMISSIONS

Flexibility. A single fuel cell normally generates power at approximately 0.5 to 1 volt and can be connected in series stacked with other cells to obtain almost any desired voltage. The current produced is a function of the size (the area) of a single cell. The range of sizes, the modularity, and the load-following capabilities make the fuel cell system an attractive candidate for power generation in a variety of applications, including on-site and central plants for commercial, industrial, and residential uses. With modular design,

fuel cell efficiency is independent of size; small units can operate as efficiently as large ones (Figure 1.3). Efficiency is relatively constant over a wide range of load (Figure 1.4).

Figure 1.3.. POWER SYSTEM EFFICIENCY COMPARISON AS A FUNCTION OF SIZE⁵

Efficiency. Fuel cells are inherently more efficient than conventional power generation devices because they do not suffer from the Carnot limitation, as discussed in the next section.

Fuel Cell Efficiency

Chapters 2 and 5 will discuss fuel cell efficiency and factors affecting the efficiency in detail. However, it is important to mention the theoretical efficiency of fuel cells here. The following includes a comparison of maximum fuel cell efficiency with conventional power generation techniques to illustrate the basic attractiveness of fuel cells.

The process of galvanic oxidation that produces electricity in a fuel cell resembles that of a conventional storage battery. The fuel cell does not store electrical energy; instead, it combines electrochemical oxidation (a property

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Figure 1.4. COMPARISON OF POWER SYSTEM EFFICIENCIES⁶
 (From "Fuel-Cell Power Plants" by A. P. Fickett.
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of the storage battery) with continuous feeding of sufficient fuel (a feature of the mechanical engine) to maintain a desired output.

The efficiency, ϵ , of steam or internal combustion engines, two of the most widely used conventional methods of generating electricity, is limited by the temperatures at which heat is supplied (T_{2C}) and rejected (T_{1C}), according to the Carnot cycle -

$$\epsilon = \frac{T_{2C} - T_{1C}}{T_{2C}} \quad (1.1)$$

The maximum practical theoretical efficiency for heat engines is 40% to 50%. Fuel cells convert energy isothermally (not Carnot-cycle limited), and most of the chemical energy of the fuel may be converted to electricity.

For example, in a hydrogen/oxygen fuel cell, the following reactions occur:

For the overall reaction at 298° K, based on lower heating values (LHV),

$$\Delta G = -54.6 \text{ kcal/g-mol}$$

$$\Delta H = -57.8 \text{ kcal/g-mol}$$

The maximum amount of heat energy that can be produced isothermally and isostatically by the overall reaction is the enthalpy change, ΔH , but the fuel cell can only convert to electricity an amount equivalent to the Gibbs free energy, ΔG . The difference, $T\Delta S = \Delta H - \Delta G$, is the minimum amount of heat that is produced in an isothermal, isostatic process. Therefore, the maximum efficiency of a hydrogen/oxygen fuel cell at 298° K is* -

$$\epsilon_{\max} = \left(\frac{\Delta G}{\Delta H} \right) (100) = \left(\frac{-54.6}{-57.8} \right) (100) = 94.5\% \quad (1.5)$$

The standard potential of a fuel cell, E^0 , is directly related to the standard free-energy change for the overall reaction, according to the expression -

* This quantity is often based on higher heating values. Then $\epsilon_{\max} = 83\%$.

$$\Delta G^{\circ} = -nFE^{\circ} \quad (1.6)$$

where n is the number of electrons transferred, or g-equiv/g-mol, and F is the Faraday constant, which is equal to 23.06 kcal/V · g-equiv.

In a fuel cell, all the free energy, ΔG , of the reaction is available as cell electromotive force (emf) and a large fraction of the $T\Delta S$ heat can be recovered in a bottoming cycle or cogeneration scheme. In contrast, in any heat engine a smaller fraction of the ΔH of the combustion reaction is available for useful work as a result of the Carnot efficiency limitation.

Fuel Cell System

The fuel cell system consists of a fuel processor, a fuel cell, a power conditioner, and optional cogeneration or bottoming cycle schemes, depending on application. A hydrocarbon fuel (natural gas, mined coal, solid waste, refined petroleum products or resids, synthetic natural gas, naphtha, methanol, etc.), steam, and heat recycled from the fuel cell section are fed into the fuel processor to generate a gas rich in hydrogen. The fuel processor could be a reformer, a gasifier, or a hydroprocessor, depending on the hydrocarbon fuel used. The hydrogen-rich mixture is then fed to the anode side of the fuel cell power section, formed by fuel cells connected electrically in series, to generate the desired voltage. The d-c power obtained is then processed by the power conditioner (at about 95% efficiency) to produce the a-c power to meet the user requirements. The efficiency of the system described above is compared with the conventional systems in Figure 1.4.

If the fuel cell is located on-site (at the point where the electricity will be used), system efficiency can be greatly improved by cogeneration — the production of electricity and the effective use of the heat generated by the inefficiencies discussed in Chapter 5.

The conservation potential of the fuel cell can be seen in comparisons of its heat rate (the number of British thermal units of fuel required to produce 1 kilowatt-hour of electric energy) with that of other types of power plants over a wide range of loads (Figure 1.4). Fuel cells installed for load-following duty would enable other generators to operate at their most efficient rate. Through cogeneration, as much as 90% of the heating value of the fuel can be put to work (Figure 1.5) for a phosphoric acid fuel cell system.

A number of fuel cell cogeneration system studies for residential and industrial applications have shown energy savings of up to 50%.^{7,8} Another study⁴ of an integrated coal gasifier/molten carbonate fuel cell power plant with a steam turbine bottoming cycle to recover waste heat reports an overall coal to a-c power efficiency of 50%.

Figure 1.5. PRELIMINARY FUEL UTILIZATION CHARACTERISTICS FOR A FUEL CELL POWER PLANT⁸

Types of Fuel Cells

Fuel cells are usually classified according to the type of electrolyte or ion-conducting media used and the temperature of operation, as shown in Figure 1.6, which also shows fuel quality requirements. A brief introduction to the four fuel cell types follows.

Solid Oxide Fuel Cells. Fuel cells with solid oxide electrolytes operate at temperatures above 800°C using non-noble metal electrodes. The electrolyte is usually yttria or calcia stabilized zirconia (ZrO_2), which conducts oxygen ions at the operating temperature. Because of their high operating temperature, solid oxide fuel cells will offer high-quality waste heat that can be utilized either in cogeneration or in a bottoming cycle, hence giving the potential for

Figure 1.6. FUEL CELL TYPES⁹

increasing overall system efficiency. Solid oxide fuel cell technology is still at the research stage. Three of the major problems yet to be solved are —

1. Efficient contact of electrodes with these electrolytes, involving a solid/solid interface, is difficult to achieve.
2. An extremely large number of cells are needed because of the brittle and fragile nature of the solid oxide electrolytes, which limits cell size to small areas (a few square centimeters).
3. Materials that are stable at high temperatures are needed, such as cell interconnecting materials and stable electrolytes.

Molten Carbonate Fuel Cells. This type of cell operates at temperatures of 600° to 700°C, using impure hydrogen and air, non-noble metal electrodes, and an electrolyte of molten alkali-metal carbonates in a porous ceramic carrier (tile). As with solid oxide cells, high-quality waste heat is available for use in cogeneration or in a bottoming cycle to increase overall system efficiency. Molten salt fuel cells are entering the pilot plant technology stage. The problems associated with molten carbonate fuel cells are —

1. Carbon dioxide must be recycled from the anode to the cathode for efficient and cost-effective operation.
2. Molten carbonate electrolytes are lost by evaporation, creepage, and corrosion.

3. Electrolyte tile integrity and corrosion resistance of cell hardware must be improved for successful long-term (approximately 40,000 hours) operation.

Acid Fuel Cells. Many acid electrolytes have been considered for use in fuel cells because acids are tolerant to carbon dioxide, which allows the use of impure hydrogen and air. H_3PO_4 fuel cells are the most advanced of all the fuel cell technologies: Pilot plants up to 1 MW have been successfully operated. The following factors are important in considering the use of H_3PO_4 cells for commercial application -

1. Platinum is poisoned by carbon monoxide (CO), reducing its electro-catalytic activity for hydrogen oxidation. Therefore, CO concentrations of 4% or less in the fuel are desirable.
2. Cathode performance must be improved to improve cell performance.
3. The acid electrolyte is lost because of evaporation and corrosion of cell components. Electrolyte carryover can also cause corrosion problems downstream of the cell.

Alkaline Fuel Cells. Aqueous KOH electrolyte fuel cells operate at lower temperatures (60° to 120°C) and have demonstrated reliability in space applications using pure H_2 and O_2 . The major drawback to commercialization of alkaline fuel cells is -

1. The electrolyte reacts with CO_2 , limiting the fuel to noncarbonaceous compounds. Even the 0.04% CO_2 in air must be removed. This can not be accomplished by present technology in a cost-effective manner.

All four fuel cell types are affected to varying degrees by impurities such as H_2S , SO_2 , Cl, NO_x , and NH_3 in the fuel. Thus, gas clean-up schemes are necessary for the systems.

Of the four types of fuel cells discussed above, the phosphoric acid and molten carbonate are in the most advanced state of development for commercial, industrial, and residential applications. The phosphoric acid fuel cell system (first generation) will be tested in realistic utility situations in 1980, when a 4.8-MW power plant is scheduled to begin operation in New York City. Molten carbonate electrolyte fuel cells (second generation) have advanced to the stack development stage, and demonstration of this technology in realistic utility situations has been projected for 1985. Because of these facts, this handbook will concentrate on these two systems, including their operation and application.

Basic Principles of Operation

General. Figure 1.7 is a schematic diagram of one repeating element in a stack of fuel cells. Each element is made up of an anode, where oxidation of the fuel occurs; an electrolyte, to separate the anode and cathode and to conduct the ions between them; and a cathode, where reduction of the oxidant occurs. The operation of the cell involves many complex mechanisms, which are conceptually simplified in the following discussions.

Figure 1.7a. CONCEPTUAL DIAGRAM OF A PHOSPHORIC ACID FUEL CELL

Figure 1.7b. ILLUSTRATIVE CELL CONFIGURATIONS¹⁰

Phosphoric Acid. Gaseous hydrogen in the fuel diffuses through the porous anode to a reaction site at the electrode (solid)/electrolyte (liquid) interface where it is electrochemically oxidized:

The electrons are transported through the external circuit, and the hydrogen ions are conducted through the electrolyte to the cathode reaction sites. Oxygen, which has diffused through the cathode, reacts with the hydrogen ions and electrons (Equation 1.8), and the product water diffuses back out of the cathode:

The net reaction is —

Molten Carbonate. The electrolyte is a mixture of alkali metal carbonates (a molten ionic conductor at the cell operating temperatures of 600° to 700°C) and ceramic particulates that retain the liquid. Fuel enters the anode, and the H_2 reacts* at the anode/electrolyte interface according to —

The product H_2O and CO_2 diffuse out of the electrode. At the cathode, Equation 1.11 takes place:

Note that CO_2 is formed at the anode and consumed at the cathode. For a cost-effective molten carbonate fuel cell system, the CO_2 in the anode effluent must be recycled back to the cathode. This can be accomplished by catalytic combustion of the anode effluent to CO_2 and H_2O (plus N_2 in the combustion air), followed by mixing with air to produce the cathode feed.

* Carbon monoxide in the fuel can also be oxidized, but a more favorable reaction for the conversion of CO is via conversion to hydrogen by the shift reaction, $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$. The hydrogen formed is then consumed according to Equation 1.10.

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CHAPTER 2. ELEMENTARY ELECTROCHEMISTRY AND FUEL CELL OPERATING PARAMETERS

Introduction

This chapter presents a brief introduction to the electrochemistry of fuel cells. It explains some of the basic electrochemical relationships and terminology necessary to understand how the chemical energy in the fuel and oxidant is converted to electricity.

The equilibrium characteristics of a fuel cell are related to ΔG° for the overall cell reaction. Deviation from ideal behavior caused by physical and chemical factors (Figure 2.1) is discussed in detail. More exhaustive details of electrochemical theory can be obtained from many texts on the subject.¹⁻⁷

Reversible (Equilibrium) Electrodes

The Nernst Equation. Consider an oxidation-reduction reaction such as Reaction 2.1 occurring at an electrode:

At equilibrium, there is no net reaction, but there is a difference in potential between the electrode and electrolyte. Based on the following thermodynamic relationships —

$$\Delta G = -nFE \quad (2.2)$$

$$\Delta G = \Delta G^\circ + RT \ln K \quad (2.3)$$

Nernst developed an equation relating this equilibrium potential, E , to the activities of the species involved in the reaction. In general, the Nernst Equation is written as —

$$E = E^\circ + \frac{RT}{nF} \ln \frac{[\text{product of the activity of reactant species}]}{[\text{product of the activity of product species}]} \quad (2.4)$$

E is the thermodynamic reversible (equilibrium) potential, and E° is the standard electromotive force or the potential when all the species involved are at unit activity. E° is related to the standard free energies of the species by —

$$\Delta G^\circ = -nFE^\circ \quad (2.5)$$

Values of E° as a function of temperature for the water formation reaction are presented in Table A.6.

Figure 2.1. SCHEMATIC FUEL CELL POLARIZATION CURVE

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For the acid fuel cell, the overall reaction was given in Equation 1.4:

At the normal operating temperature of 190°C, $E^0 = 1.14$ volts, and the Nernst Equation is —

$$E = 1.14\text{V} + \frac{RT}{2F} \ln \frac{[\text{P}_{\text{H}_2}][\text{P}_{\text{O}_2}]^{1/2}}{\text{P}_{\text{H}_2\text{O}}} \quad (2.6)$$

The molten carbonate reactions were given in Equations 1.10 and 1.11:

Because CO_2 is fed to the cathode and produced at the anode, the concentrations are not necessarily equal, so the overall reaction is written as —

$E^0 = 1.019$ volts at 650°C , and the Nernst equation can be written as —

$$E = 1.019\text{V} + \frac{RT}{2F} \ln \frac{[P_{\text{H}_2}]}{[P_{\text{CO}_2}]_a [P_{\text{H}_2\text{O}}]} + \frac{RT}{2F} \ln [P_{\text{CO}_2}]_c [P_{\text{O}_2}]^{1/2} \quad (2.8)$$

E can be less or greater than E^0 depending on the sign and magnitude of the logarithmic, concentration-dependent terms of Equations 2.6 and 2.8.

Exchange Current. Current is related to the electrochemical reaction rate by —

$$i = nFr \quad (2.9)$$

At equilibrium, the forward and reverse reaction rates of Reaction 2.1 are equal. They produce currents equal in magnitude but opposite in sign. The magnitude of the currents is called the equilibrium exchange current density, i_0 . High exchange current density indicates that the electrochemical reaction rate is high and good fuel cell performance is possible.

Non-Equilibrium Electrodes — Polarization

Chemical and physical factors associated with various elements of the cell when current is flowing limit the processes described here and in Chapter 1. These result in a reduction in voltage from the expected reversible potential, E . Knowledge of these limitations, called polarizations, overpotentials, or overvoltages, η , is useful when attempting to calculate efficiencies.

$$\eta = E - V \quad (2.10)$$

where V = cell voltage.

Although a discussion of fuel cell efficiencies will be reserved for a later section (Chapter 5), the factors that affect them will be discussed now. The total polarization of the electrode is the sum of these factors.

Activation Polarization — Tafel Equation. Most chemical reactions involve an energy barrier that must be overcome by the reacting species. This activation energy results in activation polarization, η_{act} , which is related to the current, i , by the Tafel Equation, Equation 2.11.

$$\eta_{act} = a + b' \log i \quad (2.11)$$

This can also be written as -

$$i = i_0 \exp (2.3\eta_{act}/b') \quad (2.12)$$

where b' is referred to as the Tafel slope obtained from plots of $\log i$ versus η . The exchange current can be determined experimentally by extrapolating plots of $\log i$ versus η to $\eta = 0$. Equation 2.12 describes either the fuel cell anode or the cathode when the appropriate values for i_0 , η , and b' are used.

Activation polarization is related to the slow step in the reaction sequence. The slow step could be adsorption of reactant onto the surface, electron transfer, desorption of product, or any other step in the reaction sequence. Of course, the slow step depends on the magnitude of the potential energy barrier that must be overcome. As temperature increases, activation polarization usually decreases.

Concentration Polarization - The Limiting Current. Concentration polarization occurs when the electrode reaction is hindered by mass transport effects. The controlling process in the case of concentration polarization may be slow diffusion in the gas phase through the pores of the electrode, solution/dissolution of reactants/products into/out of the electrolyte, or diffusion through the electrolyte to a reaction site. At practical current densities, the latter predominates. When the electrode is completely governed by diffusion processes because of low reactant concentration in the feed gases or because of conversions approaching 100% (reactants depleted), the limiting current, i_L , is reached. This situation is characterized by a rapid drop in cell voltage, as shown in Figure 2.1.

The limiting current, i_L , can be calculated from the diffusion coefficient of the reacting ions, D , the bulk concentration of the reacting ions, C_B , and the thickness of the diffusion layer, X , by applying Fick's Law:

$$i_L = \frac{DnFC_B}{X} \quad (2.13)$$

For an electrode free from activation polarization (that is, the reaction is fast), the concentration overpotential is -

$$\eta_{conc} = \frac{RT}{nF} \ln \left(1 - \frac{i}{i_L} \right) \quad (2.14)$$

Total Electrode Polarization. The total overpotential is the sum of the activation and concentration polarizations.

$$\eta = \eta_{\text{act}} + \eta_{\text{conc}} \quad (2.15)$$

The electrode voltage is defined as the sum of the equilibrium potential and the polarization*:

$$V_e = E_e + \eta_e \quad (2.16)$$

The signs of the quantities in Equation 2.16 are always such that $V \leq E$ so that Equation 2.16 is applicable to both anode and cathode.

Ohmic Polarization — iR Losses. When an anode and cathode are connected to an external load (Figure 1.7), the circuit is complete and current flows. Resistance to conduction of ions through the electrolyte, electrons through the electrodes and current collectors, and by contact resistances (between components) causes ohmic or iR polarization. Because both fuel cell electrodes and the electrolyte obey Ohm's Law, it is easy to calculate the voltage gradient (and loss) required to force ionic and electronic conduction:

$$\eta_{\text{ohm}} = iR \quad (2.17)$$

where R is the total cell resistance including electronic, ionic, and contact resistances.

Cell Performance

For the cell shown in Figure 1.7, both anodic and cathodic reactions contribute to the cell voltage, and the internal resistance of the cell reduces the available voltage. Therefore,

$$V_{\text{cell}} = V_{\text{anode}} + V_{\text{cathode}} - iR \quad (2.18)$$

* In Equation 2.16, E_e is not the Nernst potential for a complete cell (Equation 2.6 or 2.8), but is the Nernst potential of either the oxidation or reduction half-cell reaction, as measured against an inert reference electrode. A detailed discussion of this concept is not germane to this text, but a simplified discussion can be found in Reference 3 and rigorous treatment in References 4 and 5.

where V_{anode} and V_{cathode} are determined experimentally or by Equation 2.16. The effect of the polarizations has been shown qualitatively in Figure 2.1

Polarization cannot be eliminated, but can be minimized by cell design. The iR loss can be reduced by using thin electrolytes and by efficient contacts between electrode and leads. Temperature and electrolyte composition also influence the cell resistance.

Concentration polarization is dependent on the mass transport properties of the system. Mass transfer is a function of temperature, pressure, concentration, and the physical properties of the system. In a fuel cell, the reactants must diffuse through the tortuous paths of the porous electrode. This makes electrode structure important. The electrochemical reaction rate is a function of the concentration of the reacting species so, as the conversion increases, the concentration polarization becomes more severe.

Activation polarization depends upon the fundamental electrochemical reaction rate, which is also a function of temperature, pressure, and concentration. However, because the fuel cell reactions under consideration are catalytic, the activation polarization can be changed by using different catalysts.

Fuel Cell Operating Variables

From the previous discussion it is apparent that many of the same variables affect ohmic, concentration, and activation polarizations. In most cases, all three are present to some degree, depending on the cell operating conditions and physical configuration. Therefore, it is difficult to quantitatively predict the effect of changing variables without the aid of experimental data. Chapters 3 and 4 present data for the phosphoric acid and molten carbonate fuel cells, that are parametric for temperature, pressure, conversion, gas composition, and impurities. A brief discussion of the influence of these parameters is given below.

Temperature. Increasing temperature will enhance mass transfer, increase the reaction rate, and usually decrease cell resistance,* thus reducing

* Although resistance to electronic conduction in metals increases, resistance to ionic conduction in the electrolyte decreases with increasing temperature, resulting in a net decrease in cell resistance if the electrolyte concentration remains constant.

polarization and increasing cell performance. In the case of the acid cell, the additional benefit of increased CO tolerance at higher temperature is realized. On the other hand, increasing temperature results in increased corrosion, catalyst sintering and recrystallization, and electrolyte loss due to evaporation, so a compromise is required.

Pressure. There are multiple incentives for operating a fuel cell at elevated pressure, including integration with fuel processors,⁸ increased reactant partial pressure (Nernst gains), and higher gas solubilities in the electrolyte. There are also problems associated with high-pressure operation. Among these for the MCFC are the strict pressure control requirements to prevent reactant leakage through the electrolyte and seals and the effect that pressure has on the C/H/O thermodynamic system, which can lead to C deposition and CH₄ formation.

Utilization. Utilization in a fuel cell (an electrochemical reactor) is analogous to conversion in any chemical reactor that dictates or is dictated by operating characteristics and system economics. High utilization in a fuel cell results in increased concentration polarization, which reduces efficiency. However, low utilization also results in low fuel cell efficiency (Chapter 5). To achieve high system efficiencies the reactant must be utilized, either in the fuel cell or elsewhere in the system. For example, in a complete fuel cell system, anode exhaust containing unreacted hydrogen is often burned to supply heat to the fuel processor. Therefore, it is worthwhile to discuss fuel and oxidant utilizations and their effects on the performance of a fuel cell.

Reactant Gas Composition. The power produced in a fuel cell is directly related to the moles of fuel and oxidant that are available for reaction. Definition of the fuel processor and a system flow sheet to optimize efficiency requires knowledge of fuel cell performance as a function of fuel and oxidant gas compositions.

Impurities. Recent advances in hydrocarbon fuel processing have widened the range of fuels from which hydrogen can be obtained^{9,10} and the variety of impurities present in the fuel cell feed. Knowledge of the effects of the various impurities on cell operation is crucial to definition of fuel treatment requirements. How clean must the fuel cell feed be? Should the impurity be

removed prior to processing, before the fuel cell, prior to venting, or not at all? The answers to these questions lie in economics, fuel cell tolerance, existing impurity removal technology, and environmental considerations.

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CHAPTER 3. PHOSPHORIC ACID FUEL CELLS

Introduction

Technological advances since 1965 have been significant for the phosphoric acid fuel cell and will lead to a large-scale (4.8-MW) demonstration in a realistic utility situation in 1980. The historical development of acid cells has been discussed in detail elsewhere¹⁻⁴ and will not be presented here. Although cell performance levels have not changed significantly (Figure 3.1), several achievements are notable²:

1. Current cells require less than 4% of the noble metal catalyst used in earlier cells (0.75 mg/cm^2 vs. 20 mg/cm^2 of active cell area).
2. Life has been extended from hundreds to thousands of hours.
3. Hardware scaleability has been demonstrated.
4. Capital costs have been reduced by two orders of magnitude.

Figure 3.1. PHOSPHORIC ACID FUEL CELL POLARIZATION CURVES: (a) 160°C , 1 atm, AIR, PLATINUM LOADING OF 20 mg/cm^2 (b) 190°C , 3 atm, AIR, PLATINUM LOADING OF 0.75 mg/cm^2 HYDROGEN FUEL IN BOTH CASES (Figure originally presented at the Spring 1977 Meeting of the Electrochemical Society, Inc., held in Philadelphia)

State-of-the-art phosphoric acid fuel cells operate at 150° to 200°C and 1 to 3 atmospheres. The electrical operating point is 0.55 to 0.65 volts/cell at 100 to 400 mA/cm^2 of electrode area. The heat of reaction, iR heat, etc., are removed by the process gases and/or by air or water intercell cooling.

Fuel cell system efficiencies are 32% to 40% without cogeneration and 60% to 120% with cogeneration.⁵ The oxidant is oxygen in air, and the fuel is hydrogen with CO₂, CH₄, and small amounts of CO from the methane or naphtha steam reformer.

Energy Research Corporation (ERC, a subsidiary of St. Joe Minerals Corporation) has been involved in phosphoric acid fuel cell work for about 8 years. ERC has delivered a 1.5-kW indirect methanol-air fuel cell power plant (Figure 3.2) to the U.S. Army Mobility Equipment Research and Development Command (MERADCOM) for remote d-c power generation. The ERC hardware (Figure 3.3), mass production manufacturing techniques, and performance have been completely described in many publications.⁵⁻¹⁰

Figure 3.2. 1.5-kW INDIRECT METHANOL-AIR PHOSPHORIC ACID FUEL CELL POWER PLANT (Photo courtesy of U.S. Army MERADCOM)

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Figure 3.3 ENERGY RESEARCH CORPORATION'S PHOSPHORIC ACID FUEL CELL COMPONENTS AND STACK (Photo courtesy of ERC)

The organization with the most experience in developing, building, and running large-scale phosphoric acid fuel cell systems is Power Systems Division (PSD) of United Technologies Corporation (UTC). The team at UTC has successfully field-tested 60 units of 12.5-kW each in a variety of applications (residential, commercial, industrial) in 19 states and the District of Columbia¹¹ under the Team to Advance Research for Gas Energy Transformation (TARGET), a consortium of 32 gas utilities, program. These circa 1967 fuel cells operated on reformed natural gas supplied by a self-contained reformer. A larger (40-kW) system (Figure 3.4) had accumulated 14,000 hours as of July 1977.¹² An advanced model of the 40-kW unit is projected for field testing in 1980. Further large unit experience was gained in early 1977 with the 1100-hour test of a 1-MW system at UTC. This pilot power plant is shown in Figure 3.5. Data obtained from this test were used to design the 4.8-MW system (Figure 3.6), scheduled to go on line in 1980 in a program jointly

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Figure 3.4. (Left) UNITED TECHNOLOGIES' 40-kW PHOSPHORIC ACID FUEL CELL POWER PLANT¹³

Figure 3.5. (Right) UNITED TECHNOLOGIES' 1.0-MW PHOSPHORIC ACID FUEL CELL PILOT POWER PLANT¹³

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Figure 3.6a. UNITED TECHNOLOGIES' 4.8-MW PHOSPHORIC ACID FUEL CELL POWER PLANT DEMONSTRATOR (Fuel Cell d-c Module)¹⁴

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Figure 3.6b. UNITED TECHNOLOGIES' 4.8-MW PHOSPHORIC ACID FUEL CELL POWER PLANT DEMONSTRATOR (Power Plant Artist's Conception)¹⁵

funded by EPRI, DOE, UTC, and a utility group led by the Consolidated Edison Company of New York. Successful demonstration of the 4.8-MW phosphoric acid fuel cell system could lead to the commercialization of multi-megawatt systems in the 1980's.

Although the phosphoric acid fuel cell system is on the verge of large-scale demonstration, a number of problems are still receiving attention:

1. The platinum catalyst is expensive and suffers a reduction in surface area and performance due to sintering. The CO-poisoning problem mentioned earlier has been somewhat mitigated by operation at higher temperatures,² although increasing the temperature also increases the sintering. CO-tolerant catalysts such as mixtures of Pt, Rh and WO_3 have also been used.⁶
2. Electrolyte is lost because of evaporation. This problem can be alleviated by incorporation of an electrolyte reservoir in the cell. However, this reservoir can increase concentration polarization in the cell, and the evaporated acid condenses downstream of the cell, creating corrosion problems.
3. The most difficult challenge concerns the irreversibility (severe activation polarization) and lack of understanding of the reduction of oxygen at the cathode. This area also offers considerable opportunity for improvement of the phosphoric acid fuel cell performance.

Basic Concepts and Cell Components

The brief discussion of the basic principles of operation of the phosphoric acid fuel cell, presented in Chapter 1, will be expanded in this section. A schematic of a phosphoric acid fuel cell is shown in Figure 3.7. Both electrodes are Teflon-bonded diffusion electrodes consisting of porous agglomerates of catalyst particles held together by a Teflon binder¹⁷ and backed by a porous conductive support sheet. Pores in the hydrophobic Teflon region serve as diffusion channels for the gaseous reactants and products. The hydrogen diffuses through these pores to a catalyst agglomerate made up of electronically conductive catalyst particles of platinum (WO_3 , Rh and Ru may be used as dopants), supported on carbon to achieve lower catalyst loadings (0.25 to 0.75 mg Pt/cm^2 of anode area and 0.5 to 0.75 mg/cm^2 of cathode area). The catalyst agglomerates are believed to be flooded with electrolyte during cell operation.¹⁷ When the hydrogen arrives at a reaction site at the catalyst/electrolyte interface, it is electrochemically oxidized according to –

The electrons are transported through the external circuit, and the hydrogen ions are conducted to the cathode through the 95% to 100% phosphoric acid electrolyte held in place by an inert inorganic or polymeric matrix.

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Figure 3.7. ELEMENTAL PHOSPHORIC ACID FUEL CELL SCHEMATIC¹⁶

The basic cathode structure and materials are the same as the anode's (the cathode is not doped) although the physical parameters (pore size, thickness, etc.) may be different to achieve the desired mass transfer characteristics. When the hydrogen ions arrive at the cathode reaction sites, they react with the oxygen, which has diffused through the pores of the cathode's Teflon region. The reaction is –

The water then diffuses back out of the cathode. The overall reaction in the phosphoric acid fuel cell is –

Phosphoric Acid Fuel Cell Performance

General Considerations. Although the phosphoric acid fuel cell system is much more developed and closer to demonstration/commercialization than other fuel cell systems, it is difficult to find clear parametric data that fully describe cell performance characteristics. Therefore, the following discussions of cell performance parameters and design considerations should be taken as directional in nature.

The performance of a typical state-of-the-art hydrogen-air phosphoric acid fuel cell was presented in Figure 3.1. The magnitudes of the anode, the cathode (activation plus concentration), and ohmic polarizations are shown in Figure 3.8.^{2,3} The upper curve represents the cell performance that could be obtained if ohmic (approximately 15 mV/100 mA/cm²) and anode (approximately 5 mV/100 mA/cm²) polarizations were eliminated. It also demonstrates the significant gains possible if the cathode polarization (approximately 400 mV/300 mA/cm²) could be reduced.^{2,18} The relative magnitudes of the anode and cathode polarizations illustrate why most recent research is concentrated on the cathode.

The remainder of this chapter will discuss the parameters affecting cell performance, present supporting data and derived equations, and illustrate how this information is used to predict fuel cell performance at different conditions. For the purposes of this discussion, the performance of a cell operating on hydrogen and oxygen at low utilizations, atmospheric pressure, and 175°C will be considered as baseline. This performance is shown in Figure 3.9.

Design Considerations. Various points on the performance curve can be chosen as the operating design point. The selection affects and is affected by several factors. These include size, cost, heat removal, maximum and minimum voltage, and power constraints. The performance curve is a function of gas composition and utilization, temperature, pressure, and impurity levels.

Figure 3.8. PHOSPHORIC ACID FUEL CELL AT 190°C, 3 atm, AIR, PLATINUM LOADING, 0.75 mg/cm², H₂ FUEL

Figure 3.9. BASELINE PHOSPHORIC ACID FUEL PERFORMANCE AT 1 atm, 175°C, H₂ FUEL, O₂ OXIDANT, LOW UTILIZATION

The following illustrates assessment of the size, cost, and heat removal criteria: A cell operating at 100 mA/cm^2 (0.769 volt) generates 72 W/ft^2 , whereas a cell operating at 200 mA/cm^2 (0.702 volt) produces 131 W/ft^2 . Thus, to generate 1 kilowatt, the required areas are 14 ft^2 and 7.7 ft^2 , respectively. Because fuel cell cost is almost directly proportional to area, substantial savings can be realized by operating at higher current density. However, the fuel cell will be less efficient. Typical fuel cells will operate in the range of 100 to 400 mA/cm^2 at 0.65 to 0.55 volt/cell .

The voltage and power constraints arise from the fact that platinum and carbon components can corrode at cell potentials above approximately 0.8 volt . This maximum allowable voltage determines the minimum load at which the system can operate because the cell voltage increases at part load.

Effect of Temperature. From the discussion in Chapter 2, increasing the temperature is expected to increase cell performance. However, increasing the temperature has deleterious effects such as increases in catalyst sintering, cell component corrosion, electrolyte degradation, and electrolyte evaporation and concentration.^{13,20-24} The possibility of increased electrolyte concentration can be neglected at high utilization because the high partial pressure of product water in the gas stream maintains the electrolyte concentration. The increase in cell performance, which can be realized by increasing operating temperature,^{25,26} is shown in Figure 3.10. For a low-utilization H_2/O_2 or H_2/air fuel cell at 50 psia and 300 A/ft^2 , the change is described by —

$$\Delta V_T (\text{mV}) = 0.64 (T_2 - T_1) (^\circ\text{F}) \quad (3.4)$$

between 375° and 425°F .

Although temperature has only a minimal effect on the hydrogen oxidation reaction at the anode, it is important in terms of anode poisoning. Figure 3.11 shows that increasing the cell temperature results in increased anode tolerance to CO poisoning. This explains the higher slope for CO-containing fuels in Figure 3.11 described by —

$$\Delta V_T (\text{mV}) = 1.22 (T_2 - T_1) (^\circ\text{F}) \quad (3.5)$$

A more detailed discussion of poisons can be found in the Effect of Impurities section of this chapter.

Figure 3.10. EFFECTS OF TEMPERATURE ON PHOSPHORIC ACID FUEL CELL PERFORMANCE AT 50 psia, 300 ASF, 190°F ANODE DEWPOINT^{25,26}

Figure 3.11. EFFECTS OF TEMPERATURE ON PHOSPHORIC ACID FUEL CELL ANODE CO TOLERANCE² (Figure originally presented at the Spring 1977 Meeting of the Electrochemical Society, Inc., held in Philadelphia, Pennsylvania)

The preceding discussion of the effect of temperature on the phosphoric acid fuel cell implies that there is great incentive to increase the operating temperature. As mentioned previously, higher temperatures would result in increased catalyst sintering, cell component corrosion, and electrolyte evaporation and degradation, which could result in performance decay and/or life limitations. State-of-the-art phosphoric acid cells operate at 190°C, but cell package development work is in progress to lay the foundation for higher temperature and pressure conditions in the future.^{25,26}

Effect of Pressure. Increasing the pressure is expected to result in higher cell performance because of decreased activation polarization at the cathode due to increased oxygen and water partial pressures. The water dilutes the acid, resulting in a higher exchange current density. Additional gains (Nernst) are realized in the open circuit potential, E:

$$E = E^{\circ} + \frac{RT}{2F} \ln \frac{P_{H_2}}{P_{H_2O}} + \frac{RT}{2F} \ln [P_{O_2}]^{1/2} \quad (3.6)$$

The calculated contribution of each of these factors is compared with experimental data in Figure 3.12.²⁷ Figure 3.13 contains additional data^{25,26} that demonstrate the gains associated with higher pressure.

For Figure 3.12 at 350°F, the theoretical line is described by —

$$\Delta V_p \text{ (mV)} = 137 \log \frac{P_2}{P_1} \quad (3.7)$$

The experimental data are also described by —

$$\Delta V_p \text{ (mV)} = 137 \log \frac{P_2}{P_1} \quad (3.8)$$

The data in Figure 3.13 are for 375°F and become —

$$\Delta V_p \text{ (mV)} = 146 \log \frac{P_2}{P_1} \quad (3.9)$$

which also described data in the same reference at 425°F. This shows that the effect of pressure on cell performance is independent of temperature. Analysis of all of the data indicate that there is no dependence on the presence of 1.7% CO or the fuel and oxidant utilizations.

Figure 3.12. CELL VOLTAGE GAIN AT A FIXED CURRENT DENSITY AS A FUNCTION OF CELL OPERATING PRESSURE (Contribution of Different Factors Shown)²⁷

Figure 3.13. EFFECT OF PRESSURE ON CELL VOLTAGE AT 375°F, 190°F ANODE DEWPOINT, 300 ASF^{25,26}

Although the experimentally derived equations are slightly different, the discrepancy in voltage gain when increasing pressure from 50 to 100 psi is only 3 mV. Therefore, an average dependence is recommended:

$$\Delta V_p \text{ (mV)} = 142 \log \frac{P_2}{P_1} \quad (3.10)$$

Increases in cell performance with pressure can also be considered as increases in current density, which allow reduced fuel cell size and cost.

There are also problems associated with higher pressure such as increased component corrosion at the resulting higher voltage. The operating pressure range of interest for phosphoric acid fuel cells is 1 to 10 atmospheres.

Effect of Reactant Concentration and Utilization. Decreasing reactant utilization or inlet concentration results in decreased cell performance because of increased concentration polarization (diffusion) and Nernst losses as determined by Equation 3.6. Both are partial pressure effects and are considered simultaneously.

Oxidant. Figure 3.14 is representative of the data concerning the cathode that has been published^{13,20,23,24,28} and shows the magnitude of cathode performance improvement obtained with oxygen vs. air.²⁰ At a constant cathode potential the current varies linearly with oxygen partial pressure.²⁰ Additional data on the gains associated with using oxygen at the cathode instead of air are contained in Figures 3.10 and 3.13. The data in these figures are represented by —

$$\Delta V_{O_2} \text{ (mV)} = 103 \log \frac{(\bar{P}_{O_2})_2}{(\bar{P}_{O_2})_1} \quad (3.11)$$

where $(\bar{P}_{O_2})_1$ and $(\bar{P}_{O_2})_2$ are average oxygen partial pressures at the cathode.

Fuel. Because the phosphoric acid fuel cell anode reaction is essentially reversible, the effects of fuel composition and utilization are less critical to cell performance. The available data concerning the effects of fuel composition are more difficult to interpret because of the poisoning effect of carbon monoxide, which is contained in virtually all gaseous fuel cell feeds derived from hydrocarbon (liquid or coal) feedstocks. The cell performance change with respect to hydrogen partial pressure is derived

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Figure 3.14. EFFECTS OF OXYGEN PARTIAL PRESSURE ON CATHODE PERFORMANCE AT 192°C, 100% H₃PO₄²⁰ (Reprinted with permission from Electrochimica Acta 23, Kunz, H. R. and Gruver, G. A., "The Effect of Electrolyte Concentration on the Catalytic Activity of Platinum for Electrochemical Oxygen Reduction in Phosphoric Acid," Copyright 1978, Pergamon Press, Ltd.)

from the data in Figure 3.13:*

$$\Delta V_{H_2} \text{ (mV)} = 77 \log \frac{(\bar{P}_{H_2})_2}{(\bar{P}_{H_2})_1} \quad (3.12)$$

The hydrogen partial pressures are average values at the anode.

The loss in cell performance with hydrogen utilization has been demonstrated qualitatively on early electrodes,²⁹ and on current electrodes, a 40-mV Nernst loss has been observed at 80% fuel utilization.¹⁸

* The derivation of Equation 3.12 involved the application of Equations 3.14 and 3.18. These equations account for the voltage losses resulting from carbon monoxide and internal resistance, respectively.

The previous discussion implies that fuel cells should be operated at low conversions to achieve high performance. However, lower conversions result in lower cell current efficiency. (See Chapter 5.) A compromise is required, and present utilizations are on the order of 85% fuel and 70% oxidant.

Effect of Impurities. This section will attempt to quantify the effects of various impurities on cell performance and electrolyte stability. Synergistic effects of more than one poison will not be considered in detail although such effects are important.

Carbon Compounds. Anode feeds derived from hydrocarbons will contain varying amounts of methane, carbon dioxide and carbon monoxide depending upon the fuel processing techniques used. Carbon dioxide is inert in the phosphoric acid fuel cell acting as a diluent.¹⁶

The poisoning of Pt by CO, illustrated in Figure 3.11, is believed to be a simple site-elimination mechanism^{13,22,30,32} and results in decreased Pt activity at the anode, leading to increased anode polarization. The deleterious nature of carbon monoxide is described by Figure 3.15,¹³ which also shows that raising the temperature decreased CO poisoning.

Figure 3.15. EFFECT OF CO CONTENT AND TEMPERATURE ON ANODE PERFORMANCE,
0.35 mg Pt/cm², 269 mA/cm² ¹³

The data of Figure 3.15 can also be represented as —

$$\Delta V_{CO} \text{ (mV)} = -6.14 ((CO)_2 - (CO)_1) \text{ (\%)} \quad (3.13)$$

$$\Delta V_{CO} \text{ (mV)} = -3.54 ((CO)_2 - (CO)_1) \text{ (\%)} \quad (3.14)$$

$$\Delta V_{CO} \text{ (mV)} = -2.05 ((CO)_2 - (CO)_1) \text{ (\%)} \quad (3.15)$$

$$\Delta V_{CO} \text{ (mV)} = -1.30 ((CO)_2 - (CO)_1) \text{ (\%)} \quad (3.16)$$

The temperature-dependence of the effect of CO is shown graphically in Figure 3.16.

Figure 3.16. EFFECT OF TEMPERATURE ON SLOPE OF PERFORMANCE LOSS VS. CO CONCENTRATION

Sulfur Compounds. Advanced fuel processors operating on sulfur-containing fuels will produce H_2S that will enter the anode if not first removed. The sulfur tolerance has been studied on a fuel cell running on simulated reformer effluent containing 130 to 200 ppm H_2S , as shown in Figure 3.17.³³ The test was characterized by long periods of stable operation followed by rapid decay. The original performance could be restored by removing either CO or H_2S from the anode gas, indicating a synergistic effect, or by increasing the cell temperature from 375° to 400°F. The mechanism of H_2S -CO poisoning is not well understood. Post-test analysis of electrodes from shorter term cells showed no observable changes attributable to exposure to H_2S -containing anode gas. Work to broaden the understanding of the

Figure 3.17. EFFECT OF H_2S ON PHOSPHORIC ACID FUEL CELL PERFORMANCE³³

CO- H_2S interaction in the phosphoric acid fuel cell is continuing.

Nitrogen Compounds. Nitrogen will be present at the cathode of an air-consuming fuel cell, and nitrogen-containing hydrocarbon feedstocks will introduce nitrogen compounds (NH_3 , HCN , NO_x) into the anode. In addition, nitrogen compounds can result if nitrogen-free hydrocarbons are processed with air such as in autothermal reforming or coal gasification. The nitrogen in this case will be primarily molecular nitrogen, which acts as a diluent. Data on the interaction of nitrogen compounds other than ammonia have not been found in the literature.

Ammonia reacts with the phosphoric acid electrolyte to form ammonium dihydrogen phosphate (ADHP) according to —

The formation of the ADHP results in a performance loss, possibly by changing the conductivity of the acid³⁴ or by reducing the activity of the platinum by covering the active sites.^{35,36} The performance loss as a function of percent conversion of H_3PO_4 to ADHP is illustrated in Figure 3.18. Electrolyte conversion must be limited to less than about 0.2 mole percent to avoid unacceptable performance penalties. Diagnostic data on the cells of Figure 3.18

Figure 3.18. PERFORMANCE LOSS DUE TO AMMONIATION OF H_3PO_4 ³⁶

indicate that most of the performance loss occurred at the cathode. Figure 3.19 shows that 84% of the cathode activity is lost by only 1% conversion of the acid to ADHP.

Several long-term tests (up to 10,000 hours) have shown that the ADHP levels appear to reach a constant value significantly lower than predictions based on inlet ammonia concentrations. This observation, in conjunction with the fact that the performance was restored if the ammonia was removed from the feed (Figure 3.20), led to the hypothesis that the ammonium ion is oxidized at cell operating potential and temperature. Figure 3.21 confirms the ammonium ion oxidation premise by demonstrating the currents obtained at normal cell operating conditions.

Summary, Other Compounds. The foregoing considered the effect of carbon, sulfur, and nitrogen compounds on phosphoric acid fuel cell performance. Synergistic effects have not been discussed. Data for other possible impurities have not been reported but estimates of maximum allowable levels are summarized in Table 3.1.

Figure 3.19. RELATIVE CATHODE CATALYST ACTIVITY AS A FUNCTION OF PERCENT H_3PO_4 CONVERSION TO $(\text{NH}_4)_2\text{H}_2\text{PO}_4$ ³⁶

Figure 3.20. CELL ENDURANCE IN THE PRESENCE OF AMMONIA³⁶

Figure 3.21. POTENTIAL VS. AMMONIUM PHOSPHATE OXIDATION CURRENT³⁶

Table 3.1. ESTIMATED MAXIMUM ALLOWABLE IMPURITY LEVELS —
 PHOSPHORIC ACID FUEL CELLS^{16,37}

Impurity	Maximum Limit
CO ₂	diluent
CH ₄	diluent
N ₂	diluent
CO	Figure 3.11
H ₂ S, COS	100 ppm
C ₂ ⁺	100 ppm
Cl ⁻	1 ppm
NH ₃	1 ppm
Metal ions (Fe, Cu, etc.)	nil

Effect of Internal Resistance. The obtainable cell voltage is reduced by resistance to ionic conduction in the electrolyte and electronic conduction in the electrodes, current collectors, and interfaces. The magnitude of this loss is 15-20 mV/(100 mA/cm²).¹⁶ The sample calculations at the end of this chapter will use —

$$\Delta V_{iR} \text{ (mV)} = -0.20 i \text{ (mA/cm}^2\text{)} \quad (3.18)$$

Sample Calculations

This section will use the data and equations summarized in Table 3.2 to estimate the 4.8-MW phosphoric acid fuel cell power plant performance. The operating conditions for the baseline phosphoric acid fuel cell performance (Figure 3.9) differ from the approximate conditions of the 4.8-MW power plant operating on reformed natural gas (RNG) at 323 mA/cm² as shown in Table 3.3.

Table 3.2. SUMMARY OF PARAMETRIC DESIGN EQUATIONS FOR PHOSPHORIC ACID FUEL CELL

Parameter	Equation	Functionality	Comments
Temperature	3.4	$\Delta V_T \text{ (mV)} = 0.64 (T_2 - T_1) (^{\circ}\text{F})$	H ₂ Fuel
	3.5	$\Delta V_T \text{ (mV)} = 1.22 (T_2 - T_1) (^{\circ}\text{F})$	RM-1 Fuel
Pressure	3.10	$\Delta V_P \text{ (mV)} = 142 \log \frac{P_2}{P_1}$	
Oxidant	3.11	$\Delta V_{O_2} \text{ (mV)} = 103 \log \frac{(\bar{P}_{O_2})_2}{(\bar{P}_{O_2})_1}$	
Fuel	3.12	$\Delta V_{H_2} \text{ (mV)} = 77 \log \frac{(\bar{P}_{H_2})_2}{(\bar{P}_{H_2})_1}$	
CO	3.13	$\Delta V_{CO} \text{ (mV)} = -6.14 ((CO)_2 - (CO)_1) (\%)$	177°C
	3.14	$\Delta V_{CO} \text{ (mV)} = -3.54 ((CO)_2 - (CO)_1) (\%)$	190°C
	3.15	$\Delta V_{CO} \text{ (mV)} = -2.05 ((CO)_2 - (CO)_1) (\%)$	204°C
	3.16	$\Delta V_{CO} \text{ (mV)} = -1.3 ((CO)_2 - (CO)_1) (\%)$	218°C
Internal Resistance	3.18	$\Delta V_{iR} \text{ (mV)} = -0.2 i \text{ (mA/cm}^2\text{)}$	

Table 3.3. COMPARISON OF BASELINE AND PROJECTED 4.8-MW PERFORMANCE
AND EFFECT OF CONTRIBUTING FACTORS

Operating Variable	Baseline	4.8 MW	ΔV (mV)
Temperature, °C	175	190	+32.9
Pressure, psia	14.7	50	+75.5
Oxidant			-92.3
Composition, % O ₂	100	21 (air)	
Utilization, %	~0	70	
Fuel			-22.8
Composition, % H ₂	100	64 (RM-1)	
Utilization	~0	85	
Impurities, %			
CO	0	1.4	- 8.6
CO ₂	0	18.3	*
Internal Resistance, mV/(mA/cm ²)	-0.2	-0.2	0
Net Change, mV			-15.3

*The diluent effect is included in the effect of fuel composition and utilization.

Pressure. Use Figures 3.12 and 3.13 and Equation 3.10:

$$\Delta V_p \text{ (mV)} = 142 \log \frac{50}{14.7}$$

$$\Delta V_p = +75.5 \text{ mV}$$

Temperature. As mentioned previously, the operating temperature affects the allowable level of CO in the fuel. These two operating variables will be considered together. Their combined effect will be determined by two alternative paths yielding the same results:

- A. The first path reduces the 175°C performance because of the presence of 1.4% CO by Equation 3.13:

$$\Delta V_{CO} \text{ (mV)} = -6.14 \text{ mV (1.4)}$$

$$\Delta V_{CO} = -8.6 \text{ mV}$$

Then the temperature is increased through Equation 3.5, which includes the diminishing effect of CO:

$$\Delta V_T \text{ (mV)} = (1.22) (190-175) (9/5)$$

$$\Delta V_T = +32.9 \text{ mV}$$

The net effect is - ...

$$\Delta V_{T,CO} = 32.9 - 8.6 = +24.3 \text{ mV}$$

- B. The alternative approach evaluates the difference in loss caused by the presence of 1.4% CO at the different temperatures and then raises the temperature of the clean fuel cell:

$$\Delta V_{CO} = -8.6 \text{ mV at } 175^\circ\text{C}$$

$$\Delta V_{CO} = -5.0 \text{ mV at } 190^\circ\text{C}$$

Therefore, there is a net gain in performance of 3.6 mV.

The temperature gain is -

$$\Delta V_T = 0.64 (15) 9/5 = +17.3 \text{ mV}$$

And the total gain is -

$$\Delta V_{T,CO} = 17.3 + 3.6 = +20.9 \text{ mV}$$

Oxidant. The 4.8-MW fuel cell power plant will operate on air (21% O_2) at 70% oxygen utilization. Because most of the product water is removed at the cathode, the oxygen is diluted by 2 moles of H_2O for every mole of oxygen consumed. The inlet, exit, and average compositions are summarized in Table 3.4.

Table 3.4. COMPOSITION PROFILE OF OXIDANT AT 70% UTILIZATION

	<u>Inlet</u>	<u>Exit</u>	<u>Average</u>
N_2 , mol	0.79	0.79	0.79
O_2 , mol	0.21	0.063	0.1365
H_2O , mol	0	0.294	0.147
Total mol	1.0	1.147	1.0735
$(P_{O_2})_2$	0.21	0.055	0.127

The baseline case is for oxygen at low utilization so $(\bar{P}_{O_2})_1 = 1.0$. The loss because of the lower inlet oxygen concentration and high oxygen utilization is determined by Equation 3.11:

$$V_{O_2} = 103 \log \frac{0.127}{1.00} = -92.3 \text{ mV}$$

Fuel. The baseline cell operates on hydrogen at low utilization

so $(\bar{P}_{H_2})_1 = 1.0$. In contrast, the 4.8-MW fuel cell power plant operates on 64% hydrogen at 85% utilization.

The composition profile is summarized in Table 3.5.

Table 3.5. COMPOSITON PROFILE OF FUEL AT 85% UTILIZATION

	<u>Inlet</u>	<u>Exit</u>	<u>Average</u>
H ₂ , mol	0.64	0.096	0.368
Diluents, mol	0.36	0.36	0.36
Total mol	1.00	0.456	0.728
$(P_{H_2})_2$	0.64	0.211	0.505

Therefore, from Equation 3.12 -

$$\Delta V_{H_2} = 77 \log \frac{0.505}{1.00} = -22.8 \text{ mV}$$

Design Considerations. Analysis of the calculations shows that the increases obtained by increasing temperature and pressure are offset by using dilute oxidant and fuel gases at high utilizations and by the presence of CO in the fuel. The net effect is -15.3 mV, which indicates that the 4.8-MW fuel cell will operate at about the same level as the baseline H₂-O₂ fuel cell.

Further inspection reveals that the major loss is a result of the of air at high conversion. If the air utilization was decreased to 50% by pumping more air through the cathode, approximately 7 mV would be gained. The gain could be translated into an increase in current density to reduce capital costs or into an improvement in efficiency. However, the decreased oxidant utilization requires the pumping of additional air. The resolution of this question is not within the scope of this work, but the parametric performance equations will aid the systems engineer in tackling similar problems.

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Chapter 4. MOLTEN CARBONATE FUEL CELLS

Introduction

The molten carbonate fuel cell history has been presented in a number of sources¹⁻³ so only the significant advances of the last 10 years, shown in Figure 4.1, will be discussed.⁴

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Figure 4.1. MOLTEN CARBONATE PERFORMANCE HISTORY
ON RNG FUEL AT DESIGN VOLTAGE REQUIRED TO
ACHIEVE 7500 Btu/kWhr HEAT RATE⁴

1. From 1968 to 1972 the electrolyte was changed from a ternary ($\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3/\text{Na}_2\text{CO}_3$) to a binary ($\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3$) electrolyte, and higher surface area electrodes were used. These changes increased the initial performance, but rapid decay occurred because of sintering of the high surface area nickel anode.
2. The anode pore structure was stabilized by adding sintering inhibitors to the nickel (metals and metal oxides) to achieve the performance and endurance of the 1975 cell. This cell was thermally cycled without losing performance. Electrolyte was added to make up for evaporation, creepage, and corrosion losses, allowing operation of the cell for 15,000 hours.

3. The increased performance of the 1976 cell was the result of refinement of the anode structure (mean pore size, thickness, porosity, pore size distribution, etc.). The change in the slope of the decay curve around 3000 hours is typical of cells without electrolyte addition. Many current cells have an electrolyte reservoir, eliminating the need for periodic addition of electrolyte.
4. The improved performance of the 1977 cell, which almost meets design goals, resulted from improving the nickel cathode structure and using thinner electrolyte tiles to reduce iR losses.

Binary eutectic cells operate at 650 to 700°C; ternary eutectic systems can potentially operate at 500 to 550°C. To achieve a 7500 Btu/kWhr heat rate, the Energy Conversion Alternatives Study (ECAS)^{5,6} has specified that a molten carbonate fuel cell, integrated with an air-blown coal gasifier having a product composition of 16 mole percent H₂, 21 mole percent CO, 9.5 mole percent H₂O, 6 mole percent CO₂, and 46 mole percent N₂, must have a design point of 150 A/ft² at 0.85 volts/cell (110 A/ft² has been demonstrated).

Estimates show molten carbonate fuel cell systems are about 45% efficient when operating on petroleum liquids without a bottoming cycle⁷ and possibly over 90% efficient with cogeneration⁸. The oxidant gas must contain O₂ and CO₂, and the fuel gas is a mixture of H₂, CO₂, CO, CH₄, H₂O, and N₂ from the fuel processing subsystem. The heat is removed by the cathode gas. Cells have been successfully operated at pressures as high as 10 atmospheres.

The Electric Power Research Institute (EPRI) and the U. S. Department of Energy (DOE) are funding molten carbonate fuel cell research, development, and engineering at General Electric Company (GE), United Technologies Corporation (UTC), Energy Research Corporation (ERC), and the Institute of Gas Technology (IGT).^{6,9} The work concentrates on electrolyte management, tolerance to sulfur and other impurities, engineering scale-up (cell design and mass production of components), and systems analysis.

Although molten carbonate fuel cell technology has made impressive advances, a number of questions concerning cell performance and life remain:

1. The sulfur and chlorine tolerance of the cell is only a few parts per million; the tolerance to other impurities has not been defined.

2. Electrolyte losses result in decreases in electrolyte tile strength and bubble pressure, increased tile porosity, and diffusion of reactants across the tile causing decreases in cell voltage and efficiency. A partial solution to the evaporation problem is the incorporation of a reservoir with enough electrolyte to achieve the design life of 40,000 hours. The electrolyte may not be evenly distributed, however, and redistribution can cause performance loss. In addition, new tile and electrode structures and materials that inhibit carbonate evaporation are being sought.¹⁰
3. Electrolyte creepage and corrosion result in failure of the wet-seal and leakage of reactants out of the cell. The wet-seal is now protected by aluminizing¹¹ although it is uncertain whether this approach will be effective for 40,000 hours.¹⁰
4. Effects of structural changes in the electrolyte support (LiAlO_2) on cell performance have not been defined.
5. Cost-effective cell components (tile, electrodes, and hardware) and manufacturing techniques must be identified.

A system problem arises from the production of CO_2 at the anode and its consumption at the cathode. System efficiency requires transfer of the CO_2 from the anode to the cathode. Current transfer technology involves catalytic combustion of anode exhaust (CO , H_2 , CH_4 , H_2O , N_2 , and CO_2) to H_2O and CO_2 , mixing this stream with air and feeding it to the cathode. For this system to be economical, the anode must be run at 90% H_2 utilization, but such high utilization results in increased Nernst losses (Equation 2.8). More desirable would be a physical separation of the CO_2 from the rest of the anode exhaust, which can be recycled to the anode. To date, studies on ways to exchange the CO_2 are not complete.

Basic Concepts and Cell Components

A schematic of one repeating element in a stack of molten carbonate fuel cells is shown in Figure 4.2. The electrolyte tile, described below, is held in place between the two stainless-steel cell housings that form the anode and cathode cavities. The holding force maintains low-resistance contacts between the electrodes and the stainless steel current collectors and causes the housings to bite into the electrolyte tile, forming a wet-seal that prevents leakage of fuel from the anode chamber and oxidant from the cathode chamber. In a stack of several cells (series connection)

the cell separator must be able to withstand both the high-humidity reducing environment of the anode and the oxidizing environment of the cathode.

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Figure 4.2. MOLTEN CARBONATE FUEL CELL SCHEMATIC⁸

Carbon dioxide and oxygen diffuse from the bulk gas through the pores of the cathode to a reaction site at the electrode/electrolyte interface where they react according to -

The cathode is 70% to 80% porous NiO with a mean pore size of about $10\mu\text{m}$,⁸ formed by the oxidation of sintered nickel at operating temperatures.

The CO_3^{2-} is conducted through the liquid electrolyte, a mixture of alkali carbonates (commonly binary: 62 or 50 mole percent Li_2CO_3 , balance K_2CO_3) molten at cell operating temperatures. The electrolyte is held in place by inert LiAlO_2 particles to form the electrolyte tile (40 weight percent inert, 60 weight percent electrolyte). Because iR loss is a function of tile thickness, tiles are kept as thin as possible, 1.0 to 2.5 mm in current cells.

At the anode/electrolyte interface, carbonate ions react according to Reaction 4.2, and the external circuit is completed:

The anode is sintered nickel about 60% to 70% porous with a 5 μm mean pore size.⁸ The product H_2O and CO_2 diffuse out of the cell through the porous anode into the gas stream. The overall reaction in the molten carbonate fuel cell is —

Molten Carbonate Fuel Cell Performance

General Considerations. The performance of a typical 1977 molten carbonate fuel cell operating at 0.785 volt was shown in Figure 4.1. For a cell operating on reformed natural gas fuel at 75% total H_2 utilization and on an oxidant mixture of 70% air and 30% CO_2 at 50% CO_2 utilization, at 200 mA/cm^2 , losses are approximately 68 mV ohmic and 260 mV polarization losses.⁸ Of course, these losses depend on fuel and oxidant concentrations and utilizations and other fuel cell operating variables. It is difficult to separate the effects when relating cell performance to a single operating parameter.

For example, at the operating temperature 650°C, changes in temperature and pressure cause changes in the reactant gas composition through the following chemical equilibria:

Although the following analyses take this problem into account, results should still be considered directional.

The remainder of this chapter considers the effect of operating parameters on cell performance through data, derived equations, and an illustration of the use of this information to predict cell behavior at different conditions. For the purposes of this discussion, molten carbonate fuel cell performance at atmospheric pressure and 650°C, using a cell operating on simulated reformed methane fuel* at low utilization and on an oxidant consisting of 67 mole percent

* The composition is 60 mol % H_2 , 10 mol % CO , 7.4 mol % CO_2 , and 22.6 mol % H_2O . Pure hydrogen data are unavailable because the absence of CO_2 in the fuel gas causes compositional changes in the electrolyte.¹²

CO₂ and 33 mole percent O₂* at low utilization, will be considered as baseline. The electrolyte tile composition is 40 weight percent inert LiAlO₂ particles to provide structural integrity and 60 weight percent binary eutectic mixture of Li₂CO₃ and K₂CO₃ as the electrolyte.** The baseline performance is shown in Figure 4.3.¹²

Figure 4.3. BASELINE MOLTEN CARBONATE FUEL CELL PERFORMANCE AT 1 atm, 650°C, 67 mol % CO₂/33 mol % O₂ OXIDANT AT 15% UTILIZATION, 60 mol % H₂/10 mol % CO/7.4 mol % CO₂/22.6 mol % H₂O FUEL AT 25% UTILIZATION

Design Considerations. The factors involved in choosing the operating design point are the same as for the phosphoric acid fuel cell: size, cost, heat removal, and voltage and power constraints. Gas composition and utilization, temperature, pressure, and impurity concentrations define the performance curve. For the baseline cell operating at 100 mA/cm² (0.977 volt), 91.5 W/ft² are generated, and 1 kilowatt requires 11 ft². At 200 mA/cm²

* This composition results in equal utilization of CO₂ and O₂ by Equation 4.1 and has no diluents.

** The eutectic composition is approximately 47 weight % Li₂CO₃ and 53 weight % K₂CO₃.

(0.895 volt), 168 W/ft² are produced, and 6 ft² are required to produce 1 kilowatt. Molten carbonate fuel cells operating on leaner fuel and oxidant gases are expected to generate about 0.75 volt/cell at 160 mA/cm².

Effect of Temperature. As the molten carbonate fuel cell operating temperature is increased through its range of 600 to 700°C, hydrogen is consumed for a gas in water gas shift equilibrium because the equilibrium constant K_p is proportional to temperature:

$$K_p = \frac{P_{\text{CO}} P_{\text{H}_2\text{O}}}{P_{\text{H}_2} P_{\text{CO}_2}} \quad (4.8)$$

Thus, the middle term of the Nernst equation decreases. Because E_o also decreases with increasing temperature, the open-circuit potential decreases as temperature increases:

$$E = E^o + \frac{RT}{2F} \ln \left(\frac{P_{\text{H}_2}}{(P_{\text{CO}_2})_a P_{\text{H}_2\text{O}}} \right) + \frac{RT}{2F} \ln (P_{\text{CO}_2})_c (P_{\text{O}_2})^{1/2} \quad (4.9)$$

However, ohmic, activation, and concentration polarizations all decrease, more than offsetting the decrease in the open-circuit potential. Figure 4.4 is representative of the resulting net increase in cell performance and also shows that the anode is only slightly affected by changes in cell temperature. Data for the fuel compositions listed in Table 4.1 are similar.¹² Because all these cases exhibit similar behavior, a composite curve was constructed and the voltage gains determined (Figure 4.5). The data are represented by —

$$\Delta V_T \text{ (mV)} = 1.5 (T_2 - T_1)^\circ\text{C for } 600^\circ \text{ to } 650^\circ\text{C} \quad (4.10)$$

$$\Delta V_T \text{ (mV)} = 0.26 (T_2 - T_1)^\circ\text{C for } 650^\circ \text{ to } 700^\circ\text{C} \quad (4.11)$$

In conclusion, the diminishing gains in cell performance above 650°C, coupled with increased electrolyte loss resulting from evaporation⁴ and increased component corrosion,¹³ point to an optimum operating temperature of 650°C for molten carbonate fuel cells with an electrolyte tile composed of 40% LiAlO₂, 28% K₂CO₃, and 32% LiCO₃ by weight.

Figure 4.4. EFFECT OF TEMPERATURE ON CELL, ANODE, AND CATHODE PERFORMANCE AT 1 atm, 650° C, 200 mA/cm², AND LOW UTILIZATIONS

Table 4.1. SIMULATED FUEL PROCESSOR PRODUCT GAS COMPOSITIONS¹²

Fuel Treatment	Product Gas Composition, mol % at 650°C					
	CO	CO ₂	H ₂	H ₂ O	CH ₄	N ₂
Methane Steam Reforming	10.0	7.4	60.0	22.6	--	--
Naphtha Steam Reforming	10.7	10.4	52.7	26.2	0.2	--
Partial Oxidation of Heavy Oils*	25.1	14.5	45.1	13.3	0.2	0.2
Air-Blown Low-Btu Coal Gasification*	14.0	11.4	18.6	7.8	2.4	45.8
Advanced Coal Gasification/Steam Reforming	29.1	14.0	44.3	10.9	1.6	0.1

* Additional water added to prevent carbon formation.

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Figure 4.5. EFFECT OF TEMPERATURE ON MOLTEN CARBONATE FUEL CELL PERFORMANCE
AT 1 atm, 200 mA/cm², 70 mol % AIR/30 mol % CO₂ OXIDANT AT 50%
UTILIZATION, 75% FUEL UTILIZATION

Effect of Pressure. Cell performance increases with pressure because of increased reactant partial pressures (Equation 4.9), increased reactant solubilities, and increased mass transport rates. Analysis of cell behavior must consider the chemical equilibria –

Higher pressures tend to favor carbon formation and consumption of CO and H₂ fuel.^{15,16} The addition of water controls carbon formation, because it reduces the amount of CO (by Equation 4.14) and methanation (by forcing Equation 4.13 toward H₂).¹²

Figure 4.6 shows the effect of pressure on cell performance. As shown

in Table 4.2, the fuel gas was humidified to inhibit carbon and methane formation. The equilibrium compositions can be obtained by adjusting the compositions in Table 4.1 according to Equations 4.13 and 4.14 and the dew point.

Table 4.2. FUEL GAS DEW POINT FOR DATA IN FIGURE 4.6

Fuel	Pressure, atm	Dew Point, °F
Simulated Air-Blown Low-Btu Coal Gas	1	164
	5	260
	10	300
Simulated Reformed Methane	1	145
	5	190

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Figure 4.6. EFFECT OF PRESSURE ON MOLTEN CARBONATE FUEL CELL PERFORMANCE AT 650°C, 160 mA/cm², 70 mol % AIR/30% mol CO₂ OXIDANT AT 50% UTILIZATION, 75% FUEL UTILIZATION¹⁴

For the product gas of an air-blown low-Btu coal gasifier, the relationship between changes in cell performance and operating pressure in atmospheres is -

$$\Delta V_p \text{ (mV)} = 70 \log \frac{P_2}{P_1} \quad (4.15)$$

and for reformed methane, it is -

$$\Delta V_p \text{ (mV)} = 83 \log \frac{P_2}{P_1} \quad (4.16)$$

Because these two cases represent a wide range of gas composition, other fuels should obey the average relationship:

$$\Delta V_p \text{ (mV)} = 76.5 \log \frac{P_2}{P_1} \quad (4.17)$$

Optimization of cell operating pressure must also consider the strict pressure control required to prevent wet-seal and tile failure, compatibility with the fuel processor pressure, and the possible corrosion of cell components at the resulting higher voltages. Molten carbonate fuel cells are expected to operate between 1 and 10 atmospheres.

Effect of Reactant Concentration and Utilization. Although considerable data have been published, the effect of reactant partial pressure on molten carbonate fuel cell performance is difficult to analyze because of the participation of CO at the anode via the water-gas shift reaction (Equation 4.14) and because of consumption of CO₂ and O₂ at the cathode (Equation 4.1). Figure 4.7 is representative of data published on reactant utilization.^{7,12,17} The data indicate that increasing oxidant utilization causes less cell potential loss than increases in fuel utilization. Once again a compromise is required, because operating at low fuel utilization increases cell performance but decreases the current efficiency. (See Chapter 5.) Current molten carbonate fuel cells commonly run at 75 to 85% fuel utilization and 50% oxidant utilization.

Oxidant. According to the Nernst equation, cell performance should be related to oxidant (CO₂, O₂) partial pressure by $\ln [(P_{CO_2})(P_{O_2})^{1/2}]$. The range of conditions listed in Table 4.3 have been used to define this functionality at 1 atmosphere total pressure, as shown in Figure 4.8.

Figure 4.7. EFFECT OF REACTANT UTILIZATION ON MOLTEN CARBONATE FUEL CELL PERFORMANCE AT 1 atm, 650°C, 160 mA/cm², 70 mol % AIR/30 mol % CO₂ OXIDANT, SIMULATED REFORMED METHANE FUEL¹²

Figure 4.8. EFFECT OF OXIDANT PARTIAL PRESSURE ON MOLTEN CARBONATE FUEL CELL PERFORMANCE AT 1 atm TOTAL PRESSURE, 650°C, 160 mA/cm²

Table 4.3. SUMMARY OF DATA IN FIGURE 4.8

	OXIDANT					FUEL
	COMPOSITION		UTILIZATION, %		$\frac{P_{CO_2}}{P_{O_2}}$	
	CO ₂	O ₂	CO ₂	O ₂		
▲	0.67	0.33	25-75	AVG	2	SIMULATED REFORMED METHANE AT 75% UTILIZATION
□	0.30	0.15	15	15	2	
▣	0.30	0.15	25	25	2	
■	0.30	0.15	50	50	2	
▤	0.30	0.15	75	75	2	
○	0.30	0.05	25	69	6	
●	0.30	0.08	25	48	3.75	
◐	0.30	0.12	25	33	2.5	
◑	0.30	0.15	25	25	2	
◒	0.30	0.20	25	19	1.5	
◓	0.30	0.12	50	65	2.5	
◔	0.30	0.15	50	50	2	SIMULATED REFORMED NAPHTHA AT 75% UTILIZATION
◕	0.30	0.20	50	38	1.5	
●	0.125	0.17	25	68	0.74	
■	0.21	0.14	50	68	1.5	SIMULATED AIR-BLOWN COAL GAS AT 75% UTILIZATION

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At low oxidant partial pressures, the gains are caused by diminishing mass transfer effects in addition to the Nernst gains. As the partial pressures increase further, mass transfer losses become negligible and the gains become governed by Nernst effects, that is, the slope approximates 2.3 RT/2F. The mathematical representation of the data in terms of atmospheres is —

$$\Delta V_{ox} \text{ (mV)} = 250 \log \frac{(\bar{P}_{CO_2} \bar{P}_{O_2}^{1/2})_2}{(\bar{P}_{CO_2} \bar{P}_{O_2}^{1/2})_1} \quad (4.18)$$

$$\text{for } 0.04 \leq \bar{P}_{CO_2} \bar{P}_{O_2}^{1/2} \leq 0.11$$

$$V_{ox}(\text{mV}) = 99 \log \frac{(\bar{P}_{CO_2} \bar{P}_{O_2}^{1/2})_2}{(\bar{P}_{CO_2} \bar{P}_{O_2}^{1/2})_1} \quad (4.19)$$

$$\text{for } 0.11 \leq \bar{P}_{CO_2} \bar{P}_{O_2}^{1/2} \leq 0.38$$

Equations 4.18 and 4.19 should be used cautiously when the oxidant composition deviates significantly from the stoichiometric ratio of $P_{CO_2}/P_{O_2} = 2$. In such cases, a low partial pressure of either CO_2 or O_2 could result in severe concentration polarization, even though $\bar{P}_{CO_2} \bar{P}_{O_2}^{1/2}$ is within the range of Figure 4.8.

Fuel. Based on the data in Figure 4.7 and Table 4.4 and the assumption that the anode gas is always in shift equilibrium, the effect of the average hydrogen partial pressure in atmospheres is shown in Figure 4.9 and represented by —

$$\Delta V_F(\text{mV}) = 173 \log \frac{[\bar{P}_{H_2}/\bar{P}_{CO_2} \bar{P}_{H_2O}]_2}{[\bar{P}_{H_2}/\bar{P}_{CO_2} \bar{P}_{H_2O}]_1} \quad (4.20)$$

Figure 4.9. EFFECT OF FUEL PARTIAL PRESSURE ON MOLTEN CARBONATE FUEL CELL PERFORMANCE AT 1 atm TOTAL PRESSURE, 650°C, 160 ma/cm²

Table 4.4. APPLICABLE RANGE OF DATA FOR EQUATION 4.20

Composition	Fuel	Oxidant		P_{CO_2}/P_{O_2}	Current Density, mA/cm ²
	Utilization, %	Composition, mol %	Utilization, %		
Table 4.1	25 to 75	70 Air/30 CO ₂ 33 O ₂ /67 CO ₂	15 to 75	2	80 to 200

Effects of Impurities. Many discussions have centered on integrating the molten carbonate fuel cell with advanced fuel processors because of its tolerance to CO at the anode and CO₂ at the cathode. Other compounds likely to be present in the effluent of advanced fuel processors include NH₃, NO_x, SO_x, H₂S and COS. As with the acid system, possible synergistic effects will not be considered.

Carbon. Solid carbon can form in the cell or in system plumbing if thermodynamically favored by Equation 4.12. The addition of water prevents carbon deposition by reducing CO concentrations through the water-gas shift reaction.

Carbon dioxide present in the anode feed and produced at the anode acts only as a diluent, reducing the hydrogen partial pressure. In fact, a small amount of CO₂ is required to maintain the LiCO₃/K₂CO₃ electrolyte composition.¹² Of course, CO₂ is required at the cathode.

Methane at the anode can be reformed to hydrogen by adding sufficient water to the fuel gas.¹⁴ If the methane is not reformed, fuel cell efficiency will decrease; energy in the methane must be recovered elsewhere in the system to maintain the total system efficiency.

Although carbon monoxide dilutes the hydrogen, it is also consumed indirectly through the water-gas shift reaction.

Sulfur. Sulfur species affect cell operation in many ways: electrodes may be covered by adsorbed sulfur species at low sulfur levels or sulfided when $\log \frac{P_{H_2}}{P_{H_2S}} \leq 2.74$;¹⁸ carbonate may react with the sulfur species, affecting its suitability as an electrolyte; and the anode hardware will corrode more severely in the presence of sulfur. Also, CO₂ formed at the anode must be transferred to the cathode for efficient operation of the system. If it

is transferred by burning anode exhaust containing H_2S , then some SO_x will be present at the cathode, primarily in the form of SO_2 .

Cells with nickel anodes exhibit an immediate performance reduction and continuous further decay when exposed to as little as 10 ppm H_2S . Cobalt anodes also suffer an initial performance loss but are more resistant to further decay. The kinetics of the anode reaction are unaffected by sulfur levels up to 50 ppm so the loss may be caused by changes in the electrolyte or structural changes in the electrode.¹⁹

Sulfur dioxide has little effect on the cathode. Instead, the sulfur dioxide absorbs into the electrolyte, reacts with it, and diffuses through the electrolyte to the anode, where it emerges as H_2S (and trace COS and SO_2), possibly by the following sequence:¹⁹

The overall anode reaction is -

Nitrogen. Molecular nitrogen at the anode or cathode acts as a diluent. The presence of NH_3 and NO_x is also expected at both anode and cathode, but no data on the effect of these impurities on cell performance are available, although the $\text{K}_2\text{CO}_3/\text{Li}_2\text{CO}_3/\text{Na}_2\text{CO}_3$ eutectic is known to absorb NO .²⁰

Chlorine. Recent short-term data^{21,22} indicate that anode performance is only slightly affected after 400 hours on a fuel gas containing 100 ppm HCl , but cathode performance is catastrophically affected by 100 ppm HCl in the oxidant gas. Stable cathode performance with 10 ppm HCl has been demonstrated for 120 hours. Although long-term trends have not been established, it appears that the decay results from both hardware corrosion and chlorination of the electrolyte.

Summary, Other Compounds. Discussions on the effects of carbon, sulfur, and nitrogen compounds on molten carbonate fuel cell performance did not consider synergistic effects. Table 4.5 summarizes estimates of maximum allowable impurity levels.

Table 4.5. ESTIMATED MAXIMUM ALLOWABLE IMPURITY LEVELS — MOLTEN CARBONATE FUEL CELLS

<u>Impurity</u>	<u>Maximum Limit</u>
CO ₂	diluent
CH ₄	diluent/fuel
CO	fuel
N ₂	diluent
H ₂ S, SO ₂ , COS	<1 ppm
C ₂ ⁺	unknown*
HCl (anode)	100 ppm
HCl (cathode)	10 ppm
NH ₃ , NO _x	unknown*
Metal ions (Fe, Cu, etc.)	unknown*

Effect of Internal Resistance. Resistance to ionic (CO₃⁼) conduction through the electrolyte tile and to electronic conduction through electrodes, current collectors, and interfaces results in voltage reductions of 35 to 50 mV/(100 mA/cm²).¹² Thinner components being developed will reduce this voltage loss.²³ The sample calculations below will use —

$$\Delta V_{iR} \text{ (mV)} = - 0.4 i \text{ (mA/cm}^2\text{)} \quad (4.25)$$

Sample Calculations

The data and equations summarized in Table 4.6 will be used to estimate the performance difference between the baseline cell and a cell operating on the product gas from an air-blown coal gasifier. The oxidant gas will be obtained by burning the anode effluent with excess air.⁵ Table 4.7 lists the differences in operating conditions and resulting performance changes.

Temperature. Because the operating temperature is above 650°C, use Equation 4.11:

$$\Delta V_T \text{ (mV)} = 0.26 \text{ (675-650)}$$

$$\Delta V_T \text{ (mV)} = +6.3$$

* Although data are not available, tolerance is expected to be low.

Table 4.6. SUMMARY OF PARAMETRIC DESIGN EQUATIONS FOR MOLTEN CARBONATE FUEL CELL

Parameter	Equation No.	Functionality	Comments
Temperature	4.10	$\Delta V_T(\text{mV}) = 1.5 (T_2 - T_1)^\circ\text{C}$	600° - 650°C
	4.11	$\Delta V_T(\text{mV}) = 0.26 (T_2 - T_1)^\circ\text{C}$	650° - 700°C
Pressure	4.17	$\Delta V_p(\text{mV}) = 76.5 \log \frac{P_2}{P_1}$	
Oxidant	4.18	$\Delta V_{ox}(\text{mV}) = 250 \log \frac{[\bar{P}_{CO_2} \bar{P}_{O_2}^{1/2}]_2}{[\bar{P}_{CO_2} \bar{P}_{O_2}^{1/2}]_1}$	$0.04 \leq \bar{P}_{CO_2} \bar{P}_{O_2}^{1/2} \leq 0.11 \text{ atm}^{3/2}$ Table 4.3
	4.19	$\Delta V_{ox}(\text{mV}) = 99 \log \frac{[\bar{P}_{CO_2} \bar{P}_{O_2}^{1/2}]_2}{[\bar{P}_{CO_2} \bar{P}_{O_2}^{1/2}]_1}$	$0.11 \leq \bar{P}_{CO_2} \bar{P}_{O_2}^{1/2} \leq 0.38 \text{ atm}^{3/2}$ Table 4.4
Fuel	4.20	$\Delta V_F(\text{mV}) = 173 \log \frac{[\bar{P}_{H_2} / \bar{P}_{CO_2} \bar{P}_{H_2O}]_2}{[\bar{P}_{H_2} / \bar{P}_{CO_2} \bar{P}_{H_2O}]_1}$	Table 4.4
Internal Resistance	4.25	$\Delta V_{iR}(\text{mV}) = -0.4 i(\text{mA}/\text{cm}^2)$	

Table 4.7. COMPARISON OF BASELINE AND CANDIDATE MOLTEN CARBONATE FUEL CELL PERFORMANCE AND EFFECT OF CONTRIBUTING FACTORS

<u>Operating Variable</u>	<u>Baseline</u>	<u>Candidate</u>	<u>$\Delta V(\text{mV})$</u>
Temperature, °C	650	675	+6.3
Pressure, atm	1	10	+76.5
Oxidant, mol %			-142
CO ₂	67	20.5	
O ₂	33	14.0	
Utilization	15	50.0	
Fuel, mol %			-106
H ₂	60.0	18.6	
CO	10.0	14.0	
CO ₂	7.4	11.4	
H ₂ O	22.6	7.8	
N ₂ + CH ₄	0	48.2	
Utilization	25.0	75.0	
Internal Resistance, mV/(mA/cm ²)	-0.4	-0.4	0
Total Change, mV			-165

Fuel. To use Equation 4.20, calculate the average partial pressures of CO₂, H₂O, and H₂ at the anode. The procedure used in this example is —

1. Determine the equilibrium inlet composition.
2. Assume the moles of hydrogen consumed and increase the moles of CO₂ and H₂O stoichiometrically to determine the initial exit partial pressures.
3. Check the assumed exit composition for shift equilibrium:

$$K_p = \frac{P_{\text{CO}} P_{\text{H}_2\text{O}}}{P_{\text{CO}_2} P_{\text{H}_2}} \quad (4.8)$$

If the exit gas is not in shift equilibrium, equilibrate by —

$$K_p = \frac{(P_{\text{CO}} + X) (P_{\text{H}_2\text{O}} + X)}{(P_{\text{CO}_2} - X) (P_{\text{H}_2} - X)} \quad (4.26)$$

4. Calculate the number of moles of H_2 from the equilibrated partial pressure and the total moles.
5. Check the utilization by —

$$U_{H_2} = \frac{(\text{moles } H_2)_{\text{in}} - (\text{moles } H_2)_{\text{out}}}{(\text{moles } H_2)_{\text{in}}} \quad (4.27)$$

6. If the utilization is not that desired, adjust the moles of hydrogen consumed and repeat the procedure until the desired utilization is achieved.

The results of the procedure for the baseline case of reformed methane at 25% utilization are summarized in Table 4.8. The following calculations illustrate these results in detail. The number of moles of hydrogen at the fuel cell exit is assumed to be 0.47. Therefore —

$$H_2 \text{ consumed} = 0.60 - 0.47 = 0.13 \text{ moles}$$

$$\text{exit } CO_2 = 0.074 + 0.13 = 0.204 \text{ moles}$$

$$\text{exit } H_2O = 0.226 + 0.13 = 0.356 \text{ moles}$$

$$\text{total exit} = 0.47 + 0.204 + 0.356 + 0.100 = 1.13 \text{ moles}$$

and the exit partial pressures are —

$$(P_{H_2})_{\text{out}} = \frac{0.470}{1.130} = 0.416$$

$$(P_{CO_2})_{\text{out}} = \frac{0.204}{1.130} = 0.181$$

$$(P_{CO})_{\text{out}} = \frac{0.100}{1.130} + 0.088$$

$$(P_{H_2O})_{\text{out}} = \frac{0.356}{1.130} = 0.315$$

The equilibrium constant at $650^\circ C$ is —

$$K_p = 0.509 \neq \frac{(0.088)(0.315)}{(0.416)(0.181)} = 0.401$$

The gas is equilibrated by —

$$0.509 = \frac{(0.088 + X)(0.315 + X)}{(0.416 - X)(0.181 - X)} \quad (4.28)$$

$$0.491X^2 + 0.707X - 0.0105 = 0 \quad (4.29)$$

$$X = 0.0145$$

Table 4.8. COMPOSITION PROFILE — REFORMED METHANE AT 25% UTILIZATION

	$(P_i)_{in}$	Assumed Moles out	$(P_i)_{out}$	$(P_i)_{out, eq}$	$(P_i)_{ave, eq}$	Equilibrium Exit Moles
H ₂	0.600	0.47	0.416	0.402	0.500	0.454
CO ₂	0.074	0.204	0.181	0.166	0.120	0.188
CO	0.100	0.100	0.088	0.102	0.101	0.115
H ₂ O	0.226	0.356	0.315	0.329	0.278	0.372
Total	1.000	1.130	1.000	0.999	0.999	1.129

Table 4.9. COMPOSITION PROFILE — AIR-BLOWN COAL GAS AT 75% UTILIZATION

	$(P_i)_{in, eq}$	Assumed Moles out	$(P_i)_{out}$	$(P_i)_{out, eq}$	$(P_i)_{ave, eq}$	Equilibrium Exit Moles
H ₂	0.183	-0.045	-0.037	0.036	0.109	0.044
CO ₂	0.111	0.338	0.275	0.348	0.229	0.427
CO	0.144	0.144	0.117	0.044	0.094	0.054
H ₂ O	0.082	0.309	0.252	0.179	0.130	0.220
Other	0.482	0.482	0.393	0.393	0.438	0.393
Total	1.002	1.228	1.000	1.000	1.000	1.138

The equilibrium exit partial pressures are -

$$(P_{H_2})_{out, eq} = 0.416 - 0.0145 = 0.402$$

$$(P_{CO_2})_{out, eq} = 0.166 - 0.0145 = 0.166$$

$$(P_{CO})_{out, eq} = 0.088 + 0.0145 = 0.102$$

$$(P_{H_2O})_{out, eq} = 0.315 + 0.0145 = 0.329$$

and

$$\text{equilibrium exit } H_2 = (0.402)(1.13) = 0.454 \text{ moles.}$$

The hydrogen utilization is -

$$U_{H_2} = \left(\frac{0.60 - 0.454}{0.60} \right) 100 = 24.3\%$$

The target utilization of 25% has been achieved. The average equilibrium partial pressures are -

$$(P_{H_2})_{ave, eq} = \frac{.60 + .402}{2} = 0.50$$

$$(P_{CO_2})_{ave, eq} = \frac{0.074 + 0.166}{2} = 0.12$$

$$(P_{CO})_{ave, eq} = \frac{0.100 + 0.102}{2} = 0.101$$

$$(P_{H_2O})_{ave, eq} = \frac{0.226 + 0.329}{2} = 0.278$$

Results of the determination of the average component partial pressures for the cell operating at 675°C ($K_p = 0.58$) on product gas from an air-blown coal gasifier and 75% hydrogen utilization are summarized in Table 4.9. Note that the inlet gas has been equilibrated at 675°C. The target hydrogen utilization has been achieved:

$$U_{H_2} = \left(\frac{0.183 - 0.044}{0.183} \right) (100) = 76\%$$

The voltage change caused by the inlet fuel composition and hydrogen utilization is obtained by substituting the average H_2 , CO_2 and H_2O partial pressures from Tables 4.8 and 4.9 into Equation 4.20:

$$\Delta V_F = 173 \log \left[\frac{0.109 / (0.229)(0.130)}{0.50 / (0.12)(0.278)} \right]$$

$$\Delta V_F = -106 \text{ mV}$$

Oxidant. To use Equations 4.18 and 4.19, determine average CO₂ and O₂ partial pressures. For the baseline cell operating on 67 mole % CO₂ and 33 mole % O₂, partial pressures are constant because there are no inerts to cause dilution as the reactants are consumed. Therefore —

$$(\bar{P}_{\text{CO}_2} \bar{P}_{\text{O}_2}^{1/2})_1 = (0.67)(0.33)^{1/2} = 0.385$$

The candidate operating conditions involve nitrogen at the cathode, so the reactants are diluted as they are consumed. Therefore, determine a concentration profile as summarized in Table 4.10.

Table 4.10. COMPOSITION PROFILE OF OXIDANT AT 50% UTILIZATION

	<u>Moles in</u>	<u>Moles out</u>	<u>(P_i)_{out}, atm</u>	<u>(P_i)_{ave}, atm</u>
CO ₂	0.205	0.065	0.082	0.144
O ₂	0.140	0.070	0.089	0.115
N ₂	0.655	0.655	0.829	0.742
Total	1.000	0.790	1.000	1.001

Thus,

$$(\bar{P}_{\text{CO}_2} \bar{P}_{\text{O}_2}^{1/2}) = (0.144)(0.115)^{1/2} = 0.049$$

and, because the range of partial pressures includes both regions of Figure 4.8,

$$\Delta V_{\text{ox}} = 250 \log \frac{0.049}{0.110} + 99 \log \frac{0.110}{0.385}$$

$$\Delta V_{\text{ox}} = -142 \text{ mV}$$

Pressure. The increase in cell performance obtained by increasing operating pressure from 1 to 10 atmospheres is determined by Equation 4.17:

$$\Delta V_p = 76.5 \log \frac{10}{1}$$

$$\Delta V_p = +76.5 \text{ mV}$$

Design Considerations. The gains realized by increasing cell operating temperature and pressure are significantly less than the losses resulting from operation on leaner oxidant and fuel gases at high utilizations. In fact, the gain of only 6 mV does not warrant increasing the temperature from 650° to 675°C. Most of the loss is a result of oxidant partial pressures and could be eliminated by using an inert free gas. This requires an oxygen plant, adding cost and complexity to the molten carbonate fuel cell system. Another option is to pump more oxidant through the cathode to decrease the oxidant utilization to 25%. This improves cell performance by about 29 mV and might also provide a means of cooling the cell.

Operating on rich fuels at lower utilization will also be an improvement. However, the fuel cell efficiency will suffer at low utilization and, unless the fuel is recovered, the fuel cell system efficiency will be adversely affected.

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CHAPTER 5. FUEL CELL EFFICIENCY AND HEAT BALANCE

Introduction

A fuel cell converts chemical energy directly into electrical energy without the losses that result from the friction of moving parts, Carnot limitations, and gas expansion. Nevertheless there are inefficiencies in a fuel cell; for example, fuel cell utilization and electronic and ionic conduction resistance through components and at contact points are less than 100%, as discussed in Chapter 2. This chapter will discuss how to determine the efficiency of a fuel cell under realistic operating conditions and will develop the necessary equations to be applied to actual fuel cell data.

Fuel Cell Efficiency

In the following sections, the efficiency of converting gaseous fuels to d-c power in a fuel cell will be described in terms of thermodynamic, voltage, and current efficiencies.¹⁻⁴ In addition, the efficiency equation will be generalized to account for the presence of conventionally combustible species that do not react electrochemically, such as methane.

Thermodynamic Efficiency. The overall reaction of a fuel cell operating on air and on hydrogen from a hydrocarbon fuel processor is —

The thermodynamic efficiency is defined based on the relationship

$$\Delta G_r = \Delta H_r - T\Delta S_r \quad (5.2)$$

where the enthalpy change of Equation 5.1, ΔH_r , is the maximum amount of heat energy that can be produced isothermally and isostatically. The Gibbs free energy change, ΔG_r , is the maximum amount of energy available for conversion to electricity, and $T\Delta S_r$ is the minimum amount of heat produced. Therefore the thermodynamic or maximum efficiency is —

$$\epsilon_{\text{Th}} \equiv \frac{\Delta G_r}{\Delta H_r} \quad (5.3)$$

The appropriate enthalpy change is the lower heating value of hydrogen evaluated at the cell operating conditions of temperature and composition,^{*} because only H₂ is converted to electric power and the product water is not condensed. The heat of reaction at non-standard-state temperatures is determined by lowering the temperature of the reactants to the standard state, performing the reaction, and raising the temperature of the products back to the original temperature:

$$\Delta H_r = \Delta H_R + \Delta H_{298} + \Delta H_P \quad (5.4)$$

or

$$\text{LHV}_{\text{H}_2} \Big|_T = \sum_{\text{reactants}} m \int_T^{298} C_p dT + \text{LHV}_{\text{H}_2} \Big|_{298} + \sum_{\text{products}} m \int_{298}^T C_p dT \quad (5.5)$$

where m is the stoichiometric coefficient of each component. The integrals of Equation 5.5 can be evaluated by using heat capacity-temperature equations or by using mean heat capacities.⁵ (See Figure A-1 for graphs of mean heat capacities with respect to temperature.) Equation 5.5 can then be written -

$$\text{LHV}_{\text{H}_2} \Big|_T = \text{LHV}_{\text{H}_2} \Big|_{298} + \left(\sum_{\text{products}} m C_p^m - \sum_{\text{reactants}} m C_p^m \right) (T - 298) \quad (5.6)$$

For fuels containing less than 100% hydrogen,

$$\Delta H_r = \text{LHV}_{\text{H}_2} \Big|_{T, P} \frac{\text{cal}}{\text{g-mol feed gas}} \quad (5.7)$$

* For ideal gases, enthalpy is unaffected by pressure changes.

where Γ_{H_2} is the mole fraction of hydrogen available in the fuel cell feed or from chemical equilibrium. For the phosphoric acid fuel cell operating at 200°C, hydrogen available from internal shift and methane equilibria is negligible, so only the feed hydrogen participates in the power production and

$$(\Gamma_{H_2})_{\text{acid}} = X_{H_2} \quad (5.8)$$

In contrast, a molten carbonate fuel cell operates at 650°C, where the water-gas shift and methane-reforming* reactions supply additional hydrogen as the electrochemical oxidation of hydrogen proceeds:**

Therefore,

$$(\Gamma_{H_2})_{\text{carbonate}} = X_{H_2} + X_{CO} + 3X_{CH_4} \quad (5.11)$$

The Gibbs free energy change must also be evaluated at cell operating conditions. Thermodynamic data can be used, but a more convenient approach is to use the Nernst equation to determine the open-circuit voltage. The Gibbs free energy change is then calculated by Equation 5.12:

$$\Delta G_r = -nFE\Gamma_{H_2} \Big|_{T,P} \frac{\text{cal}}{\text{g-mol feed gas}} \quad (5.12)$$

* This assumes that sufficient water is present to force Equation 5.10 to the right.

** Although Equation 5.9 is exothermic and Equation 5.10 is endothermic, the heats of reaction are not included in ΔH_r because they do not contribute to the electrochemical power production. These effects will be accounted for in a heat balance around the fuel cell and in the total system energy balance and efficiency determination.

Because E is a function of partial pressure, ΔG_r is a function of the cell operating pressure.

Voltage Efficiency. The discussion of thermodynamic efficiency is based on equilibrium conditions. When a net current is drawn to drive an external load, the inefficiencies discussed in Chapter 2 become important and reduce the cell voltage to a value less than the thermodynamic equilibrium value, E . The voltage efficiency is defined as the ratio of the actual cell voltage under load to the theoretical voltage at equilibrium:

$$\epsilon_v \equiv \frac{V}{E} \quad (5.13)$$

Current Efficiency. The efficiency of an electrochemical cell is further reduced if all of the reactants are not converted to products, or if some of the electrons are involved in an alternative reaction such as corrosion. The amount of current produced by a reaction is obtained from Faraday's law:

$$I_F = nF \frac{df}{dt} \quad (5.14)$$

where df/dt is the molar flow rate of the electrochemical fuel. To minimize diffusion losses that occur at very high conversions, fuel cells operate at less than 100% utilization. The current produced is related to the amount of fuel actually consumed:

$$I = nF \left(\frac{df}{dt} \right)_{\text{consumed}} \quad (5.15)$$

The current efficiency is the ratio of the actual current to the current predicted by Equation 5.14:

$$\epsilon_I \equiv \frac{I}{I_F} \quad (5.16)$$

The current efficiency is usually reported as total fuel utilization.

Electrochemical Efficiency. The electrochemical efficiency of a fuel cell is the product of the efficiency terms that have been developed:

$$\epsilon_E \equiv \epsilon_{Th} \epsilon_v \epsilon_I \quad (5.17)$$

For a cell operating on a gas containing only inerts and electrochemically active species, Equation 5.17 is sufficient to describe the conversion

of electrochemical fuel to d-c power. The presence of conventionally combustible species requires an additional efficiency term.

Heating Value Efficiency. The product gases from most practical fuel processors will contain varying amounts of inerts and combustible H_2 , CO , and CH_4 , which can be burned in a conventional combustion device, converting all chemical energy into heat energy usable in a heat engine. The fuel cell converts only H_2 directly and, at high temperatures, CO and CH_4 indirectly to electricity. The heating value efficiency is defined as the ratio of ΔH_r to the amount of heat energy available from combustion of the fuel gas, that is, the lower heating value.*

$$\epsilon_H \equiv \frac{\Delta H_r}{\Delta H_c} \quad (5.18)$$

Only species involved in electricity production are included in ΔH_r , but ΔH_c includes all combustible species and is determined from the thermodynamics of mixtures.

$$\Delta H_c = \sum_i LHV_i X_i \Big|_T \frac{\text{cal}}{\text{g-mol feed gas}} \quad (5.19)$$

Again, the lower heating value is used because the combustion product water is not condensed in the fuel cell.

If a fuel gas containing H_2 , CO , and CH_4 is burned, the following combustion reactions occur:

* See Appendix A for a tabulation of heating values and a discussion of the relationships between ΔG , ΔH , $T\Delta S$, and higher and lower heating values.

where X, Y, and Z are mole fractions of CO, H₂, and CH₄ in the feed gas, respectively. Applying Equation 5.4 to the combustion reactions gives -

$$\text{LHV}_{\text{CO}} \Big|_T = -67636X + (X C_{P_{\text{CO}_2}}^m - X C_{P_{\text{CO}}}^m - \frac{X}{2} C_{P_{\text{O}_2}}^m) (T - 298) \quad (5.23)$$

$$\text{LHV}_{\text{H}_2} \Big|_T = -57798Y + (Y C_{P_{\text{H}_2\text{O}}}^m - Y C_{P_{\text{H}_2}}^m - \frac{Y}{2} C_{P_{\text{O}_2}}^m) (T - 298) \quad (5.24)$$

$$\text{LHV}_{\text{CH}_4} \Big|_T = -191762Z + (Z C_{P_{\text{CO}_2}}^m + 2Z C_{P_{\text{H}_2\text{O}}}^m - Z C_{P_{\text{CH}_4}}^m - 2Z C_{P_{\text{O}_2}}^m) (T - 298) \quad (5.25)$$

Equation 5.19 becomes -

$$\begin{aligned} \Delta H_C = & -(67636X + 57798Y + 191762Z) \\ & - [Z C_{P_{\text{CH}_4}}^m + Y C_{P_{\text{H}_2}}^m + X C_{P_{\text{CO}}}^m + (2Z + \frac{X}{2} + \frac{Y}{2}) C_{P_{\text{O}_2}}^m] (T - 298) \\ & + [(Y + 2Z) C_{P_{\text{H}_2\text{O}}}^m + (X + Z) C_{P_{\text{CO}_2}}^m] (T - 298) \end{aligned} \quad (5.26)$$

Fuel Cell Efficiency. The fuel cell efficiency describes the conversion of chemical energy in the feed gas to d-c power and is defined as -

$$\epsilon_{\text{FC}} \equiv \epsilon_E \epsilon_H \quad (5.27)$$

or

$$\epsilon_{\text{FC}} = \left(\frac{\Delta G_r}{\Delta H_r} \right) \left(\frac{V}{E} \right) \left(\frac{I}{I_F} \right) \left(\frac{\Delta H_r}{\Delta H_C} \right) \quad (5.28)$$

Only the fuel cell power section of a fuel cell system is described by ϵ_{FC} . The fuel processor, power conditioner, and waste heat utilization are not included.

Sample Calculations

This section will illustrate in detail the application of the efficiency equations (summarized in Table 5.1) to actual phosphoric acid and molten carbonate fuel cell data at various operating conditions.

Table 5.1. SUMMARY OF EFFICIENCY EQUATIONS

V ,	volts	Load
E ,	volts	Open-circuit
ΔG_r ,	cal/g-mol feed gas	$-nFE\Gamma_{H_2} _{T,P}$
ΔH_r ,	cal/g-mol feed gas	$LHV_{H_2} _{T\Gamma_{H_2}}$
ΔH_C ,	cal/g-mol feed gas	$\Sigma LHV_i X_i _T$
ϵ_v ,	voltage efficiency	V/E
ϵ_I ,	current efficiency	Utilization
ϵ_{Th} ,	thermodynamic efficiency	$\Delta G_r/\Delta H_r$
ϵ_E ,	electrochemical efficiency	$\epsilon_v \epsilon_I \epsilon_{Th}$
ϵ_H ,	heating value efficiency	$\Delta H_r/\Delta H_C$
ϵ_{FC} ,	fuel cell efficiency	$\epsilon_E \epsilon_H$

Phosphoric Acid Fuel Cell. A cell operating at 9.5 atm, 190°C, 0.688 volt, 323 mA/cm² and 85% fuel utilization on air and the fuel gas described in Table 5.2 will be used as an example.

Table 5.2. FUEL GAS COMPOSITION AND THERMODYNAMIC VALUES FOR PHOSPHORIC
ACID FUEL CELL SAMPLE EFFICIENCY CALCULATION, 1 atm, 190°C

	$(P_i)_{in}$	LHV 25°C cal/g-mol	C_p^m 25-190°C cal/g-mol °C
H ₂	0.639	-57798	6.9
CO	0.014	-67636	7.0
CO ₂	0.150	0	9.7
H ₂ O	0.197	0	8.15
CH ₄	0	-191762	9.5
O ₂	0	0	7.2

The open-circuit potential is -

$$E = E^0 + \frac{RT}{2F} \ln \frac{P_{H_2} P_{O_2}^{1/2}}{P_{H_2O}} \quad (5.29)$$

where*

$$E^0 = - \frac{\Delta G^0}{nF} \Big|_{190^\circ C} = \frac{52789}{2 (23060)} = 1.145 \text{ V} \quad (5.30)$$

Substituting the partial pressures and E^0 into Equation 5.29 yields $E = 1.175 \text{ V}$.
Then,

$$\epsilon_v = \frac{V}{E} = \frac{0.668}{1.175} = 0.586$$

Because the fuel utilization is 85%,

$$\epsilon_I = 0.85$$

Determination of ϵ_{Th} requires calculation of ΔG_r by Equations 5.5 and 5.12:

$$\Delta G_r = -nFE \Gamma_{H_2} = -2 (23060) (1.175) (0.639) = -34628 \frac{\text{cal}}{\text{g-mol feed gas}} \quad (5.31)$$

* See Table A-6 for a tabulation of ΔG^0 and E^0 as functions of temperature.

and ΔH_r by Equations 5.6 and 5.7.

The lower heating value of hydrogen at 190°C is obtained by —

$$\begin{aligned} \text{LHV}_{\text{H}_2} \Big|_{190} &= \text{LHV}_{\text{H}_2} \Big|_{298} + (C_{\text{P}_{\text{H}_2\text{O}}}^{\text{m}} - C_{\text{P}_{\text{H}_2}}^{\text{m}} - \frac{1}{2} C_{\text{P}_{\text{O}_2}}^{\text{m}}) (463 - 298) \\ &= -57798 + (8.15 - 6.9 - 3.6) (165) = -58186 \frac{\text{cal}}{\text{g-mol H}_2} \end{aligned} \quad (5.32)$$

For the acid cell,

$$\Gamma_{\text{H}_2} = X_{\text{H}_2} = 0.639 \frac{\text{mol H}_2}{\text{mol feed gas}}$$

thus,

$$\Delta H_r = -58186 (0.639) = -37181 \frac{\text{cal}}{\text{g-mol feed gas}}$$

Then

$$\epsilon_{\text{Th}} = \frac{\Delta G_r}{\Delta H_r} = \frac{-34628}{-37181} = 0.931$$

and the electrochemical efficiency of conversion of hydrogen to electric power is —

$$\epsilon_E = \epsilon_{\text{Th}} \epsilon_V \epsilon_I = (0.931) (0.586) (0.85) = 0.464$$

Calculation of the heating value efficiency requires determining the heat of combustion using Equation 5.26:

$$\begin{aligned} \Delta H_C &= - [67636 (0.014) + 57798 (0.0639)] \\ &\quad - [0.639 (6.9) + 0.014 (7.0) + 0.327 (7.2)] 165 \\ &\quad + [0.639 (8.15) + 0.014 (9.7)] 165 \end{aligned}$$

$$\Delta H_C = -38129 \frac{\text{cal}}{\text{g-mol feed gas}}$$

The heating value efficiency is —

$$\epsilon_H = \frac{\Delta H_r}{\Delta H_C} = \frac{-37181}{-38129} = 0.975$$

The value of ϵ_H is close to unity because the combustible fraction of

the fuel gas is mostly hydrogen, which participates in the electrochemical reaction.

Finally, the efficiency of converting chemical energy in the fuel feed to electrical energy is -

$$\epsilon_{FC} = \epsilon_E \epsilon_H = (0.464) (0.975) = 0.45$$

Molten Carbonate Fuel Cell. Table 5.3 describes the fuel gas fed to the molten carbonate fuel cell anode from the air-blown coal gasifier. At 650°C, 1 atm, 75% fuel utilization, and 160 mA/cm², 0.745 volt is generated with an oxidant gas composed of 70% air and 30% CO₂ at 50% utilization. The open-circuit voltage is -

$$E = 1.019 + \frac{RT}{2F} \ln \frac{0.186}{0.114 (0.078)} + \frac{RT}{2F} \ln [0.30 (0.15)^{1/2}]$$

$$E = 1.054 \text{ volt}$$

The voltage efficiency is -

$$\epsilon_V = \frac{0.745}{1.054} = 0.707$$

and the current efficiency is equivalent to the fuel utilization:

$$\epsilon_I = 0.75$$

Because the fuel gas contains H₂, CO, and CH₄,

$$\Gamma_{H_2} = 0.186 + 0.14 + 3 (0.03) = 0.416 \frac{\text{g-mol } H_2 \text{ available}}{\text{g-mol feed gas}}$$

Therefore,

$$\Delta G_R = -nF (1.054) (0.416) = -20222 \frac{\text{cal}}{\text{g-mol feed gas}}$$

and

$$\Delta H_R = 0.416 [-57798 - 625 (7.05 + 3.85) + 625 (8.75)]$$

$$\Delta H_R = -24603 \text{ cal/g-mol feed gas}$$

Then

$$\epsilon_{Th} = \frac{-20222}{-24603} = 0.822$$

and

$$\epsilon_E = (0.822) (0.707) (0.75) = 0.436$$

The heating value efficiency is determined through Equations 5.18 and 5.26:

$$\begin{aligned} \Delta H_C &= -[67636 (0.14) + 57798 (0.186) + 191762 (0.03)] \\ &\quad - 625 [0.03 (12.6) + 0.186 (7.05) + 0.14 (7.3) + (0.06 + .07 + .093) (7.7)] \\ &\quad + 625 [(0.186 - 0.06) (8.75) + (0.14 + 0.03) (11.2)] \\ \Delta H_C &= -26205 \frac{\text{cal}}{\text{g-mol feed gas}} \end{aligned}$$

and

$$\epsilon_H = \frac{-24603}{-26205} = 0.939$$

Finally,

$$\epsilon_{FC} = 0.436 (0.939) = 0.409$$

Table 5.3. FUEL GAS COMPOSITION AND THERMODYNAMIC VALUES FOR MOLTEN CARBONATE FUEL CELL SAMPLE EFFICIENCY CALCULATION, 1 atm, 650°C

	$(P_i)_{in}$	LHV 25°C cal/g-mol	C_P^m 25-650°C cal/g-mol °C
H ₂	0.186	-57798	7.05
CO	0.140	-67636	7.30
CO ₂	0.114	0	11.20
H ₂ O	0.078	0	8.75
CH ₄	0.030	-191762	12.60
N ₂	0.460	0	7.25
O ₂	0	0	7.70

Experimental Fuel Cell Efficiencies

The preceding techniques and the equations in Table 5.1 have been applied to actual phosphoric acid and molten carbonate fuel cell data at various temperatures, pressures, and fuel compositions. Although the efficiency values presented are based on published data, they are intended only to demonstrate trends. Cell operation at different conditions requires determination of an efficiency specific to those conditions.

Phosphoric Acid. Table 5.4 summarizes the results of the efficiency calculations for the phosphoric acid fuel cell operating at the conditions^{6,7} described in Table 5.5. Because the operating temperature of phosphoric acid fuel cells is low (190°C to 218°C), and because the exit temperature from the fuel processing section is higher than the cell operating temperature,⁸ changes in the fuel inlet composition have been neglected. The necessary values of $(C_p^m)_i$ were obtained from Figure A-1 and values of ΔG° and ΔE° from Table A-6.

As the cell temperature is increased, the results show that ϵ_{Th} decreases but ϵ_v increases. The net result is an increase in cell efficiency. Increasing pressure also improves cell efficiency because both the voltage and thermodynamic efficiencies increase.

Molten Carbonate. The results of the molten carbonate efficiencies calculations are summarized in Table 5.6. Common conditions⁹ are listed in Table 5.7. Changes in the equilibrium fuel inlet composition that result from temperature and pressure changes were considered in the calculation and are reflected in E , ΔG_r , ΔH_r , and ΔH_c and, consequently, ϵ_v , ϵ_{Th} , and ϵ_H .

The molten carbonate fuel cell efficiencies presented in Table 5.6 demonstrate the effect of changing gas composition and the importance of adequate fuel humidification to prevent methane formation. As pressure is increased for a cell operating on the simulated product gas from an air-blown coal gasifier, the methane concentration varies only slightly for the cases under consideration because of the increase in fuel dew point.

Because of insufficient humidification* and the resulting consumption of hydrogen to form methane, fuel cell efficiency does not increase with pressure for the cells operating on simulated reformed methane.

* The dew points of the data in Table 5.6 were chosen to prevent carbon formation, not to prevent methane formation.¹⁰

Table 5.4. SUMMARY OF PHOSPHORIC ACID FUEL CELL EFFICIENCY CALCULATIONS

Case	Temperature, °F	Pressure, atm	E, volts	V, volts	ΔG_r , cal/g-mol	ΔH_r , cal/g-mol	ΔH_c , cal/g-mol	ϵ_V	ϵ_I	ϵ_{Th}	ϵ_E	ϵ_H	ϵ_{FC}
1	375	3.4	1.165	0.650	-34333	-37181	-38130	0.558	0.850	0.923	0.438	0.975	0.427
2	400	3.4	1.161	0.681	-34206	-37200	-38149	0.586	0.850	0.920	0.458	0.975	0.447
3	425	3.4	1.157	0.711	-34106	-37220	-38169	0.615	0.850	0.916	0.478	0.975	0.467
4	375	1.0	1.153	0.575	-33980	-37181	-38130	0.499	0.850	0.914	0.387	0.975	0.378
5	375	3.4	1.165	0.650	-34333	-37181	-38130	0.558	0.850	0.923	0.438	0.975	0.427
6	375	9.5	1.175	0.710	-34628	-37181	-38130	0.604	0.850	0.931	0.478	0.975	0.466

Table 5.5. CELL OPERATING CONDITIONS FOR TABLE 5.4

Fuel Composition, %

 H_2 63.9

 CO_2 15.0

CO 1.4

 H_2O 19.7

 ΓH_2 0.639

Fuel Utilization, % 85.0

Oxidant Composition, % Air 100.0

Oxidant Utilization, % 70.0

Current Density, mA/cm^2 323.0

Table 5.6. SUMMARY OF MOLTEN CARBONATE FUEL CELL EFFICIENCY CALCULATIONS

Case	1	2	3	4	5
Temperature, °C	650				
Pressure, atm	1	5	10	1	5
Fuel*	Air-Blown Coal Gas			Reformed Methane	
H ₂	0.186	0.202	0.180	0.473	0.379
CO ₂	0.114	0.123	0.126	0.108	0.113
N ₂	0.460	0.245	0.262	0.000	0.000
CH ₄	0.030	0.006	0.016	0.009	0.080
CO	0.140	0.032	0.030	0.079	0.060
H ₂ O	0.078	0.399	0.392	0.331	0.368
Γ_{H_2}	0.416	0.230	0.257	0.579	0.679
Dew Point, °C	73	127	149	63	88
Utilization, %	75	75	75	75	75
E, volts	1.054	1.023	1.035	1.037	1.054
V, volts	0.745	0.793	0.805	0.790	0.843
ΔG_r , cal/g-mol	-20222	-10852	-12282	-27692	-33007
ΔH_r ,** cal/g-mol	-24603	-13603	-15217	-34243	-40157
ΔH_c , cal/g-mol	-26205	-14172	-15688	-34433	-43522
ϵ_v	0.707	0.775	0.778	0.762	0.800
ϵ_I	0.750	0.750	0.750	0.750	0.750
ϵ_{Th}	0.822	0.798	0.807	0.809	0.822
ϵ_E	0.436	0.464	0.471	0.462	0.493
ϵ_H	0.939	0.960	0.970	0.994	0.923
ϵ_{FC}	0.409	0.445	0.457	0.459	0.455

* Compositions listed are calculated equilibrium mole fractions at cell conditions.

** Both CO and CH₄ are considered sources of H₂, i.e., the fuel gas is always in shift and methane equilibrium.

Table 5.7 CELL OPERATING CONDITIONS FOR TABLE 5.6

Oxidant Composition, %	
Air	70
CO ₂	30
Oxidant Utilization, %	50
Current Density, mA/cm ²	160

Fuel Cell Heat Balance

The heat balance of a fuel cell can be determined from the same concepts used to develop the efficiency equations. Figure 5.1 and Equation 5.33 summarize the heat balance. The lower heating values of the inlet and exit streams are easily calculated if the compositions are known (Appendix A).

$$\text{LHV}_{\text{in}} = W_e + Q + \text{LHV}_{\text{out}} \quad (5.33)$$

The electrical work obtained is related to the efficiencies by Equation 5.34, where ϵ_v and ϵ_I account for iR , polarization, and utilization losses:

$$W_e = \epsilon_v \epsilon_I \Delta G_r \quad (5.34)$$

Figure 5.1. FUEL CELL HEAT BALANCE

The portion of the heat rejected, which is due to iR (Q_1), is equal to the difference between the maximum work available (ΔG_r) and the actual work obtained. For less than 100% fuel utilization,

$$Q_1 = \epsilon_I \Delta G_r - W_e \quad (5.35)$$

Combining Equations 2.2, 5.13, 5.34, and 5.35 -

$$Q_1 = \epsilon_I \Delta G_r (1 - \epsilon_V) \quad (5.36)$$

or

$$Q_1 = nF \epsilon_I (V-E) \quad (5.37)$$

The contribution of the electrochemical heat of reaction to the heat rejected (Q_2) is obtained from Equation 5.2. Again, for less than 100% fuel utilization -

$$Q_2 = \epsilon_I (-T \Delta S) \quad (5.37)$$

or, combining Equations 2.2, 5.2, 5.3, and 5.37,

$$Q_2 = \epsilon_I (\Delta G_r - \Delta H_r) \quad (5.38)$$

or

$$Q_2 = \Delta H_r \epsilon_I (\epsilon_{Th} - 1) \quad (5.39)$$

or

$$Q_2 = \frac{-\Delta H_r}{\epsilon_V} (\epsilon_I + \epsilon_E) \quad (5.40)$$

The total heat rejected and available for use in a bottoming cycle or cogeneration is Q:

$$Q = Q_1 + Q_2 \quad (5.41)$$

or, combining Equations 5.3, 5.37, and 5.39 with 5.41

$$Q = \epsilon_I (nFV - \Delta H_r) \quad (5.42)$$

but

$$\epsilon_I = \frac{I}{nF \, df/dt} \quad (5.16)$$

Therefore, the heat release per mole of fuel in the feed gas is -

$$Q = \frac{I}{nF \, df/dt} (nFV - \Delta H_r) \quad (5.43)$$

and the total heat rejected is -

$$Q' \text{ per second} = I(V - \frac{\Delta H_r}{nF}) \quad (5.44)$$

The heat rejected can be used to improve the system efficiency, which is discussed in the next chapter.

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CHAPTER 6. FUEL CELL SYSTEM EFFICIENCY

Fuel Cell System Efficiency

The preceding discussion considered only the fuel cell power section of the complete system, shown in Figure 6.1, which consists of a fuel processor, a fuel cell, a power conditioner, and an optional bottoming cycle or cogeneration scheme.

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Figure 6.1. COMPLETE FUEL CELL POWER PLANT¹

The overall efficiency for a system without waste heat utilization is —

$$\epsilon_S = \epsilon_{FP} \epsilon_{FC} \epsilon_{PC} \quad (6.1)$$

where

$$\epsilon_{FP} \equiv \frac{\text{LHV gaseous fuel from fuel processor to fuel cell}}{\text{HHV raw fuel into fuel processor}} \quad (6.2)$$

$$\epsilon_{FC} \equiv \frac{\text{d-c power produced}}{\text{LHV gaseous fuel to fuel cell}} \quad (6.3)$$

$$\epsilon_{PC} \equiv \frac{\text{a-c power}}{\text{d-c power}} \quad (6.4)$$

$$\epsilon_S \equiv \frac{\text{a-c power}}{\text{HHV raw fuel into fuel processor}} \quad (6.5)$$

Additional energy can be recovered in the system by integrating a bottoming cycle to produce additional electricity. For a system located onsite, that is, close to the point of electricity consumption, system efficiency can be increased even more by using the remaining heat for generating steam, heating water for domestic use, space heating, or direct heating of an industrial process. Because the fuel cell operating temperature is independent of power output, the quality of the waste heat is constant. For a system employing waste heat utilization, the fuel cell system efficiency becomes —

$$\epsilon_{S/H} = \frac{\text{fuel cell a-c} + \text{bottoming cycle a-c} + \text{cogeneration Btu's}}{\text{HHV raw fuel into fuel processor}} \quad (6.6)$$

Commonly quoted design system efficiencies for fuel cell power plants are listed in Table 6.1. The 150 to 600-MW central power plant does not include a cogeneration scheme because it is not located close to a market for the waste heat. However, a bottoming cycle is included. On the other hand, the onsite system provides the possibility of total heat recovery.

Table 6.1. DESIGN SYSTEM EFFICIENCIES FOR FUEL CELL POWER PLANTS²

System	Size, MW	Fuel	Efficiency, % Cogeneration	
			No*	Yes**
Phosphoric acid onsite	0.025-0.2	Natural gas	35-40	100
Phosphoric acid dispersed	10-25	Naphtha	37-39	75-80
Molten carbonate or phosphoric acid dispersed	10-25	Petroleum or coal liquids	45-47	75-80
Molten carbonate or phosphoric acid central	150-600	Coal	45-47	

* The fuel cell system efficiency may include a bottoming cycle.

** Heat that is not recoverable within the system.

System Examples

A detailed discussion of fuel cell system integration and heat recovery is not within the scope of this document and is contained in many studies.¹⁻¹² Therefore, only a few examples will be presented.

Air-Blown Coal Gasifier/Molten Carbonate Fuel Cell/Bottoming Cycle.⁵

Figure 6.2 shows the energy balance and simplified flowsheet for a molten carbonate fuel cell integrated with an air-blown coal gasifier and a bottoming cycle. The mass balance is summarized in Table 6.2. The efficiency summary,

based on higher heating values, is presented in Table 6.3; it shows that system efficiency is increased from 33.8% (10098 Btu/kWh) to 49.6% (6881 Btu/kWh) by the integration of the bottoming cycle, which operated at 40% efficiency.

Figure 6.2a. AIR-BLOWN COAL GASIFIER/MOLTEN CARBONATE FUEL CELL/BOTTOMING CYCLE - FLOW SCHEMATIC⁵

Figure 6.2b. AIR-BLOWN COAL GASIFIER/MOLTEN CARBONATE FUEL CELL/BOTTOMING CYCLE - ENERGY BALANCE⁵

Table 6.2. MASS BALANCE FOR THE SYSTEM IN FIGURE 6.2

Stream	Temp, °F	Pres, psia	Composition (lb-mol/hr)								Coal, lb/hr	Stream	
			H ₂	H ₂ O	CH ₄	CO	CO ₂	O ₂	N ₂	H ₂ S			H ₂ O(1)
1	59	15	0	0	0	0	0	0	0	0	0	404944	1
2	1900	200	11750	6826	428	15116	4337	0	33059	472	0	0	2
3	1192	155	13473	4689	408	12161	6339	0	31544	14	0	0	3
4	1300	--	1530	16631	408	2315	38035	0	31544	14	0	0	4
5	59	--	0	0	0	0	0	0	0	0	7612	0	5
6	660	155	0	828	0	0	0	16957	63758	0	0	0	6
7	1000	235	0	428	0	0	0	8770	32974	0	0	0	7
8	1100	150	0	64920	0	0	83963	21786	312368	0	0	0	8
9	1300	--	0	64920	0	0	62174	10892	312368	0	0	0	9
10	1300	--	0	19807	0	0	18969	3323	95102	0	0	0	10
11	1000	480	0	64463	0	0	0	0	0	0	0	0	11
12	1192	--	14120	4914	428	12746	6707	0	33059	14	0	0	12
13	1192	--	647	225	20	584	307	0	1515	1	0	0	13

Table 6.3. EFFICIENCY SUMMARY FOR THE SYSTEM
IN FIGURE 6.2.

ϵ_{FP}	0.75
ϵ_{FC}	0.47
ϵ_{PC}	0.96
ϵ_S	0.338
$\epsilon_{S/H}$	0.496

Oxygen-Blown Coal Gasifier/Molten Carbonate Fuel Cell/Bottoming Cycle.⁷

Figure 6.3 shows a schematic flowsheet for an integrated system consisting of an oxygen-blown coal gasifier, a molten carbonate fuel cell, and a partially cascaded bottoming cycle. The mass balance is shown in Table 6.4. Table 6.5 contains the efficiency summary and indicates that $\epsilon_{S/H} = 0.503$ (6785 Btu/kWh).

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Figure 6.3. OXYGEN-BLOWN COAL GASIFIER/MOLTEN CARBONATE FUEL CELL SYSTEM WITH PARTIALLY CASCADED STEAM BOTTOMING CYCLE⁷

Table 6.4. MASS BALANCE FOR THE SYSTEM IN FIGURE 6.3

	P (psi)	T (°F)	G lb gas lb coal	O ₂ (X _{O₂})	H ₂ (X _{H₂})	N ₂ (X _{N₂})	H ₂ O (X _{H₂O})	CO (X _{CO})	CO ₂ (X _{CO₂})	CH ₄ (X _{CH₄})	H ₂ S (X _{H₂S})	COS (X _{COS})	NH ₃ (X _{NH₃})	Ar (X _{Ar})	H Btu lb coal
1	600	2500	2.18	0	.2884	.0066	.1788	.4245	.0871	.0008	.0100	.0006	.0002	.0012	12018
2	500	1150	1.65	0	.3664	0	.0235	.5393	.0708	0	0	0	0	0	10158
3	100	1127	7.23	0	.1465	0	.1350	.2295	.4890	0	0	0	0	0	13234
4	99	1300	5.58	0	.0224	0	.1979	.0544	.7253	0	0	0	0	0	3670
5	99	1007	36.21	.1120	0	.6450	.0733	0	.1697	0	0	0	0	0	9195
6	98	1300	32.28	.0920	0	.7031	.0799	0	.1250	0	0	0	0	0	11716
7	98	1300	12.28	.0920	0	.7031	.0799	0	.1250	0	0	0	0	0	4457
8	14.7	60	10.63	.2100	0	.7900	0	0	0	0	0	0	0	0	0
9	100	492	10.63	.2100	0	.7900	0	0	0	0	0	0	0	0	1124
10	14.7	300	12.28	.0920	0	.7031	.0799	0	.1250	0	0	0	0	0	1101
11	98	1300	20.00	.0920	0	.7031	.0799	0	.1250	0	0	0	0	0	7258

Table 6.5. EFFICIENCY SUMMARY FOR THE SYSTEM IN FIGURE 6.3

	<u>Fraction of Coal HHV</u>
Gasifier Energy Output	
H ₂ + CO HHV Content	.767
Other Sensible/Latent Energy	.253
HRSG/Ducting Losses	.01
Heat Delivered to Steam (Heat Temp HRSG)	.10
Regen Hx/Cleanup Heat Loss	.08
Chemical + Sensible Energy at Regen Hx Clean Gas Outlet	.83
Fuel Gas Expander Input to Oxidant Supply Compressor	.025
Fuel Cell d-c Voltage*	.78
Fuel Cell a-c Voltage*	.76
Fuel Cell Output	<u>.399</u>
Gas TB Gen Output	<u>.069</u>
Heat Delivered to Steam in Bottoming Cycle	.278
FC/Bottoming Cycle Losses not returned to Gas Stream	.012
Stack Loss	.107
Steam TB Gen Output	<u>.140</u>
Gross Output	.548
Net Oxidant Supply Power	.020
Other Parasitic Power	.025
NET OUTPUT	<u>.503</u>

* Volts.

Methanol Reformer/Phosphoric Acid Fuel Cell/Export Steam.¹² Figure 6.4. shows a phosphoric acid fuel cell operating on the product gas from a methanol reformer. The corresponding material balance is shown in Table 6.6. In addition to the electricity that is generated, 100 psig steam is available to use in a steam bottoming cycle or to provide process heat.

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Figure 6.4. METHANOL REFORMER/PHOSPHORIC ACID FUEL CELL SYSTEM WITH EXPORT STEAM¹²

The overall system efficiency, based on the higher heating value of liquid methanol and excluding the export steam, is $\epsilon_S = 0.442$ (7718 Btu/kWh). If the heat of vaporization is recovered from the export steam, $\epsilon_{S/H} = 0.752$ (4538 Btu/kWh).

Table 6.6. MASS BALANCE FOR THE SYSTEM IN FIGURE 6.4

Components	STREAM (lb-mol/hr)										
	Reformer Feed 1	Steam 2	Anode Feed 3	Anode Exit 4	Cathode Feed 5	Cathode Exit 6	Condensate 7	Steam 8	Export Steam 9	Furnace Air 10	Flue Gas 11
H ₂			2.960	0.296							
CO			0.040	0.040							
CO ₂			0.960	0.960							1.000
H ₂ O		1.600	0.640	0.640		2.664	1.880	8.000	6.059		0.936
CH ₃ OH	1.000		< 80ppm	< 80ppm							
O ₂					2.664	1.332				0.399	0.231
N ₂					10.022	10.022				1.501	1.501
Total	1.000	1.600	4.600	1.936	12.686	14.018	1.880	8.000	6.059	1.900	3.668
Exchangers	E1	E2	E3	E4	E5	E6					
Btu/hr	4,600	15,100	129,600	21,920	39,400	9,000					

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No. 2 Fuel Oil Processing/Phosphoric Acid Fuel Cell/Export Steam.⁹ The sheet for a phosphoric acid fuel cell system operating on the product gas from a hybrid No. 2 fuel oil processor (high-temperature steam reforming followed by autothermal reforming) is shown in Figure 6.5. The heat and material balance is presented in Table 6.7. Excluding the exportable steam, $\epsilon_S = 0.38$ (8908 Btu/kWh). Recovery of the export steam heat of vaporization and superheat results in $\epsilon_{S/H} = 0.546$ (6247 Btu/kWh).

Figure 6.5. NO. 2 FUEL OIL PROCESSING/PHOSPHORIC ACID FUEL CELL/EXPORT STEAM⁹

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Figure 6.6. NAPHTHA STEAM REFORMER/PHOSPHORIC ACID FUEL CELL - FLOW SCHEMATIC⁸

Table 6.7. MASS AND ENERGY BALANCE FOR THE SYSTEM IN FIGURE 6.5

STREAM (lb-mol/hr)																	
Stream	Reformer Feed	Fuel	Super-heated Steam	Reformer Exit	ATR Air	ATR Exit	HT Shift Exit	LT Shift Exit	Anode Feed	Anode Exit	Condensate	Cathode Feed	Cathode Exit	Condensate	BFW	Net Steam Make	Export Steam
No:	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
H ₂				169.33		287.68	336.65	356.38	356.38	35.64							
CO				33.83		72.58	23.60	3.87	3.87	3.87							
CO ₂				57.53		71.34	120.32	140.05	140.05	140.05							
H ₂ O			436.87	287.98		274.76	225.78	206.05	9.11	9.11	196.94		320.74	250.65	866.62	841.38	385.86
CH ₄				54.26		1.70	1.70	1.70	1.70	1.70							
N ₂					100.30	100.30	100.30	100.30	100.30	100.30		861.86	861.86				
O ₂					26.58							229.10	68.73				
No. 2 oil	11.42	1.12															
Total	11.42	1.12	436.87	602.93	126.88	808.35	808.35	808.35	611.41	290.66	196.94	1090.96	1251.33	250.65	866.62	841.38	385.86

Exchangers E-1 E-2 E-3 E-4 E-5 E-6 E-7 E-8 E-9 E-10 E-11 E-12 CE-1 CE-2 CE-3 CE-4
Duty, 10⁶Btu/h 2.75 1.47 0.30 0.95 0.12 1.50 0.93 1.08 0.87 15.9 3.73 6.98 0.60 1.60 2.21 0.21

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Naphtha Reformer/Phosphoric Acid Fuel Cell.⁸ The integrated naphtha steam reformer/phosphoric acid fuel cell system shown in Figure 6.6 does not use a bottoming cycle or provide cogeneration heat. The mass and energy balance is shown in Table 6.8. For this system, $\epsilon_s = 0.379$ (9000 Btu/kWh).

Table 6.8. MASS AND ENERGY BALANCE FOR SYSTEM IN FIGURE 6.6

	STREAM (lb-mol/hr)											
Stream No.	1	2	3	4	5	6	7	8	9			
Component												
H ₂	--	--	--	326.2	378.0	37.8	--	--	--			
CO	--	--	--	55.6	3.7	3.7	--	--	--			
CO ₂	--	--	--	65.9	117.7	117.7	--	--	--			
H ₂ O	--	--	491.7	298.5	246.7	26.4	--	340.3	--			
CH ₄	--	--	--	1.4	1.4	1.4	--	--	--			
O ₂	--	--	--	--	--	--	378.1	207.9	89.8			
N ₂	--	--	--	--	--	--	1422.3	1422.3	337.0			
TOTAL	--	--	491.7	747.6	747.6	187.1	1800.3	1970.5	426.8			
lb/hr	2,250	1,756	8,851	10,608	10,608	5,858	29,082	29,763	12,334			
Exchangers	E-1	E-2	E-3	E-4	E-5	E-6	E-7	E-9	E-10	E-11	E-12	E-13
Duty, MMBtu/hr	1.09	3.47	0.85	5.48	1.21	8.22	2.24	9.30	2.28	4.18	0.94	0.66

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APPENDIX A. HEATING VALUES OF POTENTIAL FUEL CELL SYSTEM FUELS

Appendix A contains heating values for hydrocarbon fuels that can be fed to an appropriate fuel processor to supply hydrogen to a fuel cell. Some comments on thermodynamic nomenclature are also included.

For any reaction,

$$\Delta G = \Delta H - T\Delta S \quad (\text{A.1})$$

where ΔH is the enthalpy change associated with the reaction. For a combustion reaction, ΔH is called the heat of combustion or heating value. For complete combustion of compounds containing carbon and hydrogen, the products are carbon dioxide and water. When the state of the product water is liquid, that is, when the water is condensed (Equation A.2), the heating value is the higher or gross heating value.

If the water is not condensed (Equation A.3), the lower or net heating value is obtained.

The difference between the higher and lower heating values is the heat of condensation of the product water.

Thus, Equation A.1 describes both Equation A.2 and A.3 with the appropriate (higher or lower) heating value. It should be clear, though, that ΔG is not the lower heating value; rather, ΔG is simply related to ΔH by Equation A.1.

The development of the equations describing fuel cell efficiency found in Chapter 5 was based on lower heating values, because the operating temperatures of both phosphoric acid and molten carbonate fuel cells prevent the condensation of water within the cell. On the other hand, in Chapter 6, the development of the equations describing fuel cell efficiency was based on the higher heating value of the raw fuel (coal, oil, etc.) fed to the fuel processor, because the product water can be condensed in a heat recovery scheme.

Table A-1. FUEL OIL HIGHER HEATING VALUES¹

<u>Fuel</u>	<u>lb/gal</u>	<u>Btu/gal</u>
# 1	6.879-7.085	135800-138800
# 2	7.128-7.490	139400-144300
# 4	7.538-7.587	145000-145600
# 5	7.686-7.891	146800-149400
# 6	7.998-8.108	150700-152000

Table A-2. HIGHER HEATING VALUE OF BENZENE AND ALCOHOLS¹

<u>Fuel</u>	<u>Btu/lb</u>
Methanol CH_3OH	9550
Ethanol $\text{C}_2\text{H}_5\text{OH}$	12780
Benzene C_6H_6	18000

Table A-3. COMPOSITION AND HIGHER HEATING VALUE OF NATURAL GAS¹

<u>Gas</u>	<u>CO₂</u>	<u>N₂</u>	<u>CH₄</u>	<u>C₂H₆</u>	<u>Btu/ft³</u>	<u>SG*</u>
Texarkana	0.80	3.2	96	0	967	.57
Cleveland	0	1.3	80.5	18.2	1131	.65
Oil City, Pa.	0	1.1	67.6	31.3	1232	.71

* air = 1.0

Table A-4. HIGHER HEATING VALUE OF COAL¹

Rank	State	Seam	Heating Value Btu/lb
Anthracitic:			
Meta-anthracite	Rhode Island	Uncorrelated	9,620
Anthracite	Pennsylvania	Mammoth	13,540
Anthracite	Pennsylvania	Big Lykens	13,480
Semianthracite	Virginia	Merrimac	12,270
Bituminous:			
Low-volatile	West Virginia	Pocahontas No. 3	14,550
Medium-volatile	West Virginia	Sewell	14,290
High-volatile A	Pennsylvania	Pittsburgh	13,610
High-volatile A	Kentucky	Elkhorn	14,290
High-volatile B	Ohio	Middle Kittanning	12,160
High-volatile B	Kentucky	No. 6	12,950
High-volatile C	Illinois	No. 2	11,480
High-volatile C	Indiana	No. 6	11,420
Subbituminous:			
Subbituminous A or high-volatile bituminous C	Wyoming	Uncorrelated	9,740
Subbituminous B	Wyoming	Monard	9,420
Subbituminous C	Wyoming	Uncorrelated	8,610
Lignite:			
Lignite	North Dakota	Beulah	7,210

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Table A-5. IDEAL GAS HEATING VALUES²

	Ideal Gas Specific Gravity*	Ideal Gas Gross Calorific Value** Btu/ft ³	Ideal Gas Net Calorific Value,** Btu/ft ³	Compressibility Summation Factor
Hydrocarbon:				
Methane	0.5539	1012.0	911.2	0.0436
Ethane	1.0382	1772.9	1621.6	0.0917
Propane	1.5224	2523.0	2321.4	0.1342
Isobutane	2.0067	3260.1	3008.0	0.1744
n-Butane	2.0067	3269.6	3017.5	0.1825
Butanes, avg	2.0067	3265	3013	0.178
Isopentane	2.4910	4009.4	3706.4	0.2276
n-Pentane	2.4910	4018.5	3716.0	0.2377
Pentanes, avg	2.4910	4014	3711	0.233
Hexanes, avg	2.9753	4758	4405	0.283
Ethylene	0.9686	1602.9	1502.0	0.0775
Propene	1.4528	2339.0	2187.8	0.1269
1-Butene	1.9371	3087.3	2885.6	0.1749
cis-2-Butene	1.9371	3079.7	2878.0	0.1863
trans-2-Butene	1.9371	3073.4	2871.7	0.1860
2-Methylpropene	1.9371	3068.0	2866.3	0.1769
Butenes, avg	1.9371	3077	2875	0.181
1-Pentene	2.4214	3835.3	3583.1	0.230
cis-2-Pentene	2.4214	3828.2	3576.1	0.230
trans-2-Pentene	2.4214	3823.4	3571.3	0.230
2-Methyl-1-butene	2.4214	3819.2	3567.1	0.230
3-Methyl-1-butene	2.4214	3827.5	3575.3	0.230
2-Methyl-2-butene	2.4214	3812.3	3560.2	0.230
Pentenenes, avg	2.4214	3824	3572	0.230
Acetylene	0.8990	1476.2	1425.7	0.0833
1:3-Butadiene	1.8675	2887.7	2736.4	0.158
1:3-Cyclopentadiene	2.2822	3362.0	3210.0	0.224
Benzene	2.6969	3750.6	3599.3	0.266
Toluene	3.1812	4485.2	4283.5	0.311
CgAromatics, avg	3.6654	5224	4972	0.36
Nonhydrocarbons:				
Air	1.0000	--	--	0.0202
Carbon dioxide	1.5194	--	--	0.0640
Carbon monoxide	0.9671	321.3	321.3	0.0217
Helium	0.1382	--	--	-0.017
Hydrogen	0.0696	324.9	274.5	--
Hydrogen sulfide	1.1765	638.6	588.2	0.0985
Nitrogen	0.9672	--	--	0.0164

* Ratio of molecular weight (1971) of component to that of air (28.9644).

** Combustion at 60°F (15.6°C); volume of a pound mole of ideal gas at 14.73 psia (101 kPa) = 378.601 ft³ (10.798 m³) on the dry basis. Source of data is the "Selected Values of Properties of Hydrocarbons and Related Compounds" from the American Petroleum Institute Research Project 44. Additional details are available from ASTM Research Report No. D03-1000.

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Table A-6. THERMODYNAMIC VALUES FOR $\text{H}_2 + 1/2 \text{O}_2 \rightarrow \text{H}_2\text{O}(\text{g})^3$

<u>Temperature, °K</u>	<u>ΔG°, cal/g-mol</u>	<u>ΔH°, cal/g-mol</u>	<u>E°, V</u>
298	54583	57973	1.184
600	51147	58342	1.109
800	48610	58757	1.054
1000	46005	59034	0.997
1250	42615	59633	0.924
1500	39202	59702	0.850

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Figure A-1. MEAN HEAT CAPACITIES OF GASES IN THE IDEAL-GAS STATE
(Base Temperature, 77°F)⁴

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APPENDIX B. CONVERSION FACTORS AND FUEL CELL CONSTANTS

Table B-1. VALUE OF UNIVERSAL GAS CONSTANT R IN VARIOUS UNITS

<u>R</u>	<u>Units</u>
1.987	Btu/lb-mol °R or cal/g-mol °K
0.730	atm-ft ³ /lb-mol °R
10.730	psia-ft ³ /lb-mol °R
1545.000	(lb/ft ²)(ft ³)/lb-mol °R or ft-lb/lb-mol °R
1.314	atm-ft ³ /lb-mol °K
82.060	atm-cm ³ /g-mol °K

Table B-2. VALUE OF FARADAY'S CONSTANT F IN VARIOUS UNITS

<u>F</u>	<u>Units</u>
96490	C/g-equivalent
23.06	kcal/volt-g-equivalent

Table B-3. MISCELLANEOUS CONVERSION FACTORS

<u>Multiply</u>	<u>by</u>	<u>to get</u>
Btu	252	cal
cal/g-mol °C	1.0	Btu/lb-mol °F
C	1.0	A-sec
mA/cm ²	0.929	A/ft ²
watt	1.0	V-A

Table B-4. ENERGY UNIT CONVERSION CHART

BRITISH THERMAL UNITS (Btu)	NATURAL GAS **		KILOWATT HOURS ELECTRICITY (kWhr)	BARRELS OIL (bbl)	SHORT TONS BITUMINOUS COAL (T)
	CF	Therms			
1	-	-	0.000293	-	-
1000	1	0.01	0.293	0.00017	0.00004
3413	3.413	0.03413	1	0.00059	0.00014
100,000	100	1	29.3	0.017	0.004
1 MILLION	1000 (1 MCF)	10	293	0.17	0.04
3.41 MILLION	3413	34.1	1000 (1 MWhr)	0.59	0.14
5.8 MILLION	5800	58	1700	1	0.23
25 MILLION	25,000	250	7325	4.31	1
1 BILLION	1 MILLION (1 MMCF)	10,000	293,000	172	40
3.41 BILLION	3.41 MILLION	34,100	1 MILLION (1 GWhr)	588	136
1 TRILLION	1 BILLION (1 BCF)	10 MILLION	293 MILLION	172,000	40,000
5.8 TRILLION	5.8 BILLION	58 MILLION	1.7 BILLION	1 MILLION (1 MMbbl)	232,000
25 TRILLION	25 BILLION	250 MILLION	7.32 BILLION	4.31 MILLION	1 MILLION
1 QUADRILLION (QUAD)(Q)	1 TRILLION (1 TCF)	10 BILLION	293 BILLION	172 MILLION	40 MILLION

* Based on the following nominal fuel heating values:

1 Cubic Foot Natural Gas = 1000 Btu

1 Barrel Crude Oil = 5.8 Million Btu

1 Pound Bituminous Coal = 12,500 Btu

M = 1000

MM = 1,000,000

** Substitute Natural Gas (SNG) and Liquefied Natural Gas (LNG) will have approximately the same heating value.

APPENDIX C. LIST OF SYMBOLS

LIST OF SYMBOLS

b'	=	Tafel slope, V/decade of current
C_B	=	bulk concentration of reacting ions
$(CO)_1$	=	initial inlet carbon monoxide concentration, %
$(CO)_2$	=	final inlet carbon monoxide concentration, %
C_p	=	temperature-dependent heat capacity, cal/g-mol-°K
C_p^m	=	mean heat capacity, cal/g-mol-°K
D	=	diffusion coefficient of reacting ions
df/dt	=	molar flow rate of electrochemical fuel, mol/sec
E	=	fuel cell equilibrium potential, V
E_e	=	electrode equilibrium potential, V
E°	=	fuel cell standard equilibrium potential, V
F	=	Faraday constant, 23.06 kcal/V (g-equiv)
ΔG	=	free energy change, kcal/g-mol
ΔG_r	=	free energy change of $H_2 + 1/2 O_2 \rightarrow H_2O(g)$ at fuel cell conditions, kcal/g-mol feed gas
ΔG°	=	standard free energy change, kcal/g-mol
HHV	=	higher heating value, kcal/g-mol
ΔH	=	enthalpy change, kcal/g-mol
ΔH_c	=	lower heat of combustion of fuel cell feed, kcal/g-mol feed gas
ΔH_p	=	heat of transformation of products from 298°K to cell temperature, kcal/g-mol
ΔH_R	=	heat of transformation of reactants from cell temperature to 298°K, kcal/g-mol
ΔH_r	=	enthalpy change of $H_2 + 1/2 O_2 \rightarrow H_2O (g)$ at fuel cell conditions, kcal/g-mol feed gas

ΔH_{298}	=	enthalphy change of $H_2 + 1/2 O_2 \rightarrow H_2O (g)$ at 298°K, kcal/g-mol
I	=	actual fuel cell current, A
I_F	=	current predicted by Faraday's law, A
i	=	current density, mA/cm ²
i_L	=	limiting current density, mA/cm ²
i_o	=	exchange current density, mA/cm ²
K	=	equilibrium constant
K_p	=	water-gas shift reaction equilibrium constant
LHV _i	=	lower heating value of species i, kcal/g-mol
m	=	stoichiometric coefficient
n	=	number of electrons transferred in a reaction, g-equiv/g-mol
P_1	=	initial cell pressure, atm
P_2	=	final cell pressure, atm
$(P_{CO_2})_a$	=	anode inlet CO ₂ partial pressure
$(P_{CO_2})_c$	=	cathode inlet CO ₂ partial pressure
$(\bar{P}_{CO_2} \bar{P}_{O_2}^{1/2})_1$	=	initial average oxidant partial pressure, atm ^{3/2}
$(\bar{P}_{CO_2} \bar{P}_{O_2}^{1/2})_2$	=	final average oxidant partial pressure, atm ^{3/2}
P_{H_2}	=	hydrogen partial pressure, atm
$(\bar{P}_{H_2})_1$	=	initial average hydrogen partial pressure, atm
$(\bar{P}_{H_2})_2$	=	final average hydrogen partial pressure, atm

P_{H_2O}	=	water partial pressure, atm
$(\bar{P}_{H_2}/\bar{P}_{CO_2} \bar{P}_{H_2O})_1$	=	initial average fuel composition, atm ⁻¹
$(\bar{P}_{H_2}/\bar{P}_{CO_2} \bar{P}_{H_2O})_2$	=	final average fuel composition, atm ⁻¹
P_{O_2}	=	oxygen partial pressure, atm
$(\bar{P}_{O_2})_1$	=	initial average oxygen partial pressure, atm
$(\bar{P}_{O_2})_2$	=	final average oxygen partial pressure, atm
P_i	=	partial pressure of component i, atm
Q	=	heat rejected by fuel cell, cal/g-mol feed gas
Q_1	=	heat caused by internal resistance, cal/g-mol feed gas
Q_2	=	heat produced by electrochemical reaction, cal/g-mol feed gas
Q'	=	rate of heat rejection, cal/g-mol feed gas-s
R	=	universal gas constant, 1.987 cal/g-mol-°K
R	=	resistance, ohms
r	=	reaction rate, $\frac{i}{nF}$
ΔS	=	entropy change, kcal/g-mol-°K
ΔS_r	=	entropy change of $H_2 + 1/2 O_2 \rightarrow H_2O$ (g) at fuel cell conditions, kcal/g-mol feed gas-°K

T	=	absolute temperature, °K
T_1	=	initial cell temperature, °F or °C
T_2	=	final cell temperature, °F or °C
T_{1C}	=	Carnot cycle heat sink temperature, °K
T_{2C}	=	Carnot cycle heat reservoir temperature, °K
U_{H_2}	=	fuel cell total hydrogen utilization
V	=	cell voltage, V
V_{anode}	=	anode voltage, V
$V_{cathode}$	=	cathode voltage, V
V_{cell}	=	cell voltage, V
V_e	=	electrode voltage, V
ΔV_{CO}	=	cell voltage change resulting from carbon monoxide concentration change, mV
ΔV_F	=	cell voltage change resulting from change in average fuel composition $\bar{P}_{H_2} / (\bar{P}_{CO_2} \bar{P}_{H_2O})$, mV
ΔV_{H_2}	=	cell voltage change resulting from hydrogen partial pressure change, mV
ΔV_{iR}	=	cell voltage loss resulting from internal resistance, mV
ΔV_{O_2}	=	cell voltage change resulting from oxygen partial pressure change, mV
ΔV_{OX}	=	cell voltage change resulting from change in average oxidant partial pressure $\bar{P}_{CO_2} \bar{P}_{O_2}^{1/2}$, mV
ΔV_P	=	cell voltage change associated with pressure change, mV
ΔV_T	=	cell voltage change due to temperature change, mV

$\Delta V_{T,CO}$	=	total cell voltage change resulting from temperature and carbon monoxide concentration change, mV
W_e	=	electric energy generated by fuel cell
X	=	diffusion layer thickness, cm
X	=	mol fraction of CO in feed gas
X_i	=	inlet mol fraction of component i
Y	=	mol fraction of H_2 in feed gas
Z	=	mol fraction of CH_4 in feed gas
Γ_{H_2}	=	mol fraction of available hydrogen
ϵ	=	thermal efficiency of a Carnot cycle
ϵ_E	=	electrochemical efficiency
ϵ_{FC}	=	fuel cell efficiency
ϵ_{FP}	=	fuel processor efficiency
ϵ_H	=	heating value efficiency
ϵ_I	=	current efficiency
ϵ_{PC}	=	power conditioner efficiency
ϵ_S	=	fuel cell system efficiency without waste heat utilization
$\epsilon_{S/H}$	=	fuel cell system efficiency with heat recovery
ϵ_{Th}	=	thermodynamic efficiency of fuel cell
ϵ_V	=	voltage efficiency
ϵ_{max}	=	maximum fuel cell efficiency at 298°K
η	=	polarization, overvoltage, overpotential V

η_{act}	=	activation polarization, V
η_{conc}	=	concentration polarization, V
η_e	=	electrode polarization, V
η_{ohm}	=	ohmic or resistance polarization, V