

FUEL CELL DEVELOPMENTS

By

WILLIAM BENSON LUMPKIN

Bachelor of Science

Oklahoma State University

Stillwater, Oklahoma

1960

Submitted to the faculty of the Graduate School of the
Oklahoma State University of Agriculture and
Applied Science in partial fulfillment
of the requirements for the degree
of MASTER OF SCIENCE
May, 1962

NOV 8 1962

FUEL CELL DEVELOPMENTS

Thesis Approved:

Wayne C Edmister
Thesis Adviser

Kenneth J Bell

James Madison
Dean of the Graduate School

504568

PREFACE

The progress and developments made in the field of fuel cells were studied. The basic principles, history, and current status are presented. An expanded reference bibliography on fuel cells is also presented.

The advice and guidance provided by Professor Wayne C. Edmister is greatly appreciated. I am indebted to Dr. F. A. L. Dullien and the entire staff of the School of Chemical Engineering for their assistance. The fellowship received from the National Department of Health, Education and Welfare during this work is appreciated.

Most of all, I am indebted to my wife, Shirley, for her encouragement and patience which have made my graduate study possible.

TABLE OF CONTENTS

Chapter	Page
✓ I. INTRODUCTION	1
✓ II. BASIC PRINCIPLES OF FUEL CELLS.....	4
✓ General Description.....	4
✓ Thermodynamic Considerations.....	6
Actual Fuel Cells.....	<u>9</u>
The Gas Diffusion Electrode.....	10
Types of Voltage Loss.....	14
Loss of Potential at Open Circuit Voltage.....	17
Loss of Potential Due to Activation Polarization.....	20
Concentration Polarization.....	30
Ion Transport Polarization.....	34
Ohmic Polarization.....	35
Side Reactions.....	35
Total Fuel Cell Polarization.....	37
Fuel Cell Efficiency.....	<u>39</u>
Discussion	41 ¹²
III. HISTORY OF FUEL CELLS.....	47 ²
IV. SELECTED FUEL CELL SYSTEMS.....	55
Low Temperature and Pressure	
✓ Hydrogen-Oxygen Fuel Cells.....	55 ³
Union Carbide Fuel Cell	56
JustiMetal Electrode Cell.....	60
Intermediate Temperature, High Pressure	
Hydrogen-Oxygen Fuel Cell (<u>Bacon Cell</u>) .	67
Intermediate Temperature, Low Pressure	
Fuel Cell	73
Ion Exchange Membrane Fuel Cells.....	76
Dissolved-Fuel Fuel Cell.....	82
Regenerative Fuel Cells.....	84
The Chemical Regenerative (Redox)....	84
The Thermal Regenerative Fuel Cell...	86
Consumable Electrode Fuel Cells.....	93
The Sodium Amalgam Fuel Cell.....	93
✓ Allis Chalmers Low Temperature and Pressure Hydrocarbon Fuel Cell.....	97
High Temperature Fuel Cells.....	100
Power Costs.....	111
Discussion.....	111

Chapter	Page
V. CONCLUSIONS AND RECOMMENDATIONS	119 3
A SELECTED BIBLIOGRAPHY.....	121
APPENDIX A - NOMENCLATURE.....	126
APPENDIX B - A COMPREHENSIVE BIBLIOGRAPHY ON FUEL CELLS.....	129

LIST OF TABLES

Table	Page
I. Heats of Chemisorption.....	19
II. Standard State Thermodynamic Properties of Various Fuel Cell Reactions.....	44
III. Operating Characteristics: Union Carbide Low Temperature and Pressure Hydrogen-Oxygen Fuel Cell.....	63
IV. Operating Characteristics: Justi Low Temperature and Pressure Hydrogen-Oxygen Fuel Cell.....	66
V. Operating Characteristics: Bacon Intermediate Temperature High Pressure H ₂ -O ₂ Fuel Cell.....	72
VI. Operating Characteristics: General Electric Ion Exchange Electrolyte Fuel Cell.....	81
VII. Esso Dissolved-Fuel Fuel Cell.....	83
VIII. Operating Characteristics: General Electric Chemical Regenerative Fuel Cell.....	88
IX. Hydride Decomposition Temperatures.....	90
X. Operating Characteristics: Mine Safety Appliance Thermal Regenerative Cell.....	92
XI. Operating Characteristics: Union Carbide Sodium-Amalgam Fuel Cell.....	96
XII. Operating Characteristics: Allis Chalmers Hydrogen-Propane Fuel Cell.....	99
XIII. Electrode Materials for High Temperature Fuel Cells.....	103
XIV. Operating Characteristics: Consolidation Coal Company High Temperature Fuel Cell.....	110
XV. Fuel Cost.....	115

Table	Page
XVI. Minimum Fuel Cost of Fuel Cells.....	116
XVII. Initial Fuel Cell Costs.....	117
XVIII. Estimated Electrode Costs.....	117
XIX. Power Density Comparison: Fuel Cells and Storage Batteries.....	118

LIST OF FIGURES

Figure		Page
1.	Hydrogen-Oxygen Fuel Cell.....	5
2.	Three Phase Zone Diagram.....	11
3.	Reaction Zone Diagram.....	13
4.	Types of Polarization.....	16
5.	Hydrogen Electrode Free Energy Diagram.....	18
6.	Activation Polarization Diagram.....	27
7.	Electrode Fuel Concentration Diagram.....	31
8.	Total Polarization Diagram.....	38
9.	Union Carbide Low Temperature and Pressure Hydrogen-Oxygen Fuel Cell.....	64
10.	Low Temperature Low Pressure Metal Electrode Hydrogen-Oxygen Fuel Cell.....	65
11.	Bacon Type Electrode.....	68
12.	Moderate Temperature High Pressure Hydrogen- Oxygen Fuel Cell (Bacon Cell).....	70
13.	Bacon Moderate Temperature High Pressure Cell....	71
14.	Moderate Temperature Low Pressure Alkaline Cell.....	74
15.	Moderate Temperature Low Pressure Acid Cell.....	75
16.	Hydrogen-Oxygen Intermediate Temperature Low Pressure Cell.....	75
17.	General Electric Ion Exchange Fuel Cell.....	79
18.	Hydrogen-Oxygen Ion Exchange Fuel Cell.....	80
19.	Chemical Regenerative Fuel Cell.....	87

Figure	Page
20. Thermal Regenerative Fuel Cell.....	91
21. Sodium Amalgam Fuel Cell.....	95
22. High Temperature Fuel Cell.....	107
23. Increase in Internal Cell Resistance With Time.....	108
24. Effect of Adding Steam to Carbon Monoxide Fuel.....	108
25. Ohmic Polarization in High Temperature Fuel Cells.....	109
26. Methane and Kerosene Fuels in High Temperature Fuel Cells.....	109

CHAPTER I

INTRODUCTION

The search for greater efficiency in the conversion of fuel into power has been active for many years. Fuel cells have been recognized as being theoretically capable of performing this fuel-to-power conversion with a high efficiency since the latter 19th century. Until the last few years, however, fuel cells have existed mainly as "laboratory curiosities" with little promise for practical and economic applications.

The progress made on fuel cells up to about the last 20 years had not been great, but since this time a large and rapidly increasing amount of investigation has been applied to fuel cells. This increased research activity has produced many new developments that have greatly encouraged the prospects for a dependable, economical, and practical fuel cell. The perfection of such a cell, operating on conventional fuels, would have an extremely important influence on future methods of power generation (72).

The primary reason for the increased interest shown in fuel cells is the promise of increased efficiencies for the conversion of naturally occurring hydrocarbons or other conventional fuels into electrical energy. The fuel cell is theoretically capable of converting the energy released by a

fuel undergoing oxidation into direct current electrical energy with efficiencies ranging from 60-100 per cent.

Fuel cell efficiencies are well above those of conventional means such as the gas turbine (40%), internal combustion (25-30%), or the steam turbine (40%). Other reasons include the inherent simplicity because of no moving parts, quietness, cleanliness, and high power per unit weight or volume. Not all fuel cells offer these advantages to the same degree, but the fact that fuel cells as a whole promise them promotes the increased interest in fuel cells .

The fuel cell is able to attain a high efficiency because it is not a heat engine, and thus escapes the restrictions of the Carnot Cycle which limits the efficiency of many conventional methods of electrical power and generation.

At the present time fuel cells are still in an experimental state of development. Several experimental models have exhibited promising operating characteristics and results, but the cost of electrical energy produced by fuel cells is still too high for commercial use.

The new developments and the rapidly increased research activity applied to fuel cells have created a demand for technical personnel who are familiar with the concepts of fuel cells. This demand has, in turn, created a need for information on fuel cells.

The literature on fuel cells has been quite large in the last few years. Unfortunately, ^o few articles cover the complete _t scope of fuel cells. Most of the articles are either too general

to offer much information or too full of technical detail for easy understanding unless the reader is already familiar with the subject.

In view of the large interest and future potential of fuel cells, the present work was undertaken with the major purpose of gaining information and knowledge in the field. The specific objectives of the study may be stated as:

1. Assemble a literature review of past and present fuel cell systems to serve as a future reference source.
2. Present the basic principles, current status, and future outlook of fuel cells.

CHAPTER II

BASIC PRINCIPLES OF FUEL CELLS

General Description

The classic definition of a fuel cell is "an electrochemical device in which part of the energy derived from a chemical reaction maintained by the continuous supply of chemical reactants is converted to electrical energy" (57). A more practical definition is that a fuel cell is a D-C generator in which electrical energy is obtained directly from the chemical reaction between an oxidant and a fuel that are continuously fed into a cell (57).

There are two classes of fuel cells, the direct and the indirect. In the direct cell, the fuel and oxidant are fed directly into the cell. In the indirect cell, an intermediate reductant and oxidant that are regenerated by external means are utilized in the cell to produce electrical energy.

A fuel cell differs from a battery primarily in that the fuel and oxidant are fed continuously to the fuel cell while the battery contains its fuel and must be regenerated periodically.

Fuel cells may be represented in their most general form by two electrodes separated by an electrolyte, with fuel and oxidant continuously supplied to the anode and cathode, respectively.

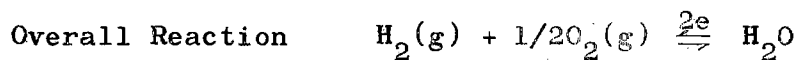
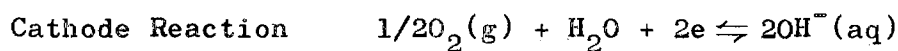
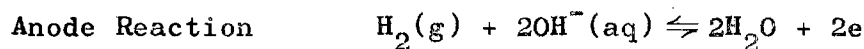
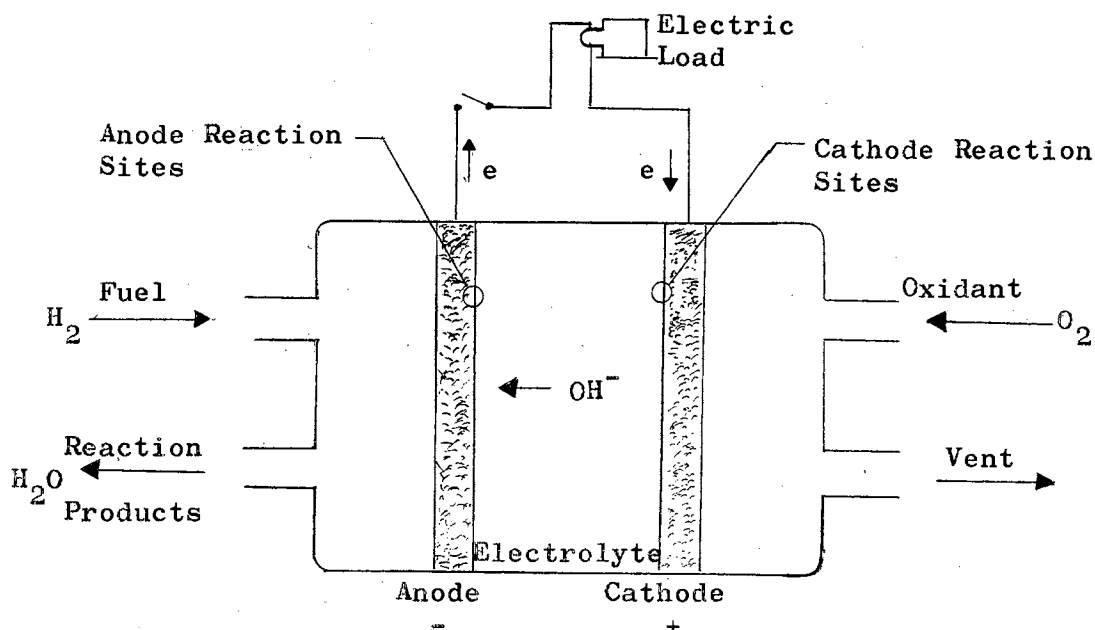


Figure 1

Hydrogen-Oxygen Fuel Cell

Figure 1 illustrates a general simplified sketch of a gaseous hydrogen-oxygen fuel cell, with an aqueous KOH electrolyte and gas diffusion porous electrodes. The fuel is oxidized at the anode, releasing electrons which flow through the external circuit to the cathode. The oxidant is reduced at the cathode, accepting electrons from the external circuit and producing ions which are transported through the electrolyte to the anode. Electrical work is produced by the electron flow through the external circuit.

Thermodynamic Considerations

The general form of the First Law of Thermodynamics for a closed system is

$$dU = \delta q - \delta W \quad (1)$$

where: dU = change in internal energy of the system, energy.

δq = infinitesimal quantity of heat absorbed by the system, energy.

δW = infinitesimal quantity of work done by the system, energy.

The use of δ instead of d for the heat and work change indicates the fact that in general δq and δW are not properties of the system but are defined only for a given path of change.

For reversible process

$$\delta W = PdV + dW' \quad (2)$$

and by the Second Law of Thermodynamics

$$dS = \delta q/T \quad (3)$$

where: dW' = reversible work done by the system other than PV work, energy.

dS = change in entropy of the system, energy/degree.

P = absolute pressure of the system, force/area.

V = volume of the system, volume

T = absolute temperature of the system, degrees

For a system at constant temperature and pressure

$$PdV = d(PV) \quad (4)$$

and

$$TdS = d(TS) \quad (5)$$

Combining equations 1 through 5, the First Law of Thermo-

dynamics may be restated for a reversible closed system under conditions of constant temperature and pressure as

$$\begin{aligned} dW' &= - dU - d(PV) + d(TS) \\ &= - d(U + PV - TS) \end{aligned} \quad (6)$$

This combination of thermodynamic properties ($U + PV - TS$) is defined as the Gibbs Free Energy Function, and is designated by G . In fuel cells, which operate at constant temperature and pressure, the free energy change represents the maximum electrical work that can be produced. This is stated in the form

$$dW' = - dG \quad (7)$$

Enthalpy is defined as $H = U + PV$. For a reversible system at constant temperature and pressure

$$dH = dU + PdV \quad (8)$$

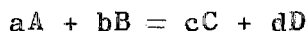
Substituting equation 8 into equation 7

$$dG = dH - TdS \quad (9)$$

or in finite difference terms

$$\Delta G = \Delta H - T\Delta S \quad (10)$$

In fuel cells, energy is produced as the result of a chemical reaction



or

$$A + \frac{b}{a} B = \frac{c}{a} C + \frac{d}{a} D$$

where: A, B, C, D , represents the species of chemical components taking part in the reaction, and a, b, c, d , represents the relative mole relationships of the amounts of reactants and products.

When applied to a chemical reaction, equation 10 may conveniently represent the change in free energy per quantity

of a particular component reacting.

The electrical work produced by a reaction yielding a reversible potential (E_{rev}) and supplying a quantity of electricity Q to an external circuit is $Q E_{rev}$. For each electrochemical equivalent reacting, Q is equal to the Faraday ($\mathcal{F} = 96500$ coulombs/gram equivalent) and for Z electrochemical equivalents reacting

$$Q = Z \mathcal{F}$$

The electrical work obtained from a reaction supplying $Z \mathcal{F}$ coulombs of electricity at a potential E_{rev} is then

$$dW' = Z \mathcal{F} E_{rev} \quad (11)$$

The electrical work is also given by

$$dW' = E_{rev} I t \quad (12)$$

where: I = current produced, coulombs/time, (Q/t)

t = time required for Z electrochemical equivalents to react, time

E_{rev} = reversible potential of the reaction, volts.

Since the electrical work also equals the free energy change for a reversible process, combining equations 7, 11, and 12

$$\Delta G = -Z \mathcal{F} E_{rev} \quad (13)$$

$$= -E_{rev} I t \quad (14)$$

The previous equations apply only to reversible processes, which do not exist as there are no truly reversible processes. To account for other than reversible conditions, equations 10, 13 and 14 may be rewritten as

$$\delta W' = Z \mathcal{F} E_a \quad (15)$$

$$= E_a I t \quad (16)$$

$$= -\Delta H + \Delta q \quad (17)$$

where: Δq = irreversible heat absorbed by the system due to the heat of reaction, energy.

E_a = actual cell potential, volts

The heat generated in an actual working fuel cell due to the reaction is found by combining equations 10, 13, 15, and 17

$$\Delta q = Z \mathcal{F} (E_a - E_{rev}) + T\Delta S \quad (18)$$

Power is defined as work produced per unit time. The electrical power supplied by a fuel cell is then

$$\begin{aligned} \text{Power} &= \delta W' / t \\ &= E_a I \quad (19) \end{aligned}$$

Actual Fuel Cells

No actual working fuel cell possesses current-voltage characteristics that would be predicted from reversible conditions. This decrease in cell potential or voltage is a result of irreversible processes, undesired processes that may occur, changes in the steady state fuel and electrolyte concentration, and imperfections in the cell construction.

To understand the reasons for these cell losses, it is necessary to examine the various processes that are active in a working cell.

The Gas Diffusion Electrode

Various types of electrodes have been proposed and investigated for use in fuel cells (5, 15, 25, 27, 36, 46), but at the present time the gas diffusion electrode seems to offer the most promise. Because of this, the gas diffusion electrode was considered in this work, although the general principles applicable to this type of electrode will apply to other types.

The gas diffusion electrode has been developed to provide a maximum surface area for the reaction zone (76). These electrodes are usually constructed of sintered metal powders or of porous carbon. Various catalysts are incorporated in them to promote desired reactions, and to inhibit undesired side reactions (76).

Gas diffusion electrodes actually consist of a very complex system of pores which would be very cumbersome to consider in a rigorous manner (46). An idealized model, consisting of cylindrical capillary pores was assumed for this treatment.

A major requirement of gas diffusion electrodes is to permit stabilization of the gas-electrolyte interface within the electrode. A stable reaction zone is necessary to prevent bubbling of the gas into the electrolyte, or of the electrolyte flowing through the electrode. Either of these will reduce the reaction zone area and decrease the cell output (76).

There are three pressure forces acting in a pore, the gas pressure P_g , the electrolyte pressure P_L , and the pressure due to surface tension P_c .

Gas diffusion electrodes used for slightly soluble gases may be classified as lyophobic (electrolyte does not wet the pore

wall) and lyophillic (electrolyte does wet the pore wall). All of the sintered porous metal electrodes currently in use appear to be of the lyophillic type while the porous carbon electrodes are of the lyophobic type (76).

The interface for each type of electrolyte-gas interface is illustrated in Figure 2, which indicates the capillary pressure forces that are acting in the pore.

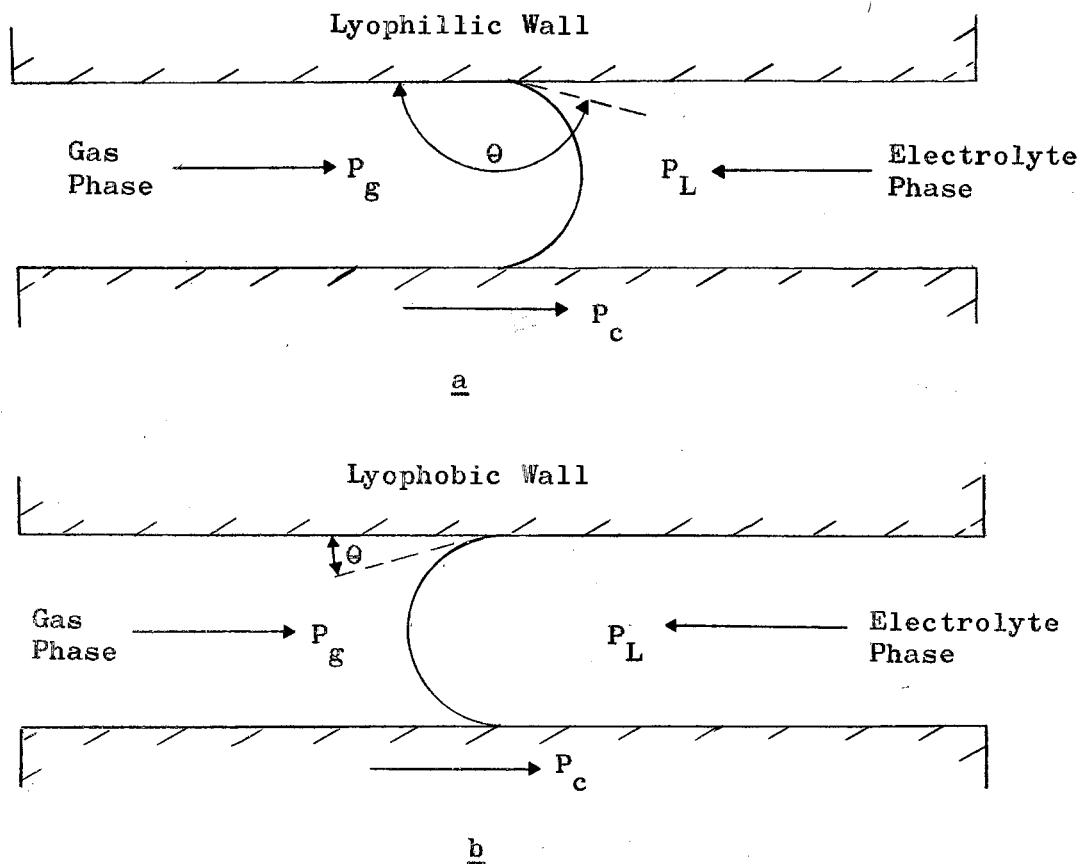


Figure 2

Three Phase Zone Diagram

The pressure due to surface tension is given (65) by

$$P_c = \frac{2\gamma}{r} \cos \theta \quad (20)$$

where: γ = surface tension, force/length

r = pore radius, length

θ = angle of wetting associated with the gas-electrolyte interface, degrees.

P_c = pressure due to surface tension, force/area.

To maintain a stable solid-gas-electrolyte interface, the capillary forces P_c , P_L , and P_g , must be in equilibrium.

This may be stated as

$$P_g + P_c = P_L \quad (21)$$

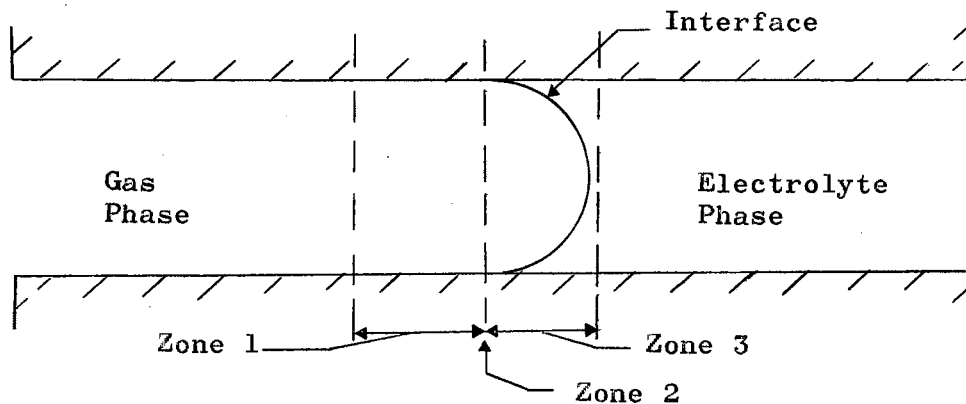
For lyophilic interfaces, (Figure 2a), θ is between 90° and 180° and $\cos \theta$ is negative in value. This indicates that P_g must be larger than P_L for a stable interface.

For lyophobic cases, (Figure 2b), θ is between 0° and 90° and $\cos \theta$ is positive in value which indicates that P_g is less than P_L for a stable interface.

In an ideal capillary, which has been assumed here, a stable gas-electrolyte would be very difficult to maintain since a small deviation of either the gas or the electrolyte pressure would displace the interface. In the actual electrode, the pore radius (r) is not uniform and a small shift of pressure will displace the interface only a small distance until the radius changes enough to again balance the pressure forces (45).

To consider the reaction mechanisms occurring at an electrode, a lyophilic type electrode wall was chosen for

illustration purposes. The interface is divided into three zones as shown in Figure 3.



Zone 1 = Gas-solid interface

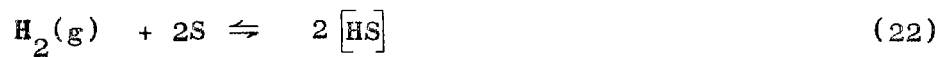
Zone 2 = Gas-solid-liquid interface

Zone 3 = Gas-liquid and liquid-solid interfaces

Figure 3

Reaction Zone Diagram

Considering the anodes of the hydrogen-oxygen fuel cell, the following reactions will occur (3, 6, 46, 49):



where: $\text{H}_2(\text{g})$ = the gas phase fuel, hydrogen

S = an active site in the electrode surface

$[\text{HS}]$ = chemisorbed fuel

OH^- = the reacting hydroxyl ion of the electrolyte

e = electrochemical equivalents transferred per stoichiometric molar reaction.

A prerequisite for reactions 22 and 23 to take place is that the chemisorbed fuel and the hydroxyl ion must come into contact. There are several methods by which this may happen (76).

First the gaseous fuel must migrate to the vicinity of the gas phase of zone 1, and the ionic species to the vicinity of the liquid phase of zone 3. After this occurrence, the reactions may take place by one or all of the following three mechanisms:

- I Fuel can be chemisorbed in zone 1 and then be transported by surface migration to zones 2 or 3.
- II Fuel can diffuse through the thin electrolyte film in zone 3 and be chemisorbed followed by reaction.
- III Fuel can be chemisorbed at zone 2 (gas-solid-liquid interface) followed by reaction.

This system of mechanisms may be applied to the cathode, and to other types of fuel in a gaseous diffusion electrode.

Types of Voltage Loss

The loss of cell potential or voltage of actual fuel cells from that predicted for theoretical cells by the overall cell reaction under reversible conditions consists of two types:

1. With zero current or open circuit.
2. With current drain.

The loss of potential at open circuit voltage (O.C.V.) is due to the loss of energy due to the chemisorption process that occurs at the electrodes, and to any undesired side reactions

that may take place (27, 77).

When a fuel cell produces current, a net reaction must take place at the electrodes, and the cell potential changes to sustain the current (65). The electrode is said to be polarized. Polarization is defined as the difference between the cell potential with current drain and the cell potential under reversible conditions with the same fuel and electrolyte concentrations (14). Fuel cell polarization is divided into three types (50):

1. Activation.
2. Concentration Polarization.
3. Ohmic Polarization.

Activation polarization indicates slow chemical reaction rates at the electrodes. This type of polarization is affected by type of catalyst, undesired side reactions, surface area of reaction zone, temperature, reaction rates, etc. (46, 50, 64).

Concentration polarization is a mass transport effect. It is caused by slow rates of mass transport as current is drawn from the cell. Gas diffusion rates, electrode construction, and electrolyte properties are some of the contributing factors to concentration polarization (46, 50, 64).

Ohmic polarization is caused by the internal resistance of the cell. This type of polarization is affected by the electrode material, electrolyte properties, cell conditions, corrosion, etc. (46, 50, 65).

The general effects of the three types of polarization on cell potential are illustrated in Figure 4 (64). This

illustration indicates the general shape of the current-voltage curve only, not magnitudes.

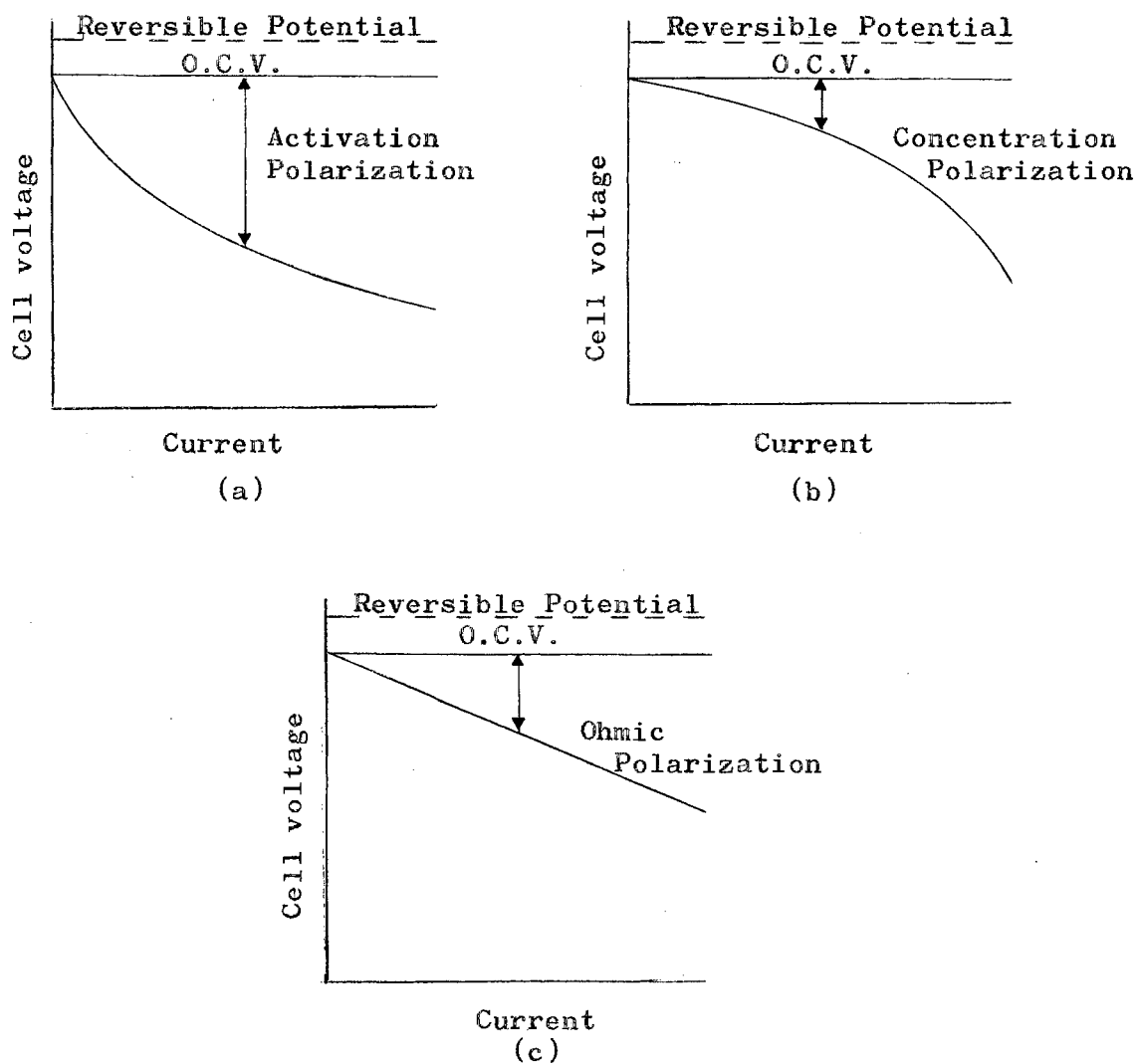


Figure 4

Types of Polarization

Each of the three types of polarization and O.C.V. potential losses are discussed separately in further detail.

Loss of Potential at Open Circuit Voltage

At open circuit voltage no net current flows and the cell potential should be that predicted for reversible conditions (equation 14). That the reversible potential is not obtained at open circuit voltage, even when the fuel is allowed to remain in contact with the electrode and in the absence of side reactions, has been confirmed by many investigators (3, 46, 50, 76).

The electrode reactions of the hydrogen-oxygen anode, equations 22 and 23, indicate that the current producing (electrochemical) reaction is the reaction between the chemisorbed fuel and the electrolyte ion. The chemisorption of the fuel is not a reversible process (77), and is always accompanied by a decrease in the chemical potential of the fuel. Since the chemisorption occurs before the electrochemical reaction and does not produce any electrical work, the free energy change available for electrical work is less. This means that the open circuit voltage is governed by the energy state of the chemisorbed fuel, and the heat of chemisorption (being always negative or exothermic) provides a convenient approximate measure of the loss of cell potential (77). The energy states of the mechanisms for the hydrogen oxygen anode are illustrated in Figure 5.

Chemisorption consists of a combination of the gas molecules to form a surface compound, which results in heats of chemisorption ranging from 20,000 to 100,000 calories per gram-mole (65). Table 1 lists the heats of chemisorption for several fuels and surfaces.

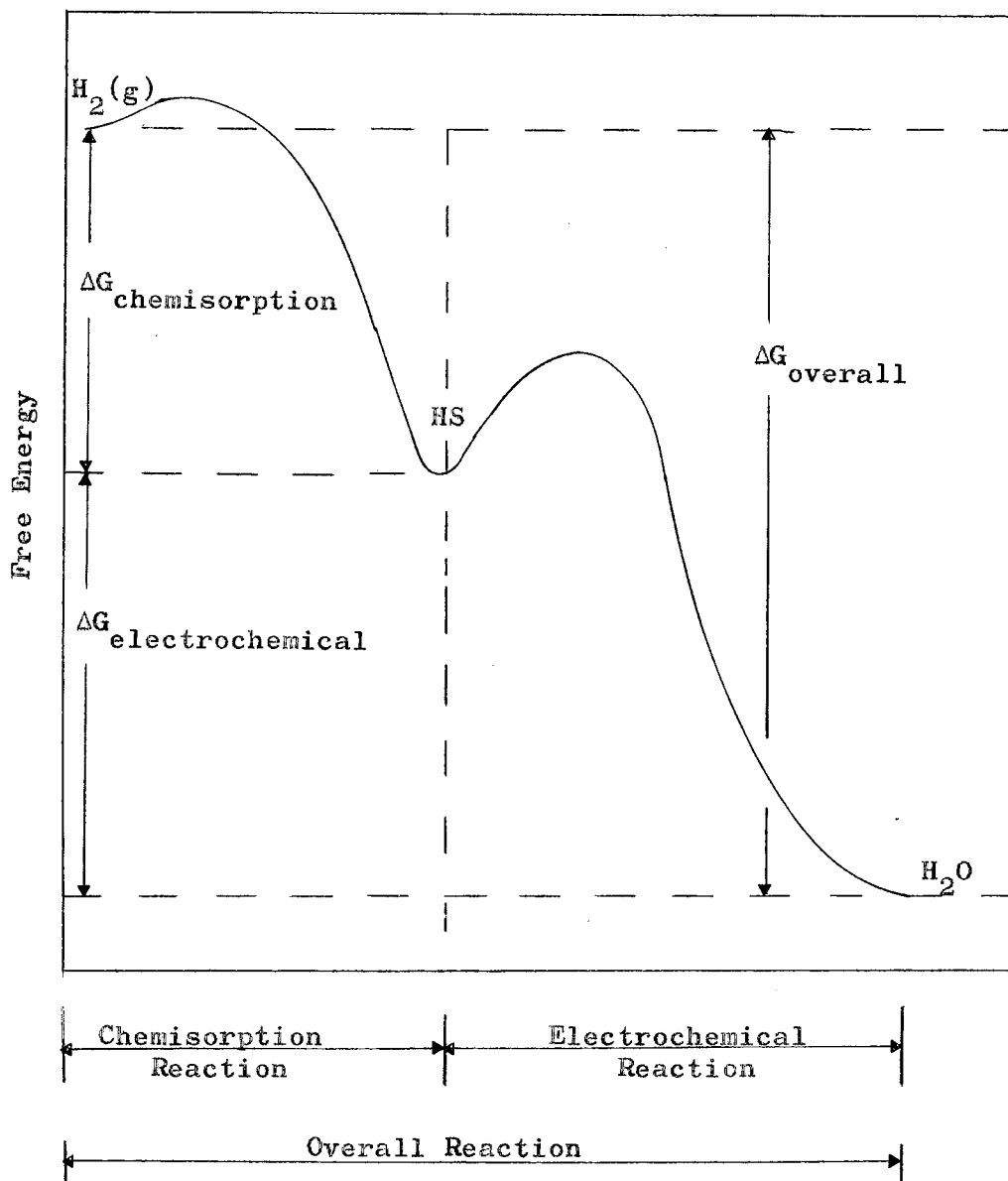


Figure 5

Hydrogen Electrode Free Energy Diagram

TABLE I

HEATS OF CHEMISORPTION*

Fuel	Material	Heat of Chemisorption cal/g-mole
H ₂	C	71000-50000
	Ni	31000
	Fe	28000
	Pt	30000
O ₂	C	72000
	Ni	130000
	Fe	75000
CO	Ni	35000
	Fe	32000
CO ₂	C	9500
NH ₃	C	17000
	Ni	37000
	Fe	45000

* Trapnell (73)

Loss of Potential Due to Activation Polarization

For the loss of potential at O.C.V., the concepts of reversible thermodynamics could be used. When a fuel cell produces current the reactions occur at a finite rate which implies irreversibility, in the thermodynamical sense of the term. The greater the current, the greater is the potential decrease or irreversibility of the process (63).

It is emphasized that the correct theory of activation polarization is uncertain. There are several theories of activation polarization and considerable differences exist between these theories (14). No theory has been proposed to account for all observed phenomena (64). However, most theories agree that activation polarization is connected with the activation free energy of the controlling step in the electrode reactions. Bockris (14) has given a thorough review of the existing theories.

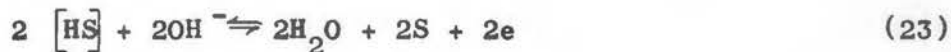
It is beyond the scope of this work to present all theories, and only the approach used by Austin (3) is presented. In this approach, the activation polarization is treated as the free energy change across the electrode-electrolyte interface as a result of current drain.

To discuss activation polarization, the anode of the hydrogen-oxygen fuel cell with the electrochemical reaction (reaction 23) as the controlling step was considered.

At open circuit voltage, the electrode reactions are in a dynamic equilibrium and the rates of the forward and reverse reactions are equal. No net reaction takes place. At open

circuit, the reactions approach reversible conditions (64).

Conforming to Eyring's (65) reaction rate theory, the forward reaction rate of reaction 23



is given by

$$(v_f) = k [(a_{\text{HS}})^2 (a_{\text{OH}^-})^2] \exp \left[\frac{-\Delta G_f^*}{RT} \right] \quad (24)$$

and the reverse reaction rate by

$$(v_r) = k' [(a_{\text{H}_2\text{O}})^2 (a_{\text{S}})^2] \exp \left[\frac{-\Delta G_r^*}{RT} \right] \quad (25)$$

At open circuit voltage, $(v_f) = (v_r)$.

where: a = activities of the various species in the electrode surface, denoted by their subscript.

(v_f) = reaction rate of reaction 23 in the forward direction (left to right as written) electrochemical equivalents/time-area.

(v_r) = reaction rate of reaction 23 in the reverse direction, electrochemical equivalents/time-area.

ΔG^* = activation free energy of the forward and reverse reactions as denoted by the subscript.

k = reaction rate constant for the forward direction.

k' = reaction rate constant for the reverse direction.

The free energy of a substance may be defined in terms of the free energy in the standard state and the activity (64).

$$G = G^\circ + RT \ln a$$

where: superscript ($^\circ$) refers to the standard state, (unit activity).

The isothermal change in free energy of a reaction



is then given by

$$\Delta G = \Delta G^\circ + RT \ln \left[\frac{(a_B)^\beta}{(a_A)^\alpha} \right]$$

Applying this concept, the free energy change of reaction 23 in the forward direction at constant temperature is given by

$$\Delta G_f = \Delta G_f^\circ + RT \ln \left[\frac{(a_{H_2O})^2 (a_s)^2}{(a_{HS})^2 (a_{OH^-})^2} \right] \quad (26)$$

and in the reverse direction by

$$\Delta G_r = \Delta G_r^\circ + RT \ln \left[\frac{(a_{HS})^2 (a_{OH^-})^2}{(a_{H_2O})^2 (a_s)^2} \right] \quad (27)$$

Equations 26 and 27 are correct whether the reactions take place reversibly or irreversibly (65). The free energy change of a reaction at constant temperature and pressure depends only on the initial and final activities. However, when a reaction takes place irreversibly, the free energy change may no longer represent the actual work (or electrochemical potential) available. The available work is a maximum only when the reaction takes place reversibly and is less than the maximum when the reaction is irreversible.

At open circuit voltage no net reaction takes place and a steady state value of the initial and final activities is established. When current is drawn from the cell, a net reaction takes place and a different steady state value of the activities is established at each current level (3). The reactions are no longer reversible when current is drawn from the cell.

Activation polarization is denoted as η_{act} and defined

as the change in potential due only to the electrode reaction processes. This is given by

$$\eta_{\text{act}} = E_{\text{rev}} - E_{\text{c}} \quad (28)$$

where: subscript (c) refers to the cell voltage with current drain.

Assuming that the activation polarization can be represented by a free energy change, the activation polarization may be stated as

$$zF\eta_{\text{act}} = -d(\Delta G) \quad (29)$$

where: $d(\Delta G)$ is the change in free energy of the reactants of the forward and reverse reactions because of current drain.

Equation 29 is not rigorous as it is based on an assumption that the activation polarization is due only to the change in activities of the reactants and products in the reaction zone because of current drain. The error due to this assumption is compensated for by the use of an experimentally determined factor and Equation 29 permits the establishment of an expression for the activation polarization of the correct form (3, 13, 65).

For a substance changing from one activity a_1 to another activity a_2 at constant temperature and pressure $\Delta G^\circ = 0$, and

$$\Delta G = RT \ln \left[\frac{a_2}{a_1} \right] \quad (30)$$

$$a_2 = a_1 \exp \left[\frac{\Delta G}{RT} \right] \quad (31)$$

Applying the concept of equation 31 to reaction 23 the activities of the reactants and products at current drain may be written as

$$\left[(a_{\text{HS}})^2 (a_{\text{OH}})^2 \right]_{\text{c}} = \left[(a_{\text{HS}})^2 (a_{\text{OH}})^2 \right]_{\text{ocv}} \exp \left[\frac{\Delta G_1}{RT} \right] \quad (32)$$

and

$$\left[(a_{\text{H}_2\text{O}})^2 (a_{\text{s}})^2 \right]_{\text{c}} = \left[(a_{\text{H}_2\text{O}})^2 (a_{\text{s}})^2 \right]_{\text{ocv}} \exp \left[\frac{\Delta G_2}{RT} \right] \quad (33)$$

where: ΔG_1 and ΔG_2 represent the free energy change of the reactants and products at open circuit voltage and with current drain. Rearranging equations 32 and 33, these are given by

$$\Delta G_1 = RT \ln \frac{\left[(a_{\text{HS}})^2 (a_{\text{OH}})^2 \right]_{\text{c}}}{\left[(a_{\text{HS}})^2 (a_{\text{OH}})^2 \right]_{\text{ocv}}} \quad (34)$$

$$\Delta G_2 = RT \ln \frac{\left[(a_{\text{H}_2\text{O}})^2 (a_{\text{s}})^2 \right]_{\text{c}}}{\left[(a_{\text{H}_2\text{O}})^2 (a_{\text{s}})^2 \right]_{\text{ocv}}} \quad (35)$$

Substituting equations 32 and 33 into equations 24 and 25, the reaction rates of the forward and reverse reactions with current drain are given by

$$v_{\text{f}} = k \left[(a_{\text{HS}})^2 (a_{\text{OH}})^2 \right]_{\text{ocv}} \exp \left[\frac{-\Delta G_{\text{f}}^*}{RT} + \frac{\Delta G_1}{RT} \right] \quad (36)$$

$$v_{\text{r}} = k' \left[(a_{\text{H}_2\text{O}})^2 (a_{\text{s}})^2 \right]_{\text{c}} \exp \left[\frac{-\Delta G_{\text{r}}^*}{RT} + \frac{\Delta G_2}{RT} \right] \quad (37)$$

The free energy change $d(\Delta G)$ is now interpreted as

$$-d(\Delta G) = \Delta G_1 - \Delta G_2 \quad (38)$$

or accepting the previous assumption

$$-Z\mathcal{F}\eta_{act} = -\Delta G_1 + \Delta G_2 \quad (39)$$

The free energy changes ΔG_1 and ΔG_2 are now defined in terms of an experimentally determined fraction α as

$$\Delta G_1 = \alpha Z\mathcal{F}\eta_{act} \quad (40)$$

$$\Delta G_2 = -(1-\alpha)Z\mathcal{F}\eta_{act} \quad (41)$$

and $-\Delta G_1 + \Delta G_2 = [-(\alpha) - (1-\alpha)] Z\mathcal{F}\eta_{act}$, which satisfies equation 39.

Equations 34 and 35 may now be written in terms of the activation polarization by using equations 40 and 41 as

$$v_f = k \left[(a_{HS})^2 (a_{OH})^2 \right]_{ocv} \exp \left[\frac{-\Delta G_f^*}{RT} + \frac{\alpha Z\mathcal{F}\eta_{act}}{RT} \right] \quad (42)$$

$$v_r = k' \left[(a_{H_2O})^2 (a_s)^2 \right]_{ocv} \exp \left[\frac{-\Delta G_r^*}{RT} - \frac{(1-\alpha)Z\mathcal{F}\eta_{act}}{RT} \right] \quad (43)$$

As seen from equations 42 and 43 the effect of η_{act} is two-fold. Part of η_{act} renders the forward reaction rate (v_f) more rapid, and the remainder diminishes the rate of the reverse reaction v_r (64).

These effects are accomplished by decreasing the free energy of activation for the forward reaction from

$$\Delta G_f^* \quad \text{to} \quad \Delta G_f^* - \alpha Z F \eta_{act} \quad (44)$$

and increasing the free energy of activation for the reverse reaction from

$$\Delta G_r^* \quad \text{to} \quad \Delta G_r^* + (1-\alpha) Z F \eta_{act} \quad (45)$$

where: α = the fraction of the polarization (η_{act}) applied to the forward reaction. α is equal to 0.5 for most electrode materials (13).

Figure 6 illustrates the effects of activation polarization on the electrode reactions (64).

These free energy effects ($\alpha Z F \eta_{act}$ and $(1-\alpha) Z F \eta_{act}$) may be interpreted as the free energy change involved in the change of the activities of the reactants and products across the electrode-electrolyte interface at open circuit and with current drain. The activities in the electrode surface change as a net reaction takes place. This change produces a concentration of electrons in the electrode surface and a concentration of positive ions from the electrolyte in the plane of closest approach to the electrode-electrolyte interface (3). It is this interface that produces the O.C.V. (3, 13, 64). The free energy change across this interface is unavailable for useful potential, and it is this free energy change that

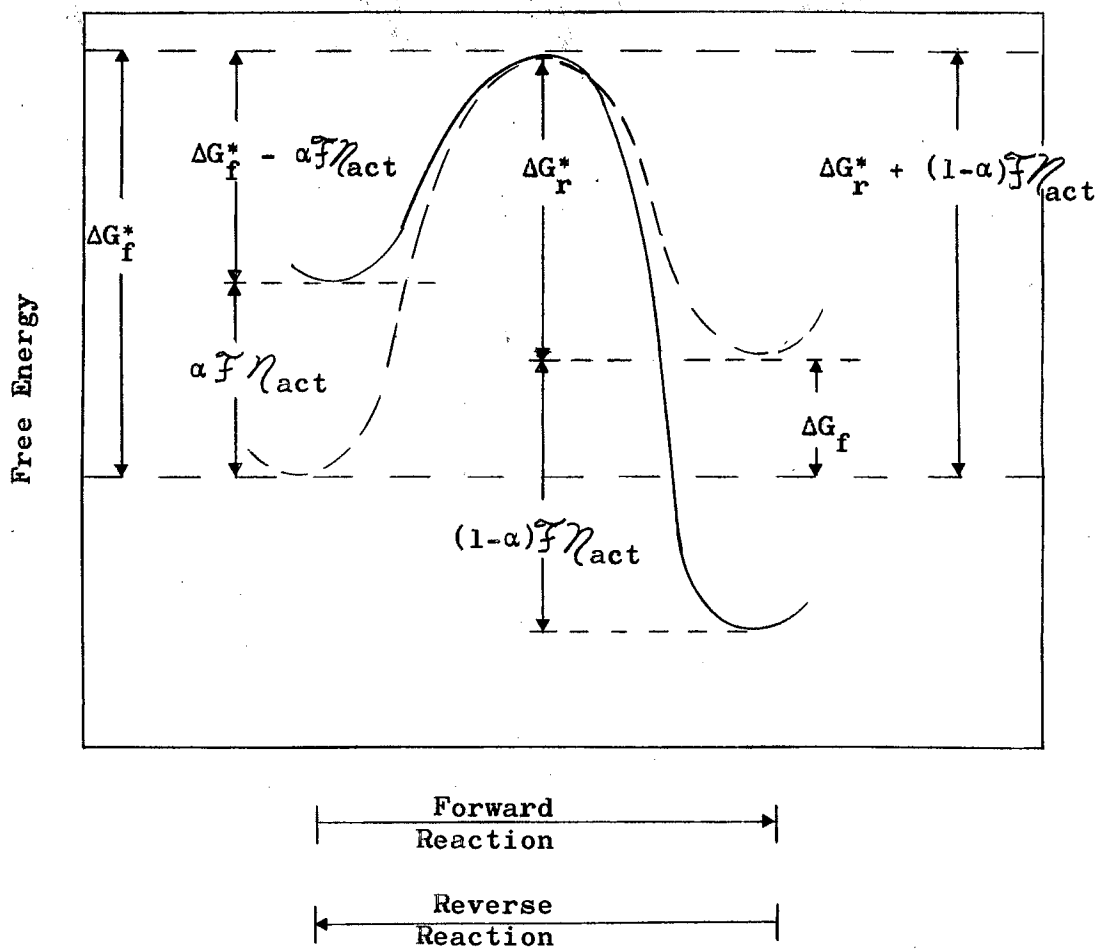


Figure 6

Activation Polarization Diagram

reduces the cell potential.

At reversible equilibrium, no net reaction occurs and $(v_f)_e = (v_r)_e$. The net reaction rate in the forward direction under irreversible conditions is given by

$$v_{net} = v_f - v_r \quad (46)$$

If the rates of reaction, denoted by the v terms, have units of electrochemical equivalents/unit time-unit area of active

electrode surface, the units may be changed to current/unit area of active electrode surface if multiplied by the Faraday.

This may be incorporated in the rate constants,

$$\text{letting } I' = \mathcal{F}(v_f)_{ocv} = \mathcal{F}(v_r)_{ocv} \quad (47)$$

$$\text{and } i' = \mathcal{F}v_{net} = \mathcal{F}(v_f - v_r) \quad (48)$$

where: I' = current in either direction, current/unit area of active electrode surface at open circuit.

i' = net current in the forward direction, current/unit area of active electrode surface.

Combining equations 42, 43, 47, and 48 an equation for the net current i' is given by

$$i' = I' \left[\exp \left[\frac{\alpha Z \mathcal{F} \mathcal{N}_{act}}{RT} \right] - \exp \left[\frac{-(1-\alpha) Z \mathcal{F} \mathcal{N}_{act}}{RT} \right] \right] \quad (49)$$

The net current i' , in terms of geometrical area, may be stated as (3):

$$i = K N_s A_o i' \quad (50)$$

where: i = net current, current/unit of geometrical area.

N_s = active site area per unit area of effective area.

A_o = effective area per unit of geometrical area.

K = constant.

Combining equations 49 and 50

$$i = I \left[\exp \left[\frac{\alpha Z \mathcal{F} \mathcal{N}_{act}}{RT} \right] - \exp \left[\frac{-(1-\alpha) Z \mathcal{F} \mathcal{N}_{act}}{RT} \right] \right] \quad (51)$$

where I is called the exchange current density, as it is the open circuit forward and reverse current per unit area of geometrical area at equilibrium.

Activation polarization is of major importance in fuel cells

when it becomes large. From equation 51, when η_{act} is large the term $\exp \left[-(1-\alpha)Z\eta_{act}/RT \right]$ becomes negligible in comparison to the term $\exp \left[\alpha Z \eta_{act}/RT \right]$ and equation 52 may be approximated by

$$i = I \exp \left[\frac{\alpha Z \eta_{act}}{RT} \right] \quad (52)$$

Taking the logarithm of both sides of equation 52 and rearranging

$$\eta_{act} = a + b \ln i \quad (53)$$

where: $a = -RT/\alpha Z \ln I$

$$b = +RT/\alpha Z$$

Equation 53 is known as the Tafel Equation and applies when the polarization is greater than 50-100 millivolts (3, 13, 63). This equation gives the activation polarization as a function of the exchange current density, the fraction α and the actual current. The assumption made in deriving this equation is compensated for by the experimental determination of the fraction α . However, it is emphasized that this treatment is based on an assumption and that α and η_{act} are not correctly defined by equations 29 and 40. Also it should be remembered that there are other theories and methods of approach to activation polarization (14).

Equation 52 was derived specifically for the electrochemical reaction (reaction 23) controlling. It is possible that the preceding chemisorption reaction is the controlling mechanism (3). If the chemisorption reaction controls, the polarization is due to this reaction and an expression identical to equation 44 can be derived by a similar treatment with the rate constant,

activation free energy, and the exchange having values for corresponding to the chemisorption reaction (3).

Concentration Polarization

For a reaction to proceed continuously at an electrode, there must be replacement of the reactants and dispersement of the reaction products. If this were not to happen the reaction would soon stop for lack of reactants. The polarization of fuel cells due to the rates of mass transport of reactants and reaction products is defined as concentration polarization. In a gas diffusion fuel electrode the concentration polarization can be of two types:

1. Gas transport polarization
2. Ion transport polarization

Each type of concentration polarization will be treated separately.

In the treatment of concentration polarization, as for activation polarization, it was assumed that the free energy change caused by a net current in the cell represents the concentration polarization. This assumption neglects any effects due to irreversible processes.

Gas Transport Polarization

Gas transport through a porous electrode is illustrated in Figure 7. p_1 and p_2 are the partial pressures of the fuel in the gas phase at the fuel side of the electrode and at the interface respectively. L is the distance from the gas side of the electrode to the gas-solid-electrolyte interface.

The rate at which the reaction at the interface occurs depends upon the partial pressure of the fuel at the interface,

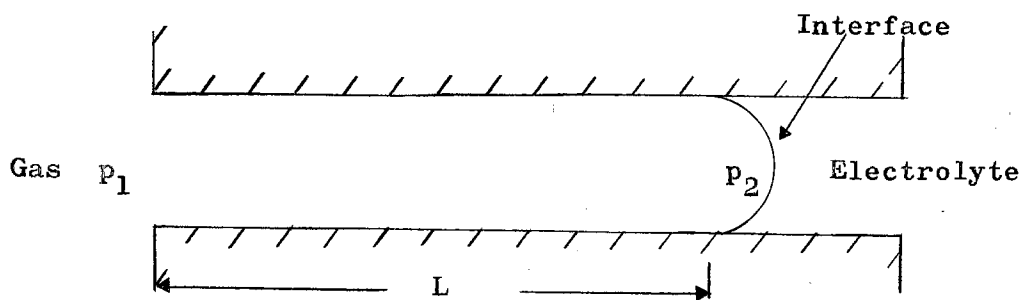


Figure 7

Electrode Fuel Concentration Diagram

and can proceed only as fast as fuel is transported to the interface. The transport of fuel to the reaction sites at the interface can occur through the following mechanisms (73):

- I. Viscous flow under a pressure gradient.
- II. Molecular diffusion.
- III. Knudsen diffusion.
- IV. Surface migration.

Viscous flow is probably non-existent because of the product or impurities built up in the pore, and surface migration will be negligible compared to diffusion mechanisms (75). Diffusion mechanisms are then the primary means for the transport of gas through porous electrodes.

The rate of gas transport due to molecular or Knudsen diffusion is given by (74)

$$\text{Rate} = D_{\text{eff}} (p_1 - p_2)/L \quad (54)$$

where: Rate = number of electrochemical equivalents transported to the reaction zone per unit area per unit time.

D_{eff} = effective diffusion coefficient, depending upon the type of diffusion, fuel concentration, fuel, and conditions.

L = distance the fuel must be transported, length.

For a given cell and operating conditions, equation 54 may be represented as

$$i = B(p_1 - p_2) \quad (55)$$

where: $i = \mathcal{F}(\text{Rate})$, and $B = \mathcal{F}(D_{\text{eff}}/L)$

Since the maximum value of $(p_1 - p_2)$ occurs at $p_2 = 0$,

$$i_L = B p_1 \quad (56)$$

where: i_L = limiting current of the cell due to gas transport.

The change in free energy of the fuel going from a partial pressure p_1 to a partial pressure of p_2 is given by equation 31.

$$a_2 = a_1 \exp \left[\Delta G/RT \right] \quad (31)$$

where: a_1 = activity of the fuel at a partial pressure p_1

a_2 = activity of the fuel at a partial pressure p_2

The activity is defined in terms of fugacity as (63)

$$a = f/f^\circ$$

where: a = activity of the substance in question

f = fugacity of the substance in question

f° = fugacity of the substance in question at the standard state.

The standard state for a gas at any given temperature is the state in which the fugacity is equal to unity (65). The activity of a gas is then equal to the fugacity. For an ideal gas, the fugacity is equal to the partial pressure. Since any gas can be brought into an ideal state by reducing the partial pressure to zero, the definition of fugacity for any gas may be further defined as (65)

$$\lim_{p \rightarrow 0} f/p = 1 \quad (57)$$

For low pressures, the fugacity may be approximated by the partial pressure (65). The free energy change for the transport of the fuel from the gas side of the electrode to the interface is then given by (assuming $f = p$)

$$\Delta G = RT \ln(p_2/p_1) \quad (58)$$

The effect of this free energy change on the cell potential is to reduce the free energy available for the electrochemical reaction, which reduces the cell potential. Denoting the concentration polarization due to gas transport as η_g at a current i , the polarization in terms of free energy is given by (assuming no effects due to irreversibility).

$$\begin{aligned} -\Delta G &= RT \ln(p_1/p_2) \\ &= -zF\eta_g \end{aligned} \quad (59)$$

Rearranging equations 55 and 56,

$$p_1/p_2 = i_L/(i_L - i) \quad (60)$$

Combining equations 58, 59, and 60

$$\eta_g = \frac{RT}{zF} \ln \left[\frac{i_L}{i_L - i} \right] \quad (61)$$

Gas transport polarization is a function of the fuel, fuel partial pressure, the distance the fuel must be transported, the current, and the temperature.

Ion Transport Polarization

Ions to replace those taking part in the electrochemical reaction may be transported to the electrode by (64):

1. Ionic migration.
2. Ionic diffusion.
3. Agitation, natural or forced.

During reaction, the first of these mechanisms inevitably occurs while the last may or may not depending on the system. If the total supply of ions to the electrodes by the first and last mechanisms is adequate, then the electrolyte concentration remains uniform up to the electrode surface and no net diffusion occurs, but if the supply is not adequate then the concentration of ions falls at the electrode surface to which the ions are being transported below that of the bulk concentration. An equilibrium is then reached in which a concentration gradient exists in a thin layer adjacent to the electrode surface. This equilibrium is controlled by the rate of diffusion, and since the electrode is essentially immersed in a solution of different concentration than that of bulk electrolyte, the potential changes accordingly (62).

Polarization due to ion transport is similar to gas transport polarization, and is given by (13, 64, 65):

$$\eta_i = \frac{RT}{Z\mathcal{F}} \ln \left[\frac{i_e}{i_e - i} \right] \quad (62)$$

where: i_e = limiting current density, given by

$$i_e = \frac{DZ\mathcal{F}}{(1-t_i)\delta} a_i$$

$$D = \frac{\lambda RT}{2}$$

$$\delta = \frac{DZ\mathcal{F}(a_i)}{i_e}$$

D = diffusion coefficient

λ = equivalent conductance of the ion

δ = thickness of the diffusion layer

t_i = transport number of the ion

a_i = bulk activity of the ion in the electrolyte.

Ohmic Polarization

Ohmic polarization η_r is due to the internal resistance of the cell. It is the combined resistances of the electrodes, electrolyte, and any films formed due to corrosion (3).

The ohmic polarization is given by Ohms Law as

$$\eta_r = i r_{\text{eff}} \quad (63)$$

where: i = current

r_{eff} = effective resistance of the cell, ohms.

Side Reactions

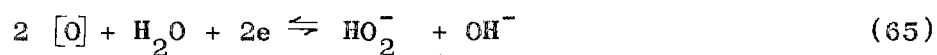
Side reactions can cause loss of potential in fuel cells by occurring as the current producing mechanism in the overall electrode reaction. When this happens, the cell performance is

a function of the side reaction rather than the fuel or oxidant.

An important example of a side reaction is the formation of perhydroxyl ions at the oxygen electrode when operated in an alkaline electrolyte (50).

The oxygen electrode deserves special attention because oxygen is the major oxidizing agent of fuel cells (28). The oxygen electrode also presents the most serious problems to be solved in low temperature fuel cells (46, 76).

The mechanism of perhydroxyl ion formation when an oxygen electrode is operated in an alkaline solution was first recognized by Berl (11) in 1943 and has since been confirmed by many others (50, 76). The mechanisms in the perhydroxyl formation and decomposition are (76)



When perhydroxyl ions are formed, part of the potential of the cell is due to this mechanism which thereby reduces the cell potential (49). Also, the accumulation of these ions at the electrode surface can cause further potential loss due to concentration polarization.

Perhydroxyl decomposing catalysts have been developed to reduce the potential loss due to this mechanism, but it appears that at room temperature the rate is not sufficiently

rapid for equilibrium to be reached and a potential loss of about 0.1 to 0.3 volts occurs (50). The catalysts to decompose this mechanism are discussed further in the description of the current fuel cells.

Another important consideration of the oxygen electrode is the polarization suffered in acid solutions and when air is used as the source of oxygen. Theoretically the oxygen electrode will operate in an acid electrolyte. Practically, they can be operated only at very low current densities in aqueous acid solutions at low temperature with a potential considerably lower than that expected (76). No electrodes have been designed that eliminate concentration polarization of the oxygen electrode when air is used as the oxidant at high current densities.

Total Fuel Cell Polarization

The total loss of potential of a fuel cell is the sum of the polarizations of the anode and the cathode. The loss of potential at O.C.V., activation polarization, and concentration polarization treated previously were for only one electrode. Both the anode and the cathode will have individual losses of potential due to O.C.V. losses, activation polarization, and concentration polarization. Since the ohmic polarization was treated for the complete cell, 1/2 of the ohmic polarization may be attributed to the anode and 1/2 to the cathode.

The total cell polarization η_T (assuming no side reactions) may be stated as

$$\eta_T = \eta_A + \eta_c \quad (67)$$

$$\eta_A = (\eta_{act} + \eta_g + \eta_i + 1/2 \eta_r)_A \quad (68)$$

$$\eta_c = (\eta_{act} + \eta_g + \eta_i + 1/2 \eta_r)_c \quad (69)$$

where: η_A = sum of the activation, gas transport, ion transport, and 1/2 of the ohmic polarization at the anode, total anode polarization, volts.

η_c = total polarization at the cathode, sum of the activation, concentration, and 1/2 of the ohmic polarization at the cathode, volts.

The resulting fuel cell potential is then given by

$$E_a = E_{rev} + \eta_T \quad (61)$$

The cell potential and the respective potential losses of the anode and cathode are illustrated in Figure 8 (31).

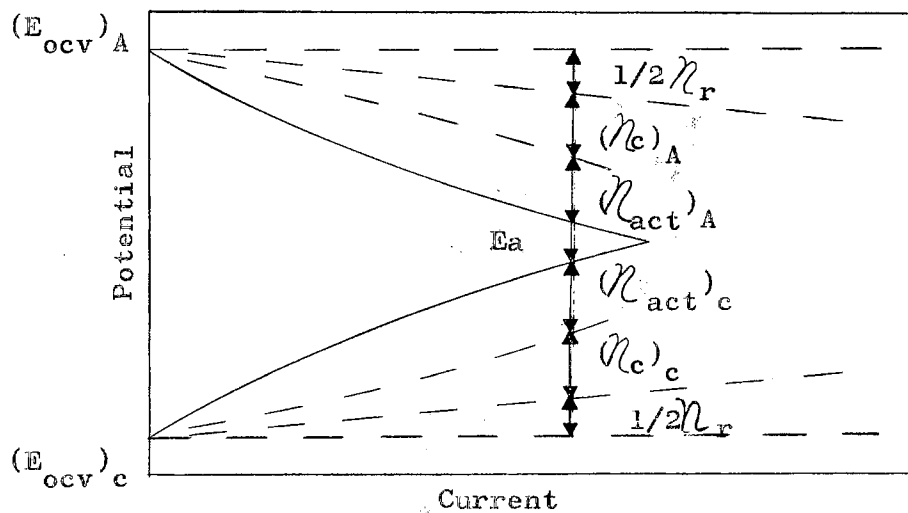


Figure 8

Total Polarization Diagram

Fuel Cell Efficiency

The attractiveness of fuel cells as a source of electrical power lies primarily in the efficient manner in which they can convert chemical energy into electrical energy, which is not limited by the familiar Carnot Cycle.

The maximum amount of useful energy (or available work) that may be recovered from a thermal engine at 100% fuel conversion is given by

$$\Delta W_m = \Delta H_c (1 - T_o/T) \quad (71)$$

where: ΔW_m = maximum available work

ΔH_c = heat of reaction of the fuel at T

T_o = absolute temperature of heat sink, degrees

T = absolute temperature of engine, degrees

$(1 - T_o/T)$ = Carnot Cycle Efficiency

Thus, even with 100% fuel conversion of fuel and no heat loss to the surroundings the thermal engine is limited to a maximum efficiency of that of the Carnot Cycle. To correct equation 71 for less than 100% fuel conversion, it must be multiplied by the fraction of fuel converted.

Efficiency is defined as the ratio of the work output to the work input. The theoretical work output of reversible fuel cells was given by equations 11, 14, and 15, and the actual work of working cells by equations 16, 17, and 18.

The efficiency of reversible fuel cells depends upon the fuel, oxidant, and the operating conditions. It represents the difference in the energy released by the chemical reaction,

and the inherent loss due to entropy changes.

The efficiency of actual cells depends upon the polarization losses, and is reflected by deviations from the theoretical reversible potential and current.

The efficiency of fuel cells has been defined in many ways in the literature (20, 50). A summary of these are:

I. Ideal Efficiency	$\phi_{ID} = \Delta G / \Delta H \times 100$
II. Free Energy Efficiency	$\phi_G = E_a It / (-\Delta G) \times 100$
III. Thermal Efficiency	$\phi_T = E_a It / (-\Delta H) \times 100$
IV. Current Efficiency	$\phi_c = I_a / I \times 100$
V. Practical Efficiency	$\phi_p = E_a It / \text{Fuel energy input} \times 100$

The ideal efficiency ϕ_{ID} represents the maximum efficiency a fuel cell may produce and is characteristic of the fuel and cell conditions. This efficiency is realistic only for reversible operation and complete fuel conversion, but it does represent a limiting value that may be compared to the Carnot Cycle of thermal engines.

The free energy efficiency ϕ_G represents the ratio of the actual electrical work produced to that theoretically produced under reversible conditions and complete fuel conversion.

The thermal efficiency ϕ_T represents the ratio of actual work produced to the heat of reaction of the fuel, assuming complete fuel conversion.

The current efficiency ϕ_c represents the ratio of the actual current of the cell to the theoretical current at 100%

fuel conversion.

The practical efficiency ϕ_p represents an overall efficiency that is the product of either the free energy efficiency and the current efficiency, or the thermal efficiency and the current efficiency.

It is emphasized that these efficiencies apply to the fuel cell only, and not to a system including other types of energy converters.

Discussion

The treatment presented in this section has emphasized the major areas to be considered in fuel cells.

The general description of fuel cells indicates the similarity between fuel cells and batteries for thermodynamic and theoretical consideration.

The voltage performance of reversible fuel cells depends upon the Gibbs free energy change of the current producing reaction, and the cell operating conditions.

Actual working fuel cells are not reversible, and can only approach as a limit the performance of reversible cells. The gas diffusion electrode provides a foundation for outlining the mechanisms and the reasons for working cells deviating from reversible cells. The gas diffusion electrode has shown the most promise of the various types of electrodes, and the principles outlined for this type of electrode will, in general, apply to the others.

Neglecting irreversible effects, the polarization and O.C.V.

losses suffered by working fuel cells are caused by free energy decreases of the fuel and oxidant before they take part in the electrochemical or current producing reactions. These losses depend largely upon the electrode materials and construction, fuel, oxidant, electrolyte, and the cell operating conditions.

The effect of temperature on fuel cell performance is of major importance mainly in the effect it has upon the reaction rates of the electrode reactions. Temperature does have other effects on fuel cell performance, but in general these are small in comparison to the reaction rates (64). Increased temperatures increase the reaction rates by decreasing the activation free energy of the electrode reactions(64).

The treatment presented in this chapter has been restricted in the sense that an important factor in fuel cell performance has been omitted. This factor is quality or technique of cell construction. Such things as electrical contacts and insulation, impurities in the fuel, oxidant, or electrolyte, and cell geometry can have a large influence on the cell performance (49)..

The general principles reviewed for fuel cells provide a basis for outlining the desirable characteristics of fuel cells.

The primary fuels should have a high energy density (free energy change per unit weight or volume), a high reactivity at the operating conditions, be stable and noncorrosive, and be low in cost (33).

The electrolyte should remain invariant. It should have a minimum of electrical resistance and have high transport properties. It should not react with any portion of the cell.

The fuel cell as a whole should be sturdy and small. It should be constructed of materials that are corrosion resistant and unreactive with the electrolyte or fuel at the cell operating conditions. The materials should not be active catalysts that promote any undesirable side reactions.

The electrode should provide a maximum area for the reaction zone (gas-solid-liquid). It should be of low electrical resistance, uniform porosity, corrosion resistant, and structurally strong at the operating conditions. The electrode should contain suitable catalysts to minimize the heat of chemisorption and activation free energy of the desired reactions. It should provide suitable catalysts to inhibit or rapidly decompose any side reaction products that may occur. The catalysts should be selective in that they chemisorb only the desired reactants.

The electrodes should be designed so that concentration polarization is at a minimum.

Table II describes the standard state thermodynamic properties of several fuels. Included in the Table are free energy, and enthalpy changes, reversible potentials and ideal efficiencies of the overall cell reaction at temperatures of 298, 500, 700 and 1000°K.

A more thorough treatment of fuel cell principles is beyond the scope of this work. Exhaustive and thorough treatments have been presented in the literature (3, 14, 16, 46, 76, 77).

The concepts outlined in this chapter are carried into Chapter IV and discussed in further detail with respect to specific cells.

TABLE II
STANDARD STATE THERMODYNAMIC PROPERTIES
OF VARIOUS FUEL CELL REACTIONS

Fuel	Reaction	Molecular wt. of fuel	(Z) <u>Equivalents</u> gm-mol	<u>Amp-hrs</u> Lb-fuel
1	Hydrogen $\text{H}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) = \text{H}_2\text{O}(\text{g})$	2.016	2	12003
2	Hydrogen $\text{H}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) = \text{H}_2\text{O}(\text{l})$	2.016	2	12003
3	Carbon $\text{C}(\text{s}) + \text{O}_2(\text{g}) = \text{CO}_2(\text{g})$	12.01	4	4029
4	Carbon $\text{C}(\text{s}) + 1/2 \text{O}_2(\text{g}) = \text{CO}(\text{g})$	12.01	2	2008
5	Carbon $\text{CO}(\text{g}) + 1/2 \text{O}_2(\text{g}) = \text{CO}_2(\text{g})$	28.01	2	864
6	Methane $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) = \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$	16.04	8	6037
7	Ethane $\text{C}_2\text{H}_6(\text{g}) + 7/2 \text{O}_2(\text{g}) = 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{g})$	30.07	14	5638
8	Propane $\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) = 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g})$	44.09	20	5493
9	n-butane $\text{C}_4\text{H}_{10}(\text{g}) + 13/2 \text{O}_2 = 4\text{CO}_2(\text{g}) + 5\text{H}_2\text{O}(\text{g})$	58.12	26	5408
10	n-pentane $\text{C}_5\text{H}_{12}(\text{g}) + 8 \text{O}_2(\text{g}) = 5\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{g})$	72.15	32	5360
11	Methanol $\text{CH}_3\text{OH}(\text{g}) + 3/2 \text{O}_2(\text{g}) = \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$	32.04	6	2262
12	Ammonia $\text{NH}_3(\text{g}) + 3/4 \text{O}_2(\text{g}) = 3/2 \text{H}_2\text{O}(\text{g}) + 1/2 \text{N}_2(\text{g})$	17.03	3	2129
13	Lithium $\text{Li}(\text{l}) + 1/2 \text{H}_2(\text{g}) = \text{Li H}(\text{l})$	6.94	1	1742
14	Sodium $\text{Na}(\text{l}) + 1/2 \text{H}_2\text{O}(\text{l}) + 1/4 \text{O}_2(\text{g}) = \text{NaOH}(\text{aq})$	23	1	520

TABLE II (Continued)

	298°K				500°K			
	$-\Delta H^\circ$ Calories gram-mol	$-\Delta G^\circ$ Calories gram-mol	E_{rev}° Volts	Ideal Efficiency (%)	$-\Delta H^\circ$ Calories gram-mol	$-\Delta G^\circ$ Calories gram-mol	E_{rev}° Volts	Ideal Efficiency (%)
1	57798	54636	1.23	94.5	58277	52361	1.18	90
2	68248	56960	1.28	83.4	66277	49101	1.11	74
3	94054	94265	1.06	100	94091	94399	1.06	100
4	26417	32783	0.739	124	26296	37144	0.837	138
5	67637	61482	1.385	90.9	67795	57295	1.29	84
6	201761	191397	1.08	94.8	191343	191182	1.08	100
7	341266	359298	1.16	105	340575	347050	1.09	102
8	+625050	646140	1.12	103	634239	653944	1.13	103
10	786908	797141	1.12	101	786607	807681	1.13	103
11	179330	166770	1.25	93	176137	167008	1.25	94.8
12	65907	66633	1.0	101	65907	65862	0.99	100
13	20610	16720	0.73	77.4	19070	11750	0.53	59.6
14	44682	71839	3.12	161	--	--	--	--

(Continued)

TABLE II (Continued)

	700°K				1000°K			
	$-\Delta H^\circ$ Calories gram-mol	$-\Delta G^\circ$ Calories gram-mol	E_{rev}° Volts	Ideal Efficiency (%)	$-\Delta H^\circ$ Calories gram-mol	$-\Delta G^\circ$ Calories gram-mol	E_{rev}° Volts	Ideal Efficiency (%)
1	58710	49915	1.12	85.1	59246	46040	103.7	77.7
2	--	--	--	--	--	--	--	--
3	94169	94510	106.4	101.4	94321	94628	106.6	99.9
4	26409	41468	0.934	157	26711	47859	107.8	179.2
5	67760	53042	1.194	78.2	67610	46769	1.053	69.2
6	191188	191290	1.077	100	191383	191318	1.077	99.97
7	340488	349665	1.125	102.7	341100	353496	1.137	103.6
8	487867	506120	1.14	103.7	489047	513724	1.157	105
9	634526	661805	1.146	104.2	635254	673212	1.166	106
10	787405	818240	1.148	104	789821	833480	1.17	105.5
11	+175772	166908	1.253	94.95	+175614	166834	1.252	94.99
12	65537	65398	0.982	99.8	65486	65355	0.981	99.8
13	20230	8220	0.37	40.63	24570	2200	0.1	8.95
14	--	--	--	--	--	--	--	--

CHAPTER III

HISTORY OF FUEL CELLS

The history of fuel cells began in 1800 when Volta constructed the first electrochemical battery known as the Voltaic Pile (75). In 1801 Davy (2, 23, 24) constructed a cell using zinc and oxygen, and in 1802 a cell with carbon and nitric acid. Grove (40) reported in 1839 that a galvanometer was permanently deflected when connected with platinum strips, both partially immersed in the same dilute sulfuric acid, with one exposed to oxygen and the other to hydrogen.

Although these first cells were crude and inefficient, they represent the beginning of the fuel cell. These men could hardly be credited with inventing the fuel cell, however, the intent of Grove (40), i.e., "to effect the decomposition of water by means of its composition," as stated in his paper of 1842, was deemed sufficient to generally concede Grove as the father of the fuel cell (2). Grove (28, 29) was also the first to recognize the significance and importance of the three-phase zone (gas-solid-electrolyte) for gaseous fuel cell electrode reactions.

During the next 100 years, many fuel cells were reported in the literature (Appendix B). It was not until 1889 that Mond and Langer (59) actually called an electrochemical cell

a fuel cell. The cell of Mond and Langer operated on hydrogen and oxygen, with platinum foil electrodes and a sulfuric acid electrolyte. The cell suffered large polarization losses, and delivered only 6 amperes per square foot of electrode surface at 0.73 volts (5).

Ostwald (61) indicated in 1894 that the fuel cell was theoretically understood and thoroughly appreciated when he proposed the use of "chemodynamic" instead of "thermodynamic" methods for the generation of electrical energy (8, 46).

Many of the early investigators attempted the direct conversion of coal and other solid fuels in fuel cells. These cells all suffered large polarization effects which prompted the increasing use of gaseous fuels such as carbon monoxide, water gas, coal gas, hydrogen, and others. The early gas cells also suffered from polarization effects, although to a somewhat lesser extent. Two major reasons for the interest in gas fuel, were ease of handling and rapid electrode reactions (30).

In the early 1900's, much interest was focused on solid or molten electrolytes in high temperature fuel cells. High temperature cells were used in an attempt to escape the high polarization losses suffered in the low temperature cells. Baur and Pries (8, 9, 10) did extensive work with solid electrolytes from 1912 to 1946, but their electrolytes did not possess sufficient electrical conductivities at reasonable temperatures (15). Davtyan (25) reported in 1946 the construction of a solid electrolyte fuel cell which was also unsuccessful due to unsatisfactory electrical conductivities of the electrolyte.

Schmid (46, 68) made a significant contribution in 1923 for gaseous fuel cells with a greatly improved gas diffusion electrode. Schmid constructed a hydrogen-oxygen fuel cell that delivered up to 37 milliamperes per square centimeter of electrode surface, which was a significant improvement in current densities over previous cells (46).

Although many of the early fuel cells used essentially the same fuel, oxidant, and catalysts that have subsequently proven very promising, practical fuel cells were not developed. The long delay in fuel cell development has been due primarily to technical and economic limitations coupled with the development and improvement of other competitive devices (2). Platinum catalysts, used almost exclusively in early fuel cells were much too expensive for the early day scientist (2). The major technical difficulties encountered were that the early scientists were adopting a purely thermodynamic point of view and were unable to understand the high polarization losses of their cells. This failing was especially emphasized in the fuel cells attempting the direct conversion of solid fuels such as coal (46). The ability to understand the failure of many early fuel cells became possible only by the consideration of the reaction rates of the electrode mechanisms (46).

Fuel cell research began to increase after World War I. Bacon (5, 6, 7) began work in 1932 on a high pressure hydrogen-oxygen fuel cell. In 1939, Bacon built a cell using nickel gas diffusion electrodes and a potassium hydroxide electrolyte. The cell delivered 75 amperes per square foot at a potential

of 0.65 volts. The cell operated at 240 °C and 1000 psia. The life of this cell was measured in hours. Further development of this cell had resulted by 1957 in outputs of 440 amperes per square foot at 0.68 volts when operated at 200 °C and 600 psia (5).

In 1943 Berl (11) made a major contribution that aided understanding of polarization losses in low temperature alkaline fuel cells. Berl was the first to recognize the perhydroxyl mechanism of oxygen electrodes operated in alkaline electrolytes.

Justi (46) has done extensive work on fuel cells, and has developed a specially activated (Double Skeleton Catalyzed, DSK) metal gas diffusion electrode. A hydrogen-oxygen fuel cell equipped with DSK electrodes has produced current densities of 600 milliamperes per square centimeter at 0.67 volts when operated at 80 °C and low pressure using a potassium hydroxide electrolyte.

Kordesch and Marko (49, 50, 51) began work in 1946 on carbon electrodes for fuel cells. They developed a hydrogen-oxygen (air) fuel cell that used porous carbon electrodes catalyzed by metals incorporated in the electrode. The development of this cell has led to current densities of 30-50 milliamperes per square centimeter at 0.8 volts at low temperature and pressure. The life of this cell ranged up to two years in 1960 (50).

Many investigators have followed the initiative of Baur and Davtyan in attempting to develop a high temperature fuel cell. The high temperature fuel cells that have resulted are

very similar, using a molten alkali carbonate electrolyte, porous gas diffusion electrodes, and operating at 500-1000 °C and 1-10 atm.

The high temperature fuel cells offer a means of utilizing the naturally occurring hydrocarbons as fuel, or possibly the products of coal gasification. Broers and Ketelaar (15, 16, 17, 18) have performed the most extensive and probably the most successful work on high temperature fuel cells (37). Other major investigators of high temperature fuel cells are Gorin and Recht (36, 37, 38, 39), Chambers and Tantrum (20), Douglas and Liebhafsky (27, 28, 29, 30), Dezubay (26), Schultz (83), and other (Appendix B). By 1960, the high temperature cell had been operated on fuels such as carbon monoxide, hydrogen, methane, natural gas, propane, and kerosene, delivering up to 50 milliamperes per square centimeter at 0.8 volts with a cell life of several months.

One type of fuel cell that is different from those mentioned previously is the Regenerative fuel cell. This type of cell does not use a gas diffusion electrode. It is an indirect cell, and uses an intermediate reductant and oxidant that supply the electrochemical reactions. The intermediates are then regenerated externally. There are two types of regenerative cells, the chemical regenerative (Redox) and the thermal regenerative.

The most significant work on the Redox type cell was done by Rideal (65) in 1921, and later by Posner (63) in 1955. The Redox cell has been hampered by the selection of the correct intermediates, and the high internal cell resistance. The

thermal regenerative cell uses an external heat source to regenerate the fuel (21). The efficiency of the thermal cell is restricted by the inclusion of a heat cycle in the regenerative process.

A new type of fuel cell developed in the 1950's by Grubb, Niedrach, Liebhafsky, Cairns, and Douglas (19, 42, 43, 54 60) is the Ion Exchange Fuel Cell. This cell uses an ion exchange resin as the electrolyte, with gas diffusion electrodes. This cell operates at low temperature and pressure with hydrogen and oxygen as the fuel and oxidant. The cell delivers 30-40 milliamperes per square centimeter at 0.20-0.6 volts. Cell life is measured in months.

The most significant example of the commercial application of fuel cells has been the development of a fuel-cell-powered farm tractor. This tractor was exhibited in 1958 by the Allis-Chalmers Corporation (48). The tractor was powered by a battery of 1008 fuel cells, connected in nine groups containing 112 cells each. The cells operated on a fuel mixture of hydrogen and propane, with oxygen as the oxidant at low temperature and pressure. The cells contained metal catalyzed electrodes and either an ion exchange resin or an aqueous potassium hydroxide electrolyte. The tractor delivered 65 watt hours/lb, as compared to 10 wh/lb for the alkali battery, 15 wh/lb for the lead battery, and 56 wh/lb for the Ag/Zn battery (46). There are numerous other applications of fuel cells in the last few years, such as the hollow porous carbon electrode hydrogen-oxygen fuel cells of the National Carbon Company used to power the Army's

Silent Sentry Portable radar set (2, 81).

Although there have been several specific applications of fuel cells, all must still be considered in the development stage. Many industrial and government organizations are currently engaged in fuel cell research (2, 57, 77, 84). Fuel cell research slowed temporarily when the advent of nuclear power made the need for energy efficiency seem unnecessary (29). The interest and research applied to fuel cells has been rapidly and steadily increasing until at the present time it is at an all time high.

A major concern of fuel cell research is the development of a low temperature cell that will operate on naturally occurring liquid hydrocarbons. In 1960 Esso Research (72) reported promising results with ethane in a low temperature cell. The DSK electrodes of Justi (95) have also exhibited encouraging results for the low temperature conversion of hydrocarbon fuels.

Much of the recent research has been in the area of catalyst development, such as that by Young and Rozelle (77).

The past and current literature on fuel cells is quite large. For this reason, many fuel cell developments were not discussed in this section, however, an excellent bibliography on fuel cells compiled by Adams (1) has been included in Appendix B. The original bibliography was complete through 1950, and has been updated to include 1960. Another excellent reference collection on fuel cells was compiled by Baur and Tobler (8). The 12th, 13th, and 14th Annual Battery Research and Development conferences (79), and the 136th through 140th National Meetings of the

American Chemical Society (80) review the more recent cells.

It is important to note that the performance data on many of the early fuel cells reported in the literature are often superficial. Often, only a certain potential difference was measured and the chemical reaction supplying the current was not thoroughly investigated. In the majority of cases, the current densities reported are short circuit currents. These high current densities result in a pronounced decrease of cell voltage and do not accurately represent the cell performance (52).

Many of the cells mentioned in this chapter are discussed in detail in Chapter IV.

CHAPTER IV

SELECTED FUEL CELL SYSTEMS

The increased research directed toward fuel cells and the progress made in fuel cell technology since just before World War II has led to the investigation and development of several types of fuel cells. These cells use various fuels, electrolytes and cell components, and operate at various temperatures and pressures.

This chapter describes the current status and operating characteristics of several selected fuel cell systems. These cells were selected to describe the various development stages of fuel cells, to outline the various types of cells, and also because of the information available.

The cells are classified according to the distinguishing characteristic that they are most often referred to in the literature.

Low Temperature and Pressure Hydrogen- Oxygen Fuel Cells

This type of fuel cell uses hydrogen as fuel and oxygen or air as the oxidant. The electrolyte is a concentrated alkaline solution. The electrodes are porous gas diffusion electrodes of carbon or sintered metals. A general illustration of this type

of cell was shown in Figure 1.

K. Kordesch (49, 50, 51) of Union Carbide Consumer Products Company and E. Justi (46, 47) of Rhur Chemie in Germany have reported the major and most successful investigation of this type of cell, although many other organizations are currently conducting research on this cell (2, 84).

The cells developed by Kordesch and Justi differ mainly in the electrode construction and are discussed separately.

Union Carbide Fuel Cell

Kordesch and Marko (49, 50, 51) began investigation on methods of activating carbon electrodes for fuel cell processes in 1946. Further development has resulted in one of the more advanced fuel cell systems existing today (2).

The Union Carbide fuel cell operates on hydrogen and oxygen (or air) at low temperatures (20-80°C) and low pressures (1-10 atm.). The cell uses porous carbon electrodes activated by metal catalysts. The porous carbon electrodes are the distinguishing characteristic of the Union Carbide fuel cell. Porous carbon electrodes have many favorable properties. They are inert at temperatures up to and exceeding 200°C (50). Many microscopic fractures produce pore sizes ranging from 10^{-3} to 10^{-7} centimeters in diameter. The internal surface area of one centimeter cube for some types of porous carbon reaches 1000 square meters (2).

The major disadvantage of present carbon electrodes is that they must be activated by metal catalysts and tend to become flooded and to wet (2, 49). Flooding occurs when the capillary

pores become totally or partially filled to such a degree that the electrode reactions are hindered.

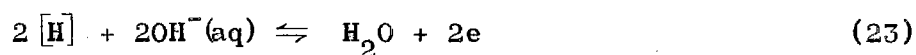
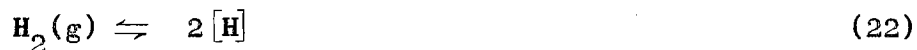
One cause of flooding occurs when capillary action due to interfacial tension draws the electrolyte into the electrode pores reducing the reaction zone area and deactivating the reaction zone. For potassium hydroxide electrolytes, Union Carbide has been able to establish a semi-permanent three-phase zone by the use of surface active agents to control the interfacial tension between the electrolyte and the pore wall (49, 50).

Another cause of flooding that is common to low temperature hydrogen-oxygen fuel cells occurs at the hydrogen electrode due to the water forming reaction (equation 23). The water formed during the electrode reaction must be removed either by diluting the electrolyte or by surface evaporation through the porous electrode by a circulating gas stream (50). If the water dilutes the electrolyte, the electrolyte must be regenerated or reconcentrated periodically. The water removed in the circulating gas stream must be removed in a condenser. If water is formed more rapidly than it can be removed by either of these methods, the pores may be filled with newly formed water and effectively flood or drown the electrode. One ampere-hour of electricity is equivalent to the formation of 0.33 cubic centimeters of water.

Flooding because of water formation becomes a major problem at high current densities, and currently limits the Union Carbide cell to around 100 amperes per square foot of electrode surface for continuous operation (2). By operating four hours and then resting the cell for one-half hour, a current density of 250

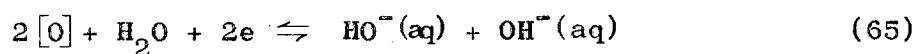
amperes per square foot can be maintained for extended periods (2).

The anode or hydrogen electrode of the Union Carbide cell is activated by metals from the platinum group (50). No hydrogen activity is observed on uncatalyzed carbon. The mechanisms occurring at the anode are

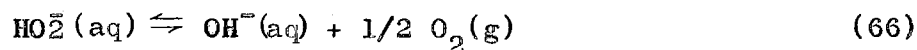


The cathode is constructed similarly to the anode. No specific metal catalysts are reported for the cathode. However, Young and Rozelle (77) report silver to be an active catalyst for the oxygen electrode in an alkaline electrolyte.

As indicated in Chapter II, the mechanisms occurring at the cathode include the undesired formation of the perhydroxyl ion



Union Carbide has accomplished the decomposition of the perhydroxyl ion by the use of catalysts such as $\text{AlO}_3\text{-CoO}$, CoAl , or Fe-Mn-Ag (49, 50, 51). These catalysts effectively reduce the perhydroxyl ion concentration to the range of 10^{-6} to 10^{-7} normal by the mechanism

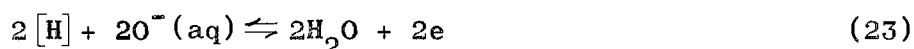


The normal potential of the hydrogen peroxide reaction (for 1 N. H_2O_2) is 0.75 volts at 25°C. Union Carbide cells

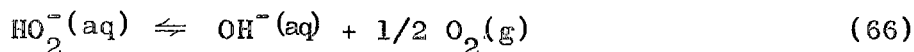
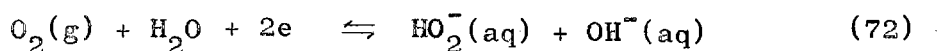
reach open circuit voltages of 1.1 to 1.15 volts, which indicates that the perhydroxyl ion formation mechanism contributes very little to the cell reaction (50).

A summary of the electrode reactions for this cell follows

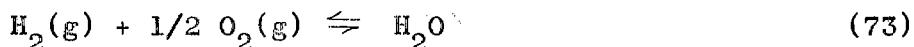
Anode Reaction



Cathode reaction



Overall Cell Reaction



Both the anode and the cathode are treated with surface active agents to prevent electrode flooding (49).

The electrolyte of the Union Carbide cell is a 30 to 60 per cent aqueous potassium hydroxide solution. The specific conductivity ranges from one to three $\text{ohm}^{-1} \text{cm}^{-1}$ (49).

The electrodes may be manufactured in the shape of tubes, plates, or blocks, but in general plates provide the most economical power package (49). Porous carbon electrodes are brittle, and are limited to 1/16 to 1/8 inches in thickness (2). Perforated metal plates are used to add structural strength.

Operation of the Union Carbide cell on air limits the current densities to around 50 amperes per square foot (2). This is due primarily to the accumulation of inert gases in the

cathode pores which limits the transport of oxygen to the reaction zone. One method to improve the hydrogen-air cell has been a concentric tube design shown in Figure 9. The design provides a maximum electrode surface for the air electrode.

One example of a Union Carbide fuel cell system is a 28 volt battery consisting of 35 fuel cells. The unit is 6 x 6 x 17 inches and weighs approximately 50 pounds. The unit is rated at between 150 to 200 watts at atmospheric pressure operating on air, and between 600 to 1000 watts at 45 psig operating on oxygen (2, 49).

The only life limiting factor of this cell appears to be the wettability of the carbon electrodes which increases with extended operation (50). Cell lives of from one to two years at 30 to 50 amperes per square foot of electrode surface at 0.8 volts have been attained.

Table III lists the general operating characteristics of the Union Carbide fuel Cell (2, 57).

Justi Metal Electrode Cell

Justi (46) has developed a "Double Skeleton Catalyzed" (DSK) hydrogen electrode for use in hydrogen-oxygen fuel cells operating at 80 to 90 C and a few atmospheres pressure in a potassium hydroxide electrolyte.

The DSK electrode combines the high activity and insensitivity to impurities of Raney Nickel catalyst powder with the mechanical strength and electrical conductivity of a normal sintered metal electrode. The oxygen electrode has a similar design and is made from silver or nickel into which a highly active silver

catalyst is imbedded.

The hydrogen electrodes are made by first alloying nickel and aluminum (or zinc) in equal parts and pulverizing the brittle alloy. The powder is then mixed with 5 μ nickel carbonyl powder (2 carbonyl: 1 nickel-aluminum alloy). The mixture is then pressed and sintered at 650 to 700°C for one-half hour. The inactive aluminum or zinc is then removed electrochemically with potassium hydroxide at low temperature (46, 47). The high activity of the Raney Nickel is due to the 3d shell electron vacancies previously occupied by the aluminum or zinc (46). This procedure produces a macro-skeleton of pressed and sintered carbonyl grains. The micro-pores of the supporting skeleton contain catalytically active Raney Nickel.

A unique feature is claimed for these electrodes. All pores of the electrodes are of approximately the same size because of the special manufacturing process. The electrodes so constructed contain about 10^5 pores per square centimeter of electrode area. The pores are of very uniform diameter. These equilibrium pores prevent bubbling of the gas into the electrolyte because of random sized pores (46).

One intermediate step due to the active electrodes is the formation of a metastable nickel hydride (Ni-H). This mechanism results in the cell having a fuel storage capacity in the form of the Ni-H and the cell will produce current for some time after the fuel supply is discontinued. The storage capacity of the DSK hydrogen electrode is 125 ampere-hours per pound of electrode (45).

Because of this storage capacity, it is possible to discharge the DSK hydrogen electrode at current densities up to 700 amperes per square foot of electrode area for some time during peak current demand periods.

Justi has studied other applications of his DSK electrodes using metals other than nickel. Most of this work is in the early development stage and few results are known. Some of the systems studied include alcohols and heavier paraffin hydrocarbon liquids mixed with the electrolyte. The active DSK electrodes dehydrogenate the fuel to allow hydrogen to react electrochemically with the electrolyte. Only very low current densities and cell lives of a few hours have been achieved (46).

Very little operating data are available on this cell. In construction it is similar to the Union Carbide cell with the exception of the electrodes. Figure 10 shows a current-voltage curve for a DSK cell. Table IV lists the available operating characteristics.

TABLE III

OPERATING CHARACTERISTICS

UNION CARBIDE LOW TEMPERATURE AND PRESSURE

HYDROGEN-OXYGEN FUEL CELL

Anode Material	Porous Carbon and Metal Catalysts
Cathode Material	Porous Carbon and Metal Catalysts
Fuel	Hydrogen
Oxidant	Oxygen and Air
Electrolyte	50 Per Cent Potassium Hydroxide
Operating Temperature (°C)	50 - 60
Operating Pressure (atm.)	1 - 5
Open Circuit Voltage (Volts)	0.95 - 1.02
Operating Voltage (Volts)	0.95 - 0.6
Current Density (amperes/ft ²)	90 - 450
Power to Weight Ratio (Watts/Lb)	2 - 3
Power to Volume Ratio (Watts/ft ³)	200 - 300
Operational Life	Thousands of Hours
Energy Efficiency (Per Cent)	65 - 70
Starting Time	Short

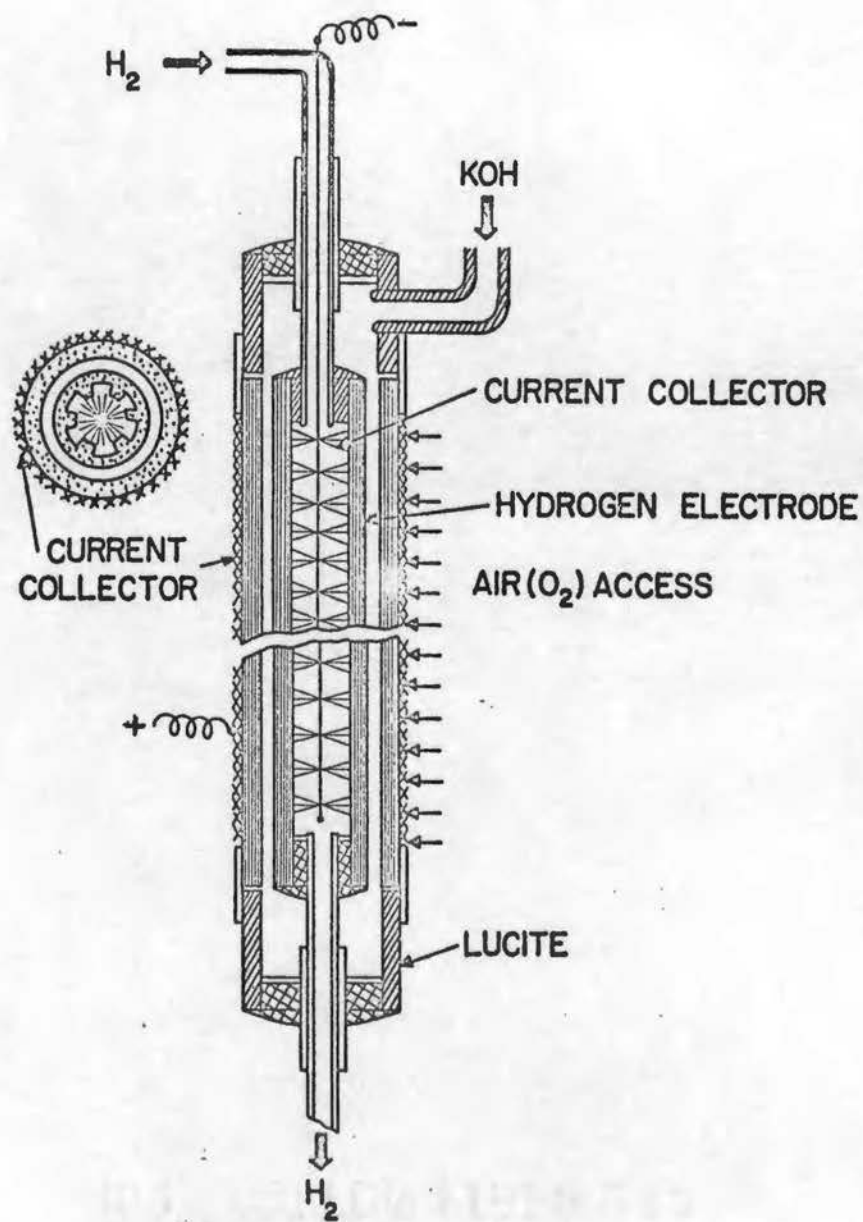


Figure 9

Union Carbide Low Temperature and
Pressure Hydrogen-Oxygen Fuel Cell

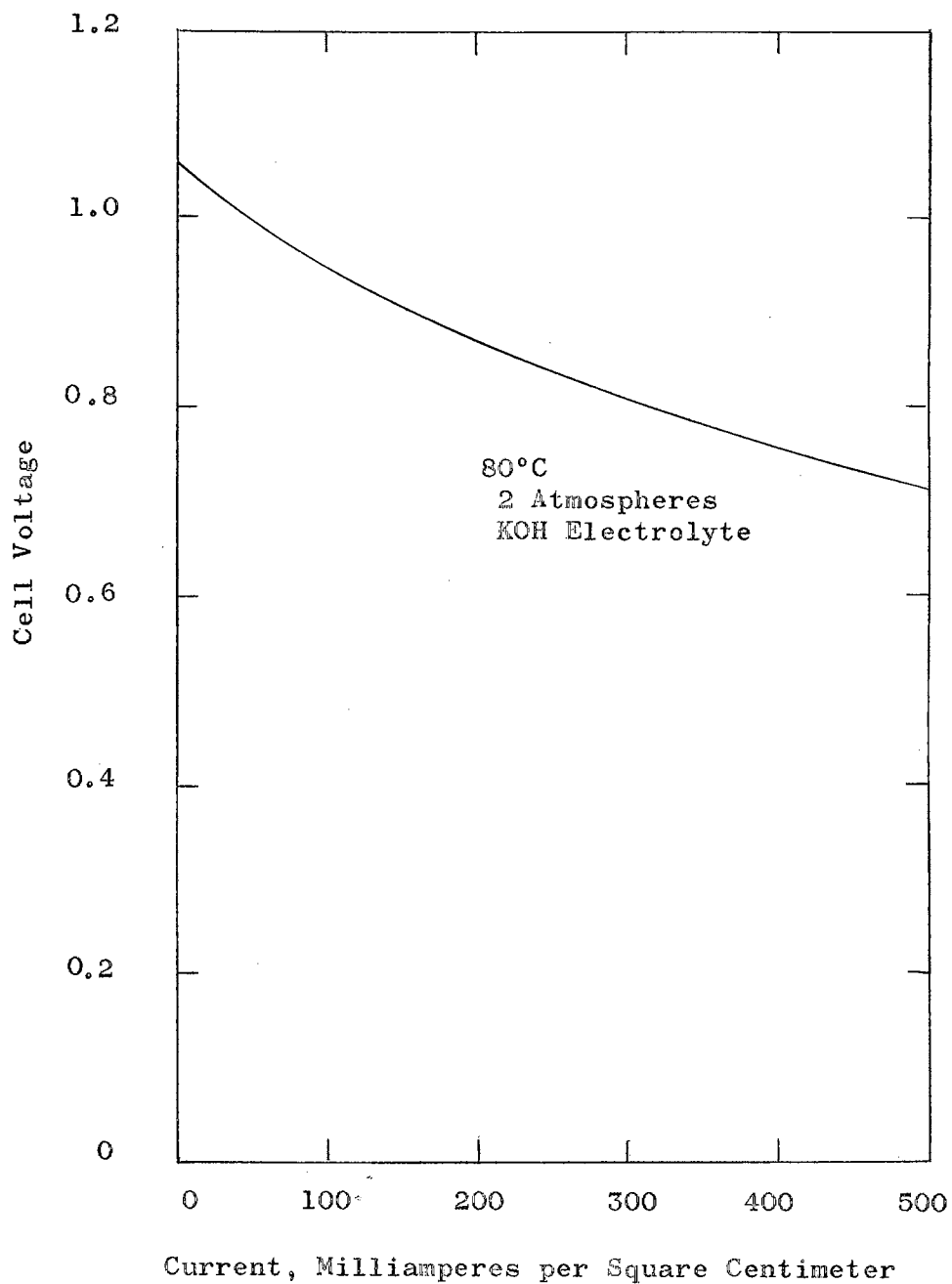


Figure 10

Low Temperature Low Pressure Metal
Electrode Hydrogen-Oxygen Fuel Cell

TABLE IV

OPERATING CHARACTERISTICS
 JUSTI LOW TEMPERATURE AND PRESSURE
 HYDROGEN-OXYGEN FUEL CELL

Anode Material	DSK - Nickel Catalyst
Cathode Material	DSK - Silver Catalysts
Fuel	Hydrogen
Oxidant	Oxygen
Electrolyte	Potassium Hydroxide
Operating Temperature (°C)	80 - 90
Operating Pressure (atm.)	1 - 5
Open Circuit Voltage (Volts)	1 - 1.1
Operating Voltage (Volts)	0.8 - 0.9
Current Density (amperes/ft ²)	200
Power to Weight Ratio (Watts/Lb)	---
Power to Volume Ratio (Watts/ft ³)	---
Operational Life	---
Energy Efficiency (Per Cent)	70
Starting Time	Short

Intermediate Temperature, High

Pressure Hydrogen-Oxygen Fuel Cell (Bacon Cell)

The intermediate temperature, high pressure fuel cell was initially developed by Bacon (5, 6, 7). Bacon began investigation of this type of cell in 1932, and by 1957 had successfully developed a high current density cell which operated at about 200°C and 400 psia on hydrogen and oxygen. Many other organizations including Leeson, Patterson Moos, and United Aircraft are currently working on this type of cell (2, 46, 57).

The electrodes are the major success of the Bacon cell. The intermediate temperatures increase the reaction rates, but require high pressure to keep from vaporizing the electrolyte. The high operating pressure makes it difficult to maintain a stable reaction zone. Bacon has minimized this difficulty by the use of dual porosity electrodes. The electrodes are constructed of porous sintered nickel with approximately 30×10^{-4} centimeter diameter pores on the gas side and 5 to 10×10^{-4} centimeter diameter pores on the electrolyte side. Figure 11 illustrates the Bacon dual porosity electrodes (2). Large differential pressures between the electrolyte and the gas are required for the interface to move from the small pores to the large pores (equation 20). These dual porosity electrodes make it possible to maintain a stable gas-liquid-solid interface at the high operating pressures. The electrodes are sintered on a 1/16" steel perforated plate for structural strength.

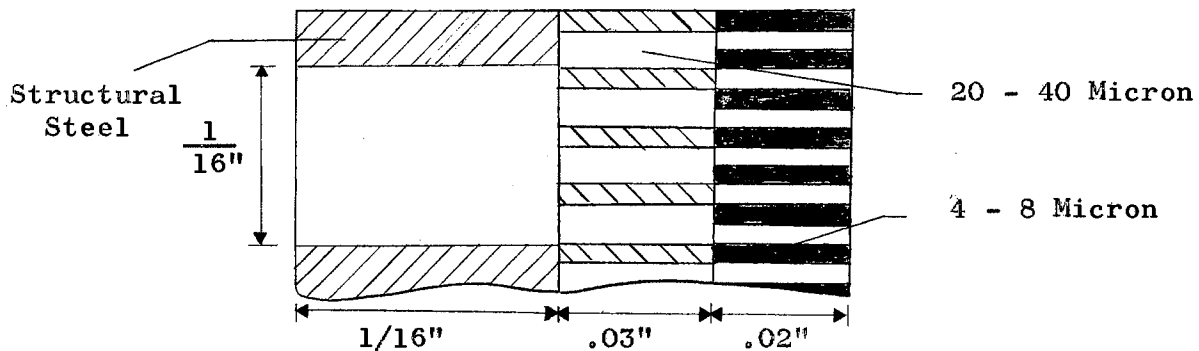


Figure 11
Bacon Type Electrode

The electrode mechanisms are identical with those of the Union Carbide Cell, (46).

The first Cell, developed in 1938, used activated nickel gauze electrodes in a potassium hydroxide electrolyte. The results were only fair. At that time, Bacon also investigated platinum, palladium, silver, and copper for electrode materials but discarded these in favor of nickel (5). Nickel electrodes were chosen because of superior performance during current drain, low cost, and good corrosion resistance.

The coarse pore layers of the hydrogen electrode are of Grade B carbonyl nickel powder (2 to 3 micron) mixed with about 20 per cent by weight 100-240 mesh ammonium bicarbonate which acts as a spacing agent. The mixture is pressed lightly and sintered for one-half hour at 850°C in a reducing atmosphere. The fine pore layer is then applied as a suspension of grade A carbonyl nickel powder (4 to 5 micron) in alcohol, then sintered for one-half hour at 800°C (5).

The hydrogen electrodes are activated by impregnation with a strong nickel nitrate solution, followed by roasting

in air at 400°C, and then reduction in a hydrogen atmosphere at about 400°C. The coarse pore layers of the oxygen electrodes are of grade D carbonyl powder (7 to 9 micron) mixed with 15 to 20 per cent by weight 100-240 mesh ammonium bicarbonate. The mixture is pressed and sintered for one-half hour at 1000 to 1150°C in a reducing atmosphere. The fine pore layer is applied as a suspension of grade A carbonyl nickel powder (4 to 5 micron) and then sintered for one hour at 950 to 1000°C.

The oxygen electrodes are impregnated with a dilute lithium hydroxide solution and then pre-oxidized in air at 700 to 800°C. A standard procedure for activating the oxygen electrode has not been established.

Serious difficulty originally arose due to gradual corrosion of the oxygen electrodes. This corrosion caused a decrease in cell performance and finally a complete cell breakdown.

Samples of nickel pre-oxidized in air at 800°C were found to be extremely resistant to corrosion in a strong potassium hydroxide solution, but the green oxide layer formed during preoxidation acts as an electrical insulator. When lithium atoms are included, pre-oxidation produces a black double oxide of nickel and lithium which acts as a semiconductor.

Using this corrosion prevention technique, oxygen electrodes have been in operation for as long as 1500 hours at 200°C without failure and with very little reduction in cell performance. Corrosion inhibitors such as potassium silicate or potassium aluminate dissolved in the electrolyte were successful in preventing corrosion but greatly reduced the cell performance.

The body of the Bacon cell is of steel, internally coated with nickel. Figure 13 shows an illustration of a Bacon cell. Figure 12 presents a current-voltage curve of a Bacon type cell. Table V lists the operating characteristics of this cell.

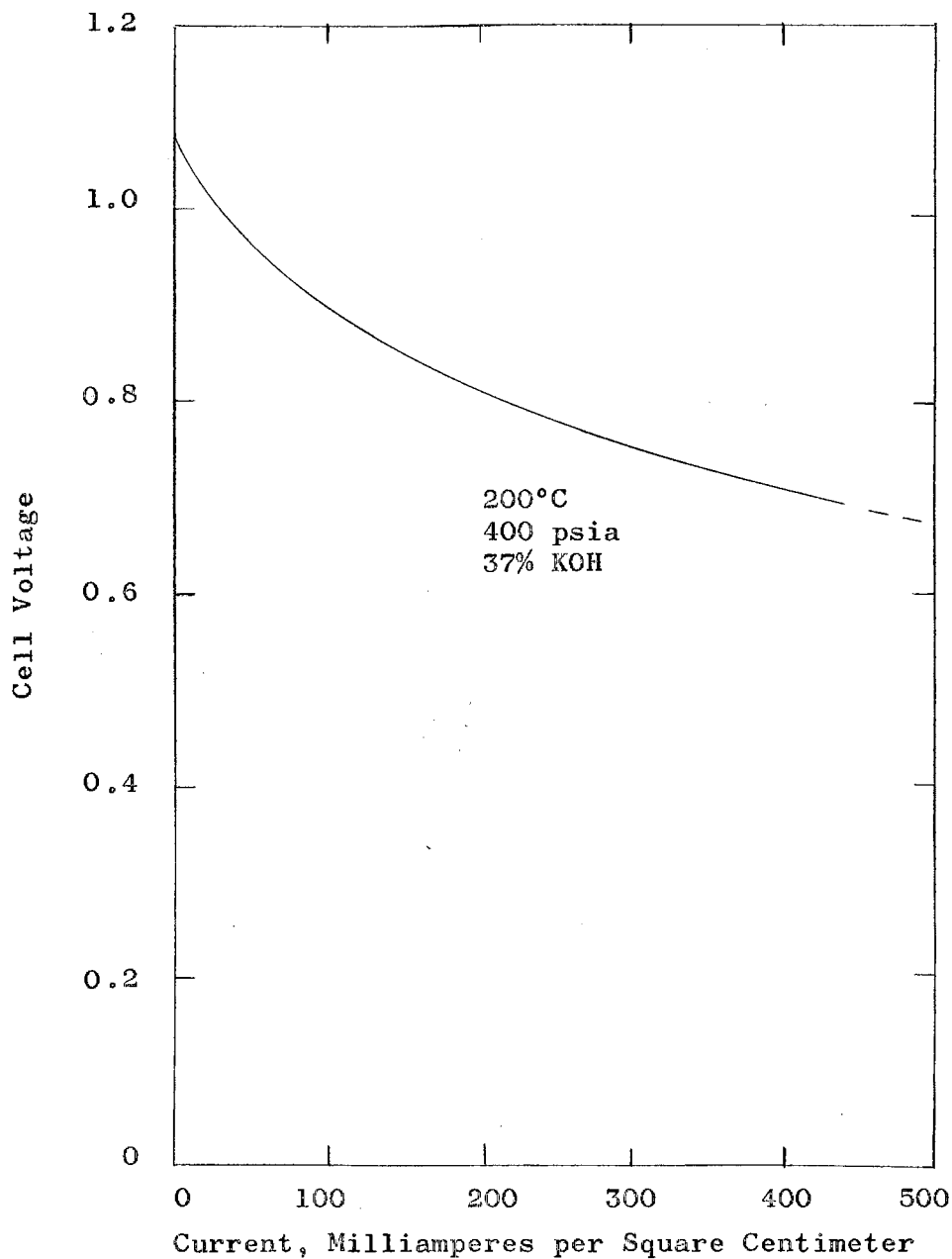


Figure 12

Moderate Temperature High Pressure
Hydrogen-Oxygen Fuel Cell (Bacon Cell)

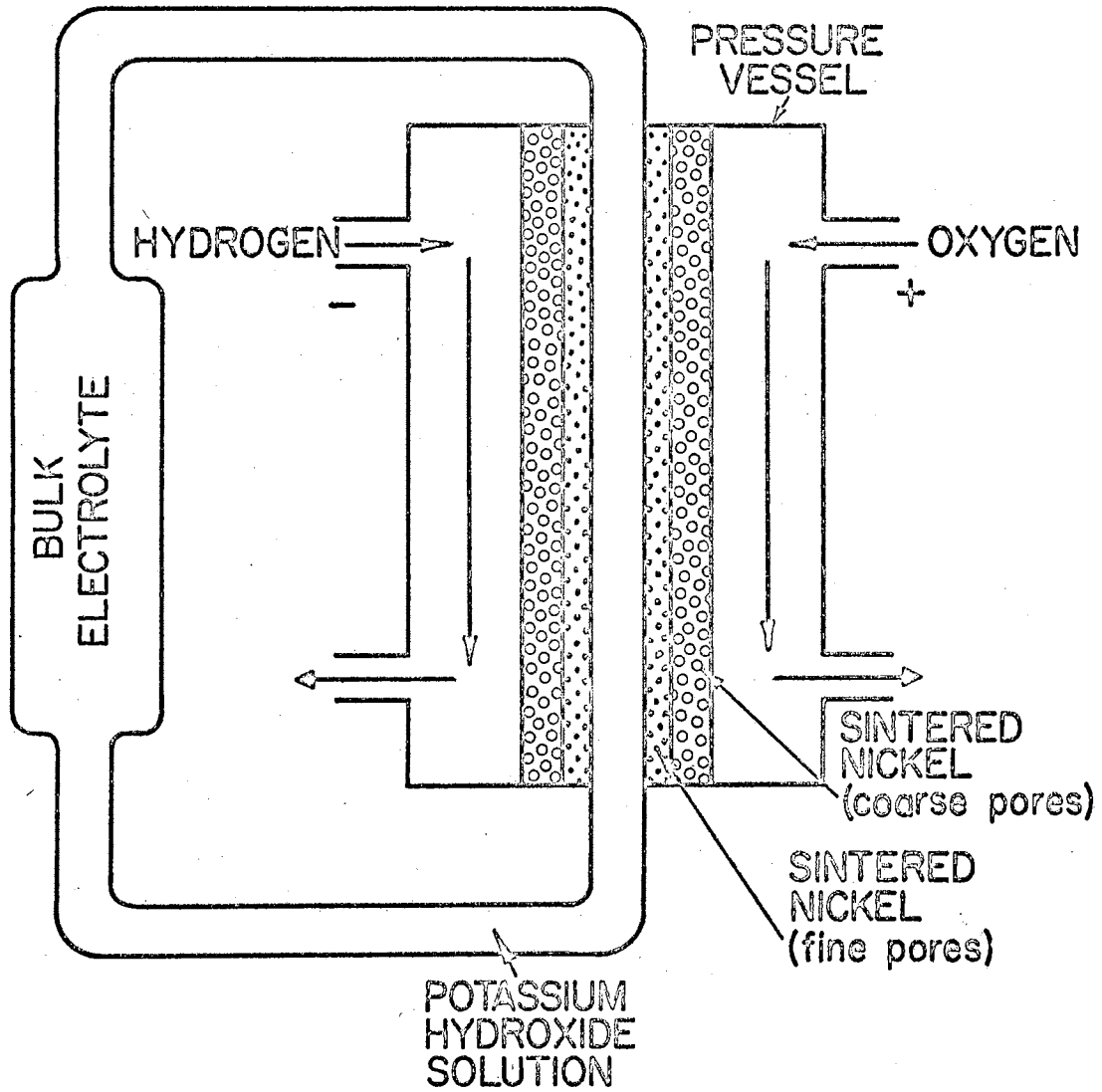


Figure 13

Bacon Moderate Temperature-High Pressure

Fuel Cell

TABLE V

OPERATING CHARACTERISTICS

BACON INTERMEDIATE TEMPERATURE

HIGH PRESSURE H₂-O₂ FUEL CELL

Anode Material	Dual Porosity, Porous Sintered Nickel
Cathode Material	Dual Porosity, Porous Sintered Nickel and Lithiated Nickel Oxide
Fuel	Hydrogen
Oxidant	Oxygen or Air
Electrolyte	26-37 Per Cent Potassium Hydroxide
Operating Temperature (°C)	200-240
Operating Pressure (atm.)	40-53
Open Circuit Voltage (Volts)	1.1
Operating Voltage (Volts)	1 - 0.6
Current Density (amperes/ft ²)	30-1000
Power to Weight Ratio (Watts/Lb)	15-20
Power to Volume Ratio (Watts/ft ³)	2000
Operational Life	1500 hours
Energy Efficiency (Per Cent)	to 80
Starting Time	Long

Intermediate Temperature - Low Pressure

Fuel Cell

An intermediate temperature low pressure fuel cell that operates on hydrogen and oxygen (or air) between 125 and 200°C and at atmospheric pressure has recently been reported by Elmore and Tanner (32).

Elmore and Tanner have investigated two cells, one using an alkaline electrolyte and one using an acidic electrolyte. Both are in an early experimental state.

The Alkaline Cell

The alkaline cell contains a paste electrolyte, consisting of 40 per cent sodium hydroxide, 40 per cent potassium hydroxide and 20 per cent calcium hydroxide. At the intermediate operating temperatures, this electrolyte retains only enough water to possess good electrical conductivity and rejects the remainder as vapor. There is no appreciable volume change due to this small water absorption.

The hydrogen electrode is palladium foil, 0.0005 inches thick. The oxygen electrode is a porous metal of silver powder with a du Pont 30 Teflon dispersion. The treated nickel powder is packed between two silver screens separated by a teflon gasket. The electrodes are separated by a teflon gasket. Figure 14 is a diagram of the alkaline cell, and Figure 16 shows a current-voltage curve.

The Acid Cell

The acid electrolyte cell uses a paste electrolyte of 35 per cent phosphoric acid and 65 per cent silicon dioxide. Unlike sulphuric acid, phosphoric acid is not reduced electrochemically under the cell operating conditions.

The electrodes are either platinum or palladium powders with a teflon dispersion. The catalyst dispersion is bonded on porous carbon electrodes. This type of cell has been operated continuously for six months at 90 milliamperes per square centimeter and 0.25 volts with no apparent cell deterioration.

Figure 15 shows a diagram of the acid cell. Figure 16 presents voltage current curves for these two cells. Several other organic fuels were used in the acid cell which resulted in about one-half the performance of hydrogen. These fuels were all reported to be oxidized to hydrogen which reacted electrochemically. No other data are presently available on these cells.

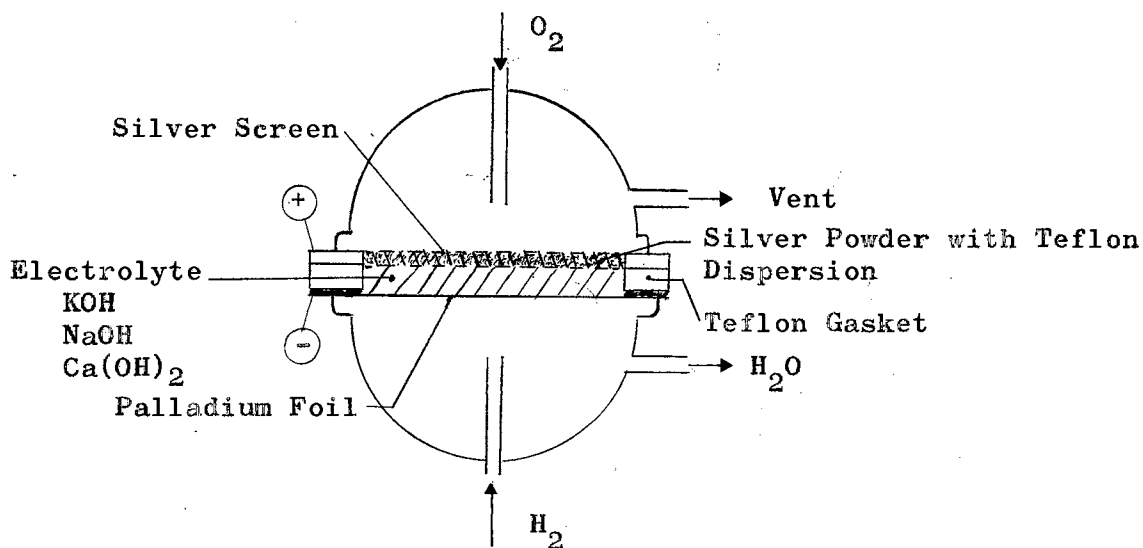


Figure 14

Alkaline Cell

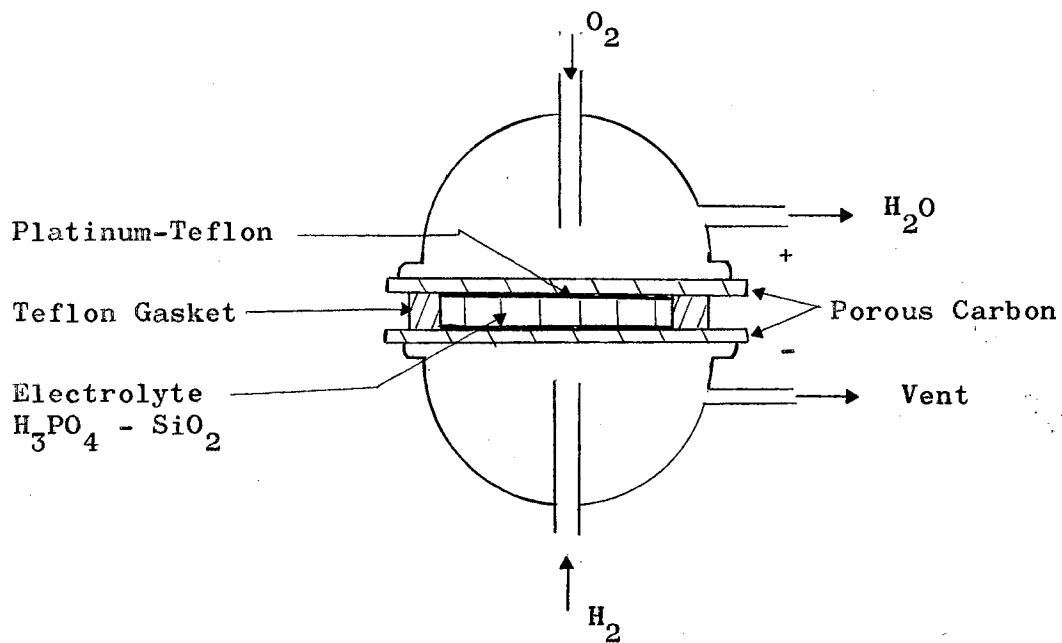


Figure 15

Acid Cell

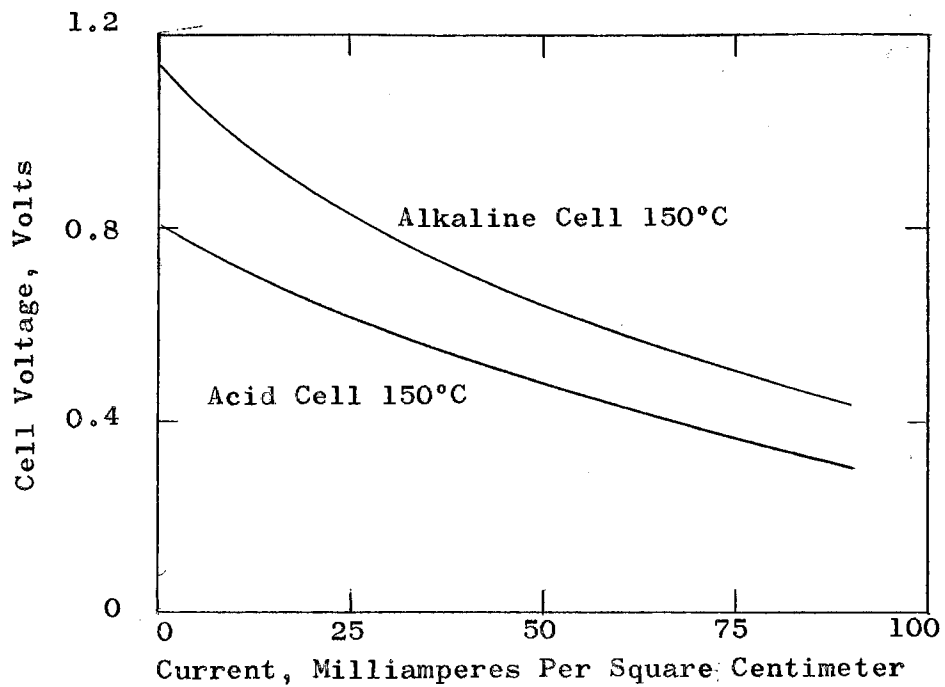


Figure 16

Hydrogen Oxygen Intermediate Temperature
Low Pressure Cell

Ion Exchange Membrane Fuel Cells

Hydrogen oxygen fuel cells based on an ion exchange electrolyte were first described by Grubb (42) in 1957. In 1959 the General Electric Company began development of this type of cell and have made considerable progress under the direction of Niedrach, Cairns, and Douglas (19, 43, 60).

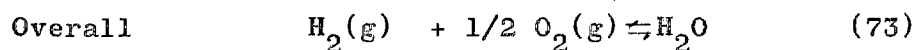
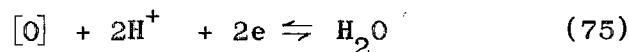
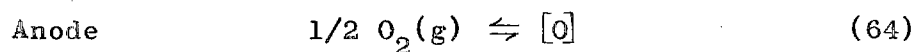
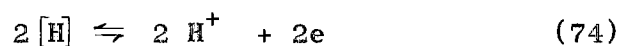
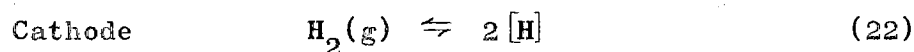
The ion-exchange fuel cell is similar to the standard hydrogen-oxygen fuel cell with the exception that the liquid electrolyte is replaced by an ion-exchange resin membrane. The essence of the ion-exchange membrane is the bonding of thin layers of electrode material and catalyst on the surfaces of the membrane electrolyte. The electrolyte is a thin sheet (0.03 inches) of a phenolsulfonic acid-formaldehyde membrane on a polyethylene matrix (2, 19). The cell is enclosed between lucite plates.

A favorable characteristic of this type of electrolyte resin is that it has a definite water saturation and absorbs only a limited quantity of the water produced by the electrode reactions. After reaching the saturation limit, excess water is rejected through the porous electrodes. This limited water saturation gives the resin electrolyte an advantage over aqueous electrolytes which tend to become diluted when operated over an extended period of time.

The electrodes for this cell consist of thin layers of porous sintered nickel treated with platinum or palladium. The platinum and palladium catalyze the electrode reactions. Catalyst loadings are in the range of 0.003 to 0.022 grams of catalyst per

square centimeter of electrode surface (19). The cells exhibit a definite catalyst saturation point at which further addition of catalyst produces no increase in cell performance other than that caused by decreased electrical resistance in the electrode material (19).

The ion exchange resin in this cell is acidic in nature and ionized hydrogen is transported across the electrolyte. This causes the water formation reaction to occur at the oxygen electrode which is the reverse of the aqueous alkaline electrolyte cells. The electrode reactions for this cell are:



An advantage of the water formation occurring at the oxygen electrode is that when air is used as the oxidant high circulation rates may be obtained to evaporate the water at a minimum of cost.

Ion exchange membrane fuel cells operate at low temperature (25°C) and atmospheric pressure. Air operation does not reduce the performance significantly from that obtained with pure oxygen, but only low current densities are obtained (19).

A major problem area of this cell is the electrode-electrolyte bonding. The properties of the resin which can be readily measured do not necessarily give an accurate index of the performance of the resin in the fuel cell. In addition to the properties such as water

saturation, physical strength, and electrolyte resistivity, the bonding properties of the electrolyte to the electrode and the catalyst are major factors in determining the cell performance.

While little is known about the membrane-catalyst electrode reaction mechanisms in this type of cell, it is believed that the resistance to ion transfer between the reaction zone and the membrane may be the controlling factor preventing operation at higher current densities (2).

The main life limiting factor for this cell is the degradation of the resin. This is thought to be due to oxidation of low molecular weight components in the resin (19). After extended operation the degradation eventually causes the electrolyte to develop a pinhole which causes cell failure. General Electric has operated this type of cell continuously for more than 100 days with no sign of deterioration.

Figure 17 shows a general diagram for an ion exchange cell. Operating characteristics of an experimental cell are given in Table VI. Figure 18 is a current voltage curve for an experimental cell.

The General Electric Company has developed a portable power pack for the United States Army which uses this type of cell (57). The power pack is fueled by a metal hydride hydrogen generator. Including the hydride source, the total weight of the pack is less than 25 pounds. It is rated at 30 watts. No other information is available on this power pack.

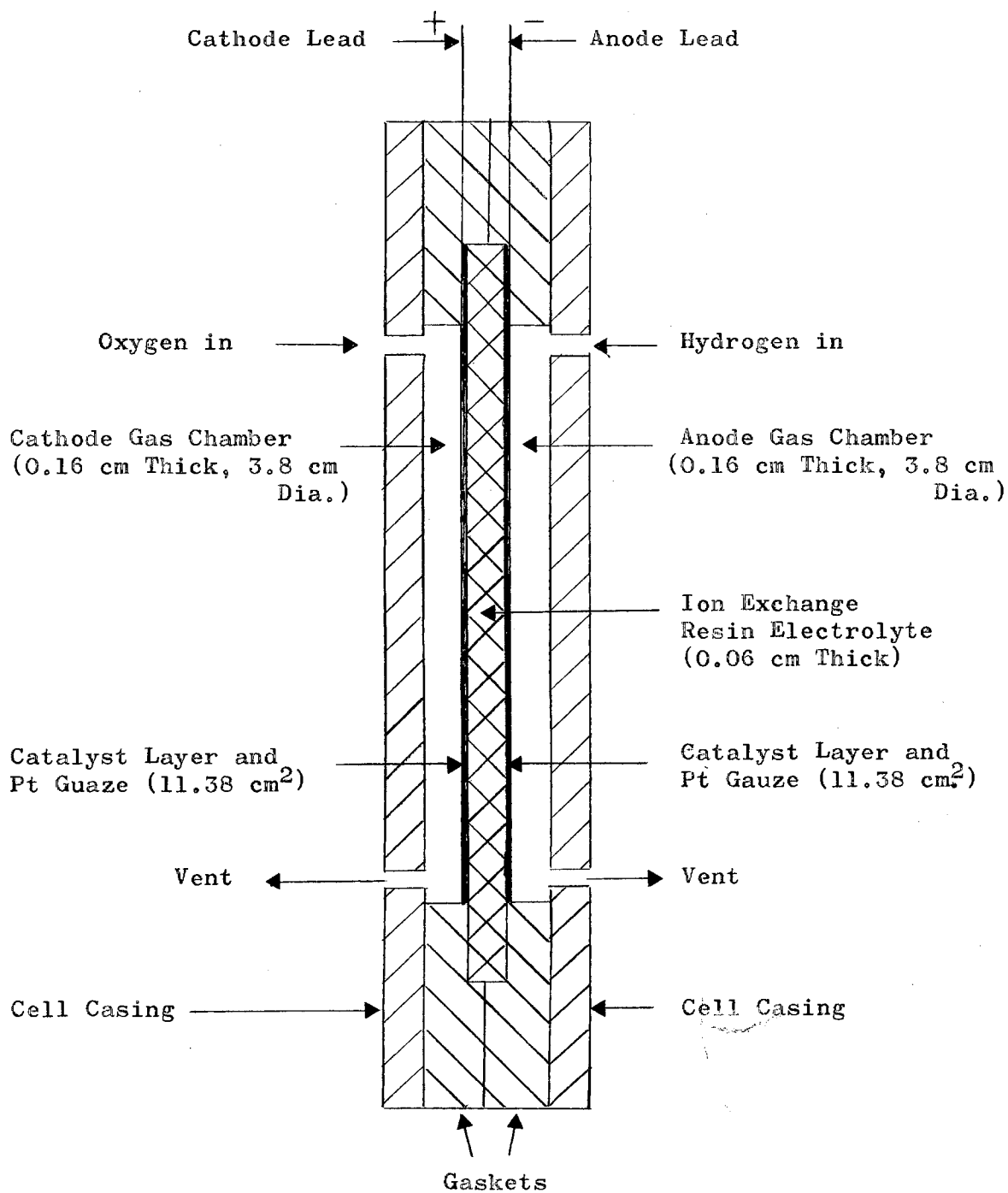
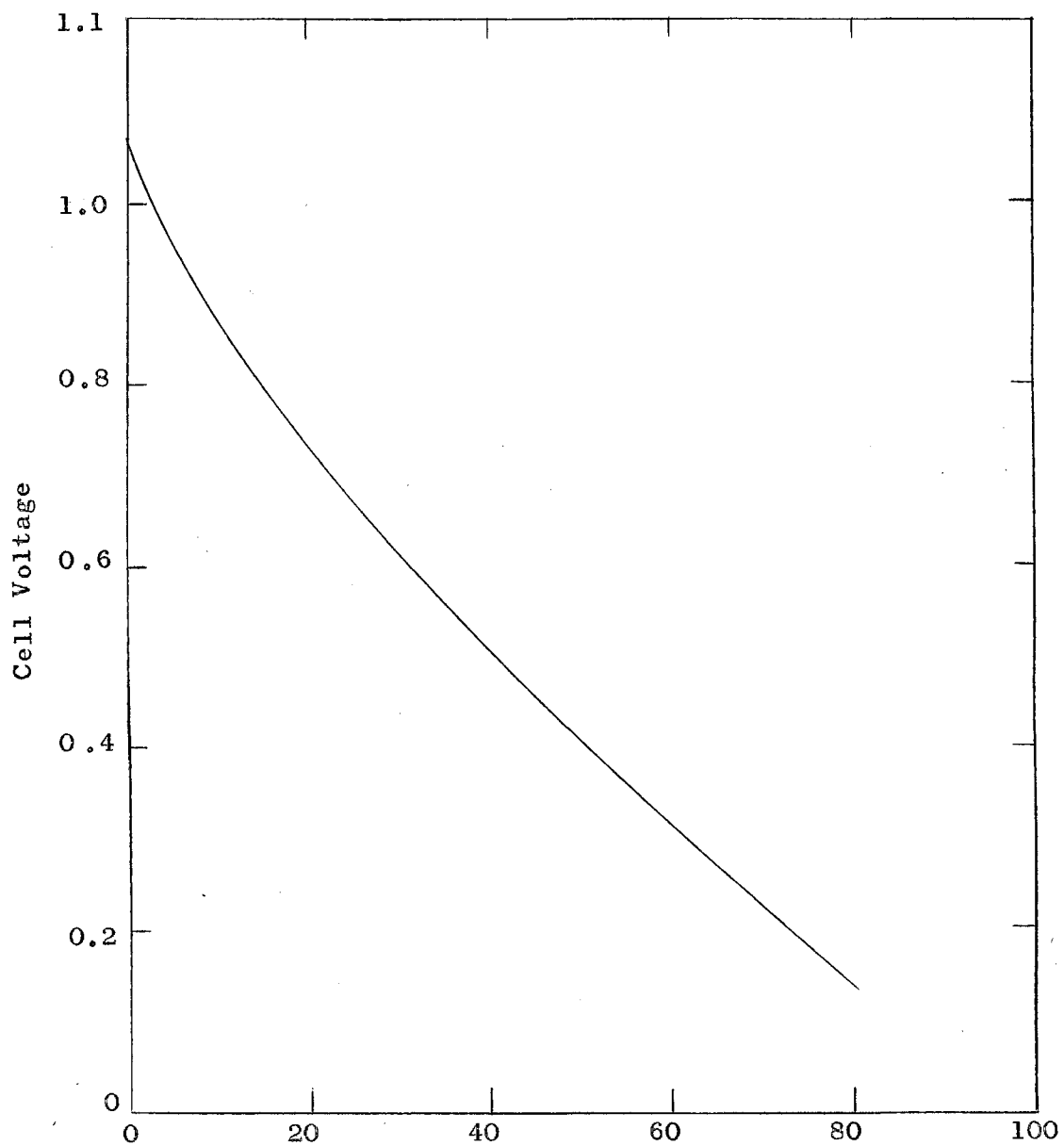


Figure 17

General Electric Ion Exchange Fuel Cell



Current, Milliamperes per Square Centimeter

27°C, 1 Atmosphere Platinum Catalyst

Figure 18

Hydrogen-Oxygen
Ion-Exchange Fuel Cell

TABLE VI
 OPERATING CHARACTERISTICS
 GENERAL ELECTRIC ION EXCHANGE ELECTROLYTE
 FUEL CELL

Anode Material	Nickel Grid and Platinum Catalyst
Cathode Material	Nickel Grid and Platinum Catalyst
Fuel	Hydrogen
Oxidant	Oxygen or Air
Electrolyte	Cation Exchange Resin Membrane
Operating Temperature (°C)	20 - 100
Operating Pressure (atm.)	1
Open Circuit Voltage (Volts)	1.08
Operating Voltage (Volts)	1 - 0.6
Current Density (amperes/ft ²)	3 - 45
Power to Weight Ratio (Watts/Lb)	10 - 20
Power to Volume Ratio (Watts/ft ³)	150 - 1000
Operational Life	---
Energy Efficiency (Per Cent)	to 75
Starting Time	Short

Dissolved-Fuel Fuel Cell

Justi (25, 46) several years ago undertook research on fuel cells where liquid fuels would be dissolved in the cell electrolyte. Justi suggested the use of such fuels as methanol, diesel oil, and other light hydrocarbons (2, 46). Justi has attempted to use his DSK electrodes for this type of cell, the scheme being that the highly active DSK electrodes dehydrogenate the liquid fuel to allow hydrogen to react electrochemically with the electrolyte. Only low current densities and a life of a few hours have been achieved (46).

More recently, Monsanto Chemical Company and Esso Research and Engineering have undertaken similar but independent research programs (2).

Although practical cells have not been obtained, fuel electrode experiments with dissolved methanol and ethane have been encouraging. This success has been due largely to the development of effective fuel and oxidant catalysts (2).

Esso Research and Engineering has recently shown that a saturated hydrocarbon, in particular ethane, can be oxidized electrochemically to carbon dioxide at relatively mild temperatures and pressures (72). Table VII shows results of the oxidation of ethane to carbon dioxide in an aqueous electrolyte (72).

The results shown in Table VII indicate that a large per cent of the fuel and oxygen consumed are used for the electrical energy producing reaction and that the amount of electrical current is very close to the theoretical. Studies at Monsanto Chemical Company have shown similar results with methanol (2).

No operating data on these experimental fuel cells are available at the present time (2, 72).

In a dissolved-fuel fuel cell, the fuel is mixed in the electrolyte. The fuel electrode could be a flat plate or porous plate impregnated with the catalyst while the oxygen electrode is a standard gas diffusion electrode. These cells are in the early experimental state, but show good promise because of cheap fuel and moderate operating conditions.

TABLE VII

ESSO DISSOLVED-FUEL

FUEL CELL (72)

Per Cent O₂ Reacted in

Electrochemical Reaction	93
Chemical Oxidation	7
Corrosion	0

Per Cent Carbon Reacted to Form

CO ₂	97
Formic Acid	3

Electron Yield/Molecule

Observed	13.8
Theoretical	14.

Regenerative Fuel Cells

Regenerative type fuel cell systems are those in which the reactants are continuously regenerated from the products formed during the cell reaction (57). There are two types of regenerative fuel cells, the chemical regenerative and the thermal regenerative.

The Chemical Regenerative (Redox)

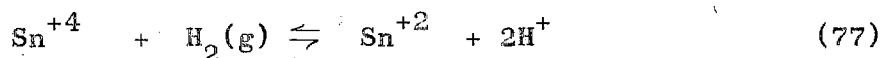
The chemical regenerative or Redox fuel cell employs an intermediate reductant and oxidant which are chemically regenerated in an external cycle by the primary fuel and oxidant. The intermediate reductant in a liquid electrolyte reacts at the anode in the conventional manner. After the electrochemical reaction the reaction products are passed through an external circuit in which the reaction products are reacted with the primary fuels to reform the intermediate reductant. A similar procedure is followed by the intermediate and primary oxidant.

Figure 19 illustrates a chemical regenerative fuel cell system (57, 84). The theoretical mechanisms occurring in this system are (84):

Anode: (HCL electrolyte)



Anode Regeneration Process



Overall Anode Reaction



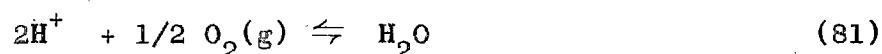
Cathode: (HBr electrolyte)



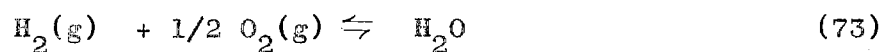
Cathode Regeneration Process



Overall Cathode Reaction



Overall Cell Reaction



To obtain proper operation of this cell, continuous recycling of the intermediate reductant and oxidant is necessary. Also, a method of removing the products of the overall cell reaction is required.

The two electrolytes used for this type of fuel cell are commonly referred to as the catholyte and the anolyte (49, 57). The catholyte is the electrolyte containing the intermediate oxidant and the anolyte contains the intermediate reductant. The anolyte and catholyte are physically separated by an ion-exchange membrane which allows the migration of a particular ion but does not allow mixing the two electrolytes.

Early investigators of this type of cell were Rideal (66) in 1921 and later Posner (63) in 1955. The major difficulties of this cell have been the selection of suitable intermediates, electrolytes and membranes (49, 82). The multiple mechanisms

that occur in this type of cell system increase the difficulty of finding suitable components.

The electrodes of this cell are inert (50). They are constructed of porous metal (platinum, nickel) or carbon.

Current work on this cell is being done at Kings College, London and the General Electric Company (50, 57).

The General Electric Company has developed a chemical regenerative fuel cell using titanous-titanyl and bromine-bromide couples (50). The anolyte is hydrogen chloride and the catholyte is hydrogen bromide. The primary fuel is hydrogen. The primary oxidant is oxygen and NO_2 . The electrodes are graphite, catalyzed by palladium black. The cell operates at low temperatures and pressures.

The primary advantage of this type of cell is the ability to operate on impure hydrogen. Also the elimination of an alkaline electrolyte which avoids contamination by carbon dioxide, and the use of air as the primary oxidant.

The operating characteristics of the General Electric chemical regenerative fuel cell are shown in Table VIII.

The Thermal Regenerative Fuel Cell

The thermal regenerative fuel cell differs from the chemical regenerative fuel cell in that the reactants are continuously regenerated by thermal rather than chemical action.

The Mine Safety Appliance Research Corporation is the only organization to report results on this type of cell (21, 57).

TABLE VIII

OPERATING CHARACTERISTICS
 GENERAL ELECTRIC CHEMICAL
 REGENERATIVE-FUEL CELL

Anode Material	Porous Graphite, Platinized
Cathode Material	Porous Graphite, Platinized
Fuel	Hydrogen
Oxidant	Oxygen or Air
Electrolyte	Anolyte Ti^{+3} - TiO^{+2} Catholyte Br^{-1} - Bi^{+2}
Operating Temperature ($^{\circ}C$)	80-85
Operating Pressure (atm.)	1
Open Circuit Voltage (Volts)	0.96
Operating Voltage (Volts)	0.8
Current Density (amperes/ft ²)	40
Power to Weight Ratio (Watts/Lb)	8
Power to Volume Ratio (Watts/ft ³)	300-400
Operational Life	One Week
Energy Efficiency (Per Cent)	to 80
Starting Time	---

The thermal regenerative cell of the Mine Safety Appliance Research Corporation uses metal hydrides as the fuel and oxidant. The electrolyte is a metal fluoride and metal chloride eutectic mixture. The metal hydride is formed in the fuel cell by the electrode reactions and is then cycled to an external thermal generator in which the hydride is decomposed to the metal and hydrogen. The metal and gaseous hydrogen are then recycled to the cell. The mechanisms occurring are

Anode



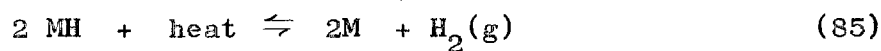
Cathode



Overall Cell Reaction



Regeneration Process



Mine Safety Appliance has operated thermal regenerative cells using lithium, sodium, potassium and calcium hydrides. The electrolytes have been molten eutectic mixtures of lithium chloride-lithium fluoride, lithium chloride-potassium chloride, and various other alkali metal halide electrolytes (21).

Figure 20 is an illustration of a Mine Safety Appliance thermal regenerative cell operating on lithium hydride.

The hydrogen electrode (cathode) consists of a porous gas diffusion metal electrode. Stainless steel and nickel have both proven successful as hydrogen electrodes. The anode or the

alkali metal electrode consists of the metal itself supported by a stainless mesh.

This cell operates in the temperature range of 400°C and the regenerator in the range of 850°C depending upon the particular hydride used. Decomposition temperatures of several hydrides are given in Table IX.

The major disadvantage of this type of fuel cell is the inclusion of a heat engine in the regeneration cycle. This heat cycle is necessarily governed by the Carnot Cycle Efficiency which must be included in the overall fuel cell system efficiency. The fuel cell efficiency is distinct from the regenerator or the overall efficiency.

The inclusion of the heat cycle decreases the attractiveness of the thermal regenerative fuel cell and reduces the overall efficiency to ranges that are obtained by conventional means (57). Table X lists the operating characteristics of the Mine Safety Appliance fuel cell.

TABLE IX

HYDRIDE DECOMPOSITION TEMPERATURES AT ONE ATMOSPHERE

Hydride	Formula	Decomposition Temperature °C
Lithium Hydride	LiH	850
Sodium Hydride	NaH	425
Potassium Hydride	KH	430
Calcium Hydride	CaH ₂	985

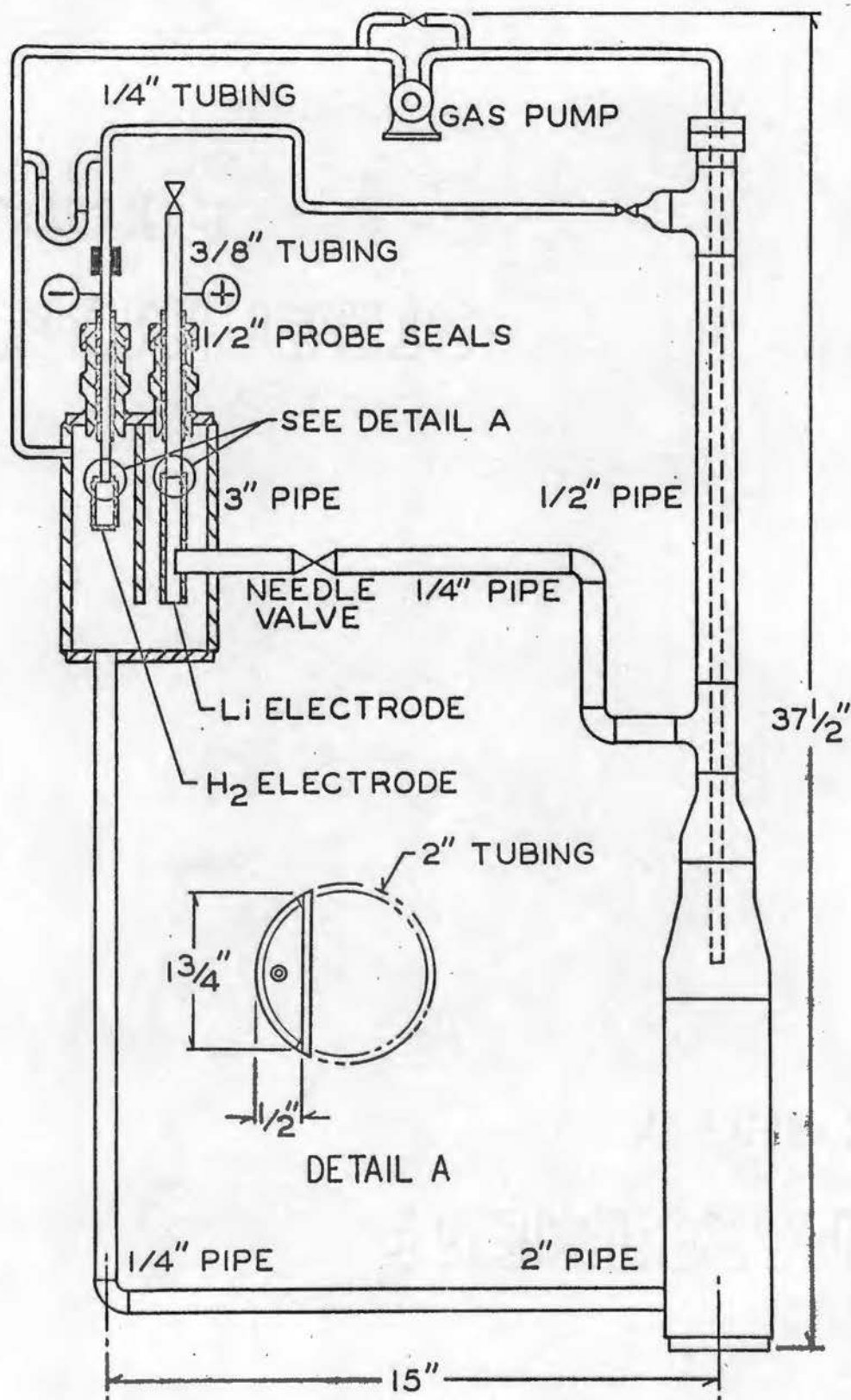


Figure 20

Thermal Regenerative Fuel Cell

TABLE X

OPERATING CHARACTERISTICS

MINE SAFETY APPLIANCE THERMAL REGENERATIVE CELL

Anode Material	Molten Lithium
Cathode Material	Porous Metal
Fuel	Molten Lithium
Oxidant	Hydrogen (gaseous)
Electrolyte	Molten Lithium Halides
Operating Temperature (°C)	450 Cell (850 Regenerator)
Operating Pressure (atm.)	1
Open Circuit Voltage (Volts)	0.3 - 0.66
Operating Voltage (Volts)	0.36 - 0.4
Current Density (Amperes/ft ²)	to 150
Power to Weight Ratio (Watts/Lb)	2
Power to Volume Ratio (Watts/ft ³)	90
Operational Life	---
Energy Efficiency (Per Cent)	Overall 10-12
Starting Time	---

Consumable Electrode Fuel Cells

The consumable electrode fuel cell is based upon the continuous consumption of materials which function in the dual capacity of both fuel and anode. Most units combine one consumable electrode, a liquid electrolyte and a gas diffusion electrode, although other arrangements are possible.

M. W. Kellogg, Union Carbide, Aerojet General, RCA, and Armour Research are conducting research on this type of cell (2, 57). There is no question regarding the feasibility of these cells (57).

The Sodium Amalgam Fuel Cell

The sodium amalgam fuel cell was originally developed at Western Reserve University in 1953 (2). Union Carbide and the M. W. Kellogg Company have reported the most advanced cells (2, 57, 58).

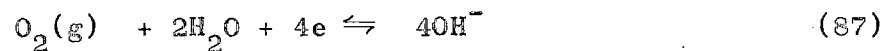
The sodium amalgam fuel cell uses sodium as fuel and oxygen or air as the oxidant. The sodium is introduced to the cell as a dilute sodium-mercury amalgam to reduce the high reactivity of sodium. The sodium amalgam electrode consists of a flat stainless steel plate down which a thin layer of the sodium amalgam flows. The oxygen electrode is a standard porous gas diffusion electrode of carbon or sintered metal powder. The electrodes are separated by an aqueous sodium hydroxide electrolyte. Figure 21 is a sketch of an M. W. Kellogg fuel cell (58).

The electrode mechanisms occurring in this cell are (57, 58).

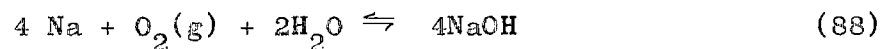
Anode



Cathode



Overall Cell Reaction



Water is consumed in the cell reaction and must be continuously supplied to the cell. Sea water has proven satisfactory for this purpose (57).

A major disadvantage of this cell is the elaborate methods required to add the raw sodium to the mercury.

Aerojet General has developed a similar cell using zinc as the anodic fuel, chlorine gas as the oxidant, and sea water as the electrolyte (2, 57).

Operating characteristics of the Union Carbide sodium amalgam fuel cell are given in Table XI.

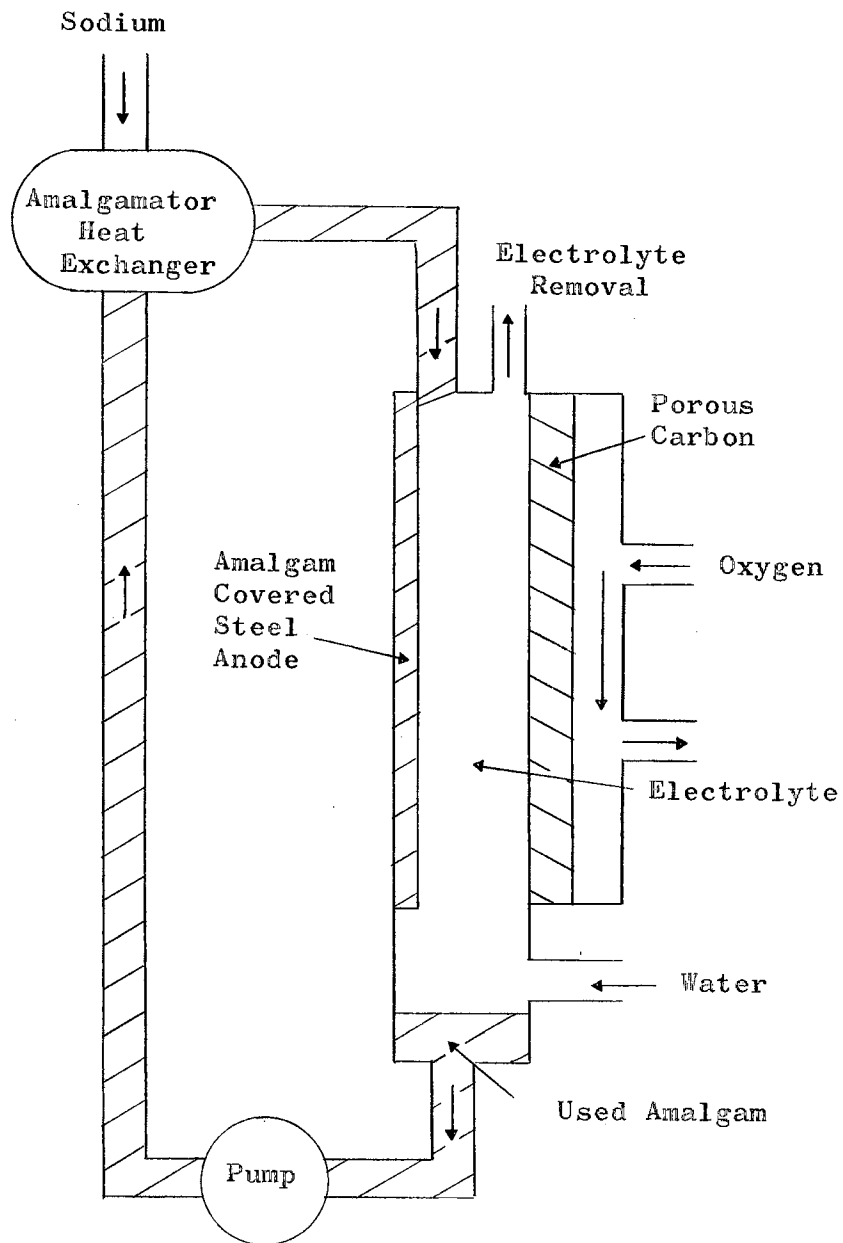


Figure 21
Sodium Amalgam Fuel Cell

TABLE XI

OPERATING CHARACTERISTICS
UNION CARBIDE SODIUM-AMALGAM
FUEL CELL

Anode Material	Steel Plate
Cathode Material	Porous Carbon
Fuel	Sodium, (5% Sodium Amalgam)
Oxidant	Oxygen
Electrolyte	5 N NaOH
Operating Temperature (°C)	45°
Operating Pressure (atm.)	1
Open Circuit Voltage (Volts)	1.95
Operating Voltage (Volts)	1.76 - 1.21
Current Density (amperes/ft ²)	25 - 150
Power to Weight Ratio (Watts/Lb)	---
Power to Volume Ratio (Watts/ft ³)	2.8
Operational Life	8 Months at 100 amp/ft ²
Energy Efficiency (Per Cent)	---
Starting Time	---

Allis Chalmers Low Temperature and
Pressure Hydrocarbon Fuel Cell

Allis Chalmers, Union Carbide, and other organizations have developed low temperature fuel cells capable of using hydrocarbon fuel mixtures (2). Allis Chalmers has reported the most successful results for this type of fuel cell.

In October of 1959, Allis Chalmers exhibited an experimental fuel cell powered farm tractor (48). This event represented the first successful attempt to construct a practical vehicle powered by fuel cells.

The tractor was powered by 1008 fuel cells. The cells were arranged in 112 units. Each unit contained nine fuel cells, weighed approximately 17 pounds, and was approximately 12 x 12 x 2 inches. Each unit was encased in an epoxy resin material. The cells of each unit were connected in parallel. Each cell was capable of delivering 20 amperes at 0.7 volts and each unit 180 amperes at 0.7 volts (44, 48).

The units of the power plant were arranged in four banks of 28 units each. The 28 units in each bank were connected in parallel for gas flow and in series for electrical flow. Separate intake and exhaust manifolds were supplied for each bank of units.

The electrical connections from each bank were connected to a controller and relayed to a 20 hp D. C. electric motor. The controller provides different speeds by making various parallels and series connections of the four banks of units, which resulted in a performance range of 360 amperes at 40 volts to 180 amperes

at 80 volts (47).

The fuel for the tractor was a mixture of gases, believed to be hydrogen and propane (2, 46). The oxidant was bottled commercial oxygen although the cells have operated on air. Gas was introduced to the cells at a pressure of about 1/2 psig and an equilibrium temperature of about 140°F was reached (48). Excess fuel gas was used to expel water formed by the cell reactions.

Energy efficiencies of 50 to 60 per cent were obtained based on fuel BTU input versus electrical BTU output. The tractor delivered about 65 watt hours per pound, as compared to 10 watt hours per pound for the alkali battery, 15 watt hours per pound for the lead battery, and 56 watt hours per pound for the silver/zinc battery (46). The power plant alone weighed 2000 pounds, however no attempts were made to limit the total weight.

There is very little information available on the details of the individual fuel cells. It is believed that the electrodes were porous nickel, and the electrolyte either an aqueous potassium hydroxide absorbed in an asbestos matrix or an ion exchange resin (2, 46).

Table XII lists the available operating characteristics of the Allis Chalmers fuel cells.

Allis Chalmers is continuing research on fuel cells and the next vehicle planned is a 4000 pound fork lift truck (48).

TABLE XII

OPERATING CHARACTERISTICS

ALLIS CHALMERS HYDROGEN-PROPANE FUEL CELL

Anode Material	--
Cathode Material	--
Fuel	Hydrocarbon Gas Mixture
Oxidant	Oxygen
Electrolyte	--
Operating Temperature (°C)	140°F
Operating Pressure (atm.)	1
Open Circuit Voltage (Volts)	1.1
Operating Voltage (Volts)	0.7
Current Density (amperes/ft ²)	20
Power to Weight Ratio (Watts/Lb)	65
Power to Volume Ratio (Watts ft ³)	
Operational Life	--
Energy Efficiency (Per Cent)	50-60
Starting Time	--

High Temperature Fuel Cells

High temperature fuel cells operating in the temperature range of 500 to 900°C on gaseous fuels have been developed largely since World War I. The most devoted of the early investigators of this type of fuel cell were Baur and Pries (8, 9, 10) and later Davtyan (25).

Baur and Pries constructed a fuel cell using solid electrolytes. Their electrolytes were based on the Nernst Mass (85% ZrO_2 , 15% Y_2O_3) and similar mixtures (18). Davtyan also used a solid electrolyte consisting of monazite sand, sodium carbonate, soda glass, tungsten oxide, and clay.

The fuel cells of Baur, Pries, and Davtyan failed to produce promising results. This failure was primarily due to the electrolytes, which failed to possess sufficient electrolytic conductivity at reasonable temperatures and did not prove to be invariant against the reducing action of the coke or fuel gases such as hydrogen and carbon monoxide (18). These solid electrolytes were later found not to be true solid ionic conductors, but owed their conductivity to the presence of low melting eutectics in a solid porous matrix (21). The Davtyan cell also used reducible iron electrodes which catalyzed the formation of carbon and caused the further complications (18, 21).

Since the work of the early investigators, many others have undertaken the task of developing an efficient high temperature fuel cell. The main reason for the interest shown in this type of cell has been to eliminate large activation polarization

losses associated with low temperature cells. Also, the high operating temperatures make it possible to use low cost fuels such as the naturally occurring hydrocarbons, coal or their by-products which are unreactive at low temperatures.

There are several organizations and investigators currently working on high temperature fuel cells (2, 84). The more recent investigators include Broers and Ketelaar (15, 16, 17, 18), Gorin and Recht (36, 37, 38, 39), Chambers and Tantrum (20), Douglas (27, 28, 29), Skelcher (70), and DeZubay (26). In general, all of the current high temperature fuel cells are similar.

The ideal electrolyte for a high temperature fuel cell would be a solid ionic oxide with anion conductance (20). However, all of the oxides with well marked ionic structures have very high melting points. It is only at temperatures near their melting point that they show any reasonable ionic conductance (20). The next best thing to a pure oxide electrolyte is an electrolyte which transports oxygen containing ions.

A necessary demand for long-term operation of high temperature fuel cells is that both the electrolyte and the electrodes remain invariant (17). This demand was not met by the cells of Davtyan and Baur (17).

Molten alkali carbonate electrolytes have been found to be the best adapted electrolytes for high temperature fuel cells (17, 20, 26, 27, 37). Decomposition of the fused carbonate by the action of carbon dioxide is impossible and concentration polarization at the oxygen electrode can be reduced by supplying carbon dioxide to the cathode (17). With carbonate electrolytes,

the transfer of oxygen ions takes place in the form of carbonate ions.

Two methods of retaining the electrolyte between the electrodes have proven satisfactory (17, 20). One method is to impregnate a porous magnesium oxide disk with the electrolyte. The porous disk has pore sizes of about 25 microns in diameter and the electrodes have pore sizes of about 160 to 270 microns. Another method is to construct dual porosity electrodes similar to the Bacon electrodes (Figure 11). For this type of electrode the coarse pore sizes on the gas side are 160 to 270 microns in diameter and the fine pore sizes on the electrolyte side are 75 to 140 microns in diameter. Both methods produce very similar cell performances (20).

The electrodes in high temperature fuel cells are either metal powders supported by gauzes of the same material or porous sintered metals (2, 17, 20, 57). The materials used provide catalysis of the desired reactions. Table XIII lists several materials that have proven satisfactory as electrode materials. Figures 22 and 23 are diagrams of experimental fuel cells of Broers and Ketelaar (17), and Chambers (20).

A primary goal of high temperature fuel cells is the use of carbonaceous fuels. With all carbonaceous fuels there is the danger of solid carbon deposits (17, 20, 37).

The formation of carbon from carbon monoxide is catalyzed specifically by iron oxides and reducible iron compounds. When these materials are not used in the cell, no trouble is experienced (20).

With hydrocarbon vapors, carbon may be deposited by thermal cracking. This occurs with propane but not methane or kerosene, and has been effectively eliminated by adding steam or carbon dioxide to the fuel gas (17, 20).

TABLE XIII

ELECTRODE MATERIALS FOR HIGH TEMPERATURE

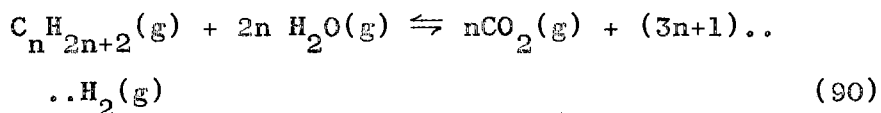
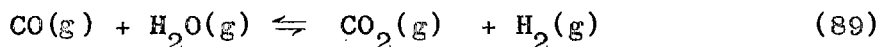
FUEL CELLS

Hydrogen	Platinum Palladium Nickel
Kerosene - Water	Nickel
Methane - Water	Nickel
Propane - Water	Nickel
Ethane - Water	Nickel
Carbon Monoxide	Platinum Nickel Cobalt
Oxygen-Carbon Dioxide	Silver Silverized Oxides

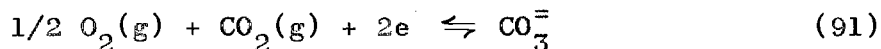
High temperature fuel cells have been operated on a variety of gaseous fuels such as carbon monoxide, hydrogen, methane, ethane, propane, kerosene, natural gas, and coal gas (17, 20, 37). The use of hydrocarbon fuels in high temperature fuel cells is enhanced by the combination of high temperatures, water vapor, and a nickel catalyst (17, 20). This combination promotes a multitude of reforming reactions in which hydrogen is formed (70). The production of hydrogen in the cell is an advantage since hydrogen is

the most galvanically reactive gas. Also, the diffusion coefficient of hydrogen is 5 to 8 times greater than that of carbon monoxide or methane (17, 74). Because of this reforming characteristic and the faster transport properties of hydrogen, the principal electrochemical reaction for mixtures of hydrocarbons, carbon monoxide, hydrogen, and water vapor will be the oxidation of hydrogen (17, 20). The general reactions that will occur in a high temperature cell of this type are

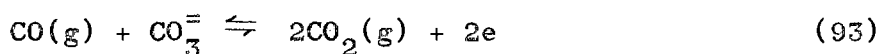
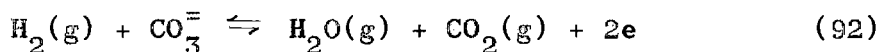
Reforming Reactions



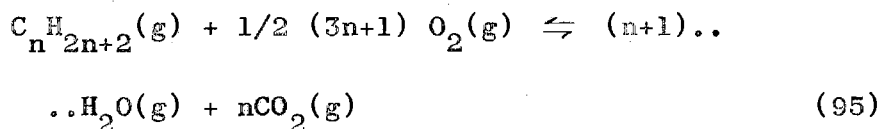
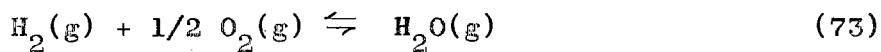
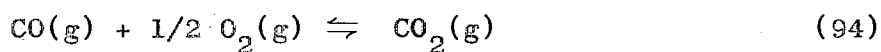
Cathode Reaction



Anode Reactions



Overall Electrochemical Reactions



The development of high temperature fuel cells has been delayed by a number of problems associated with this type of cell (57). These problems affect both the performance and

operational life of the cells.

The high operating temperatures essentially eliminate activation polarization. However, high internal cell resistance and concentration polarization currently limit the current densities of high temperature cell to about 60 amperes per square foot of electrode surface (2).

Several investigators have reported that internal cell resistance of an operating cell is much larger than that predicted by resistance measurements of the cell components (17, 20, 37). The internal cell resistance during operation is frequently 7 to 10 times greater than that predicted (37). This high cell resistance during operation has been attributed primarily to poor electrode-electrolyte contact (37). Figure 23 illustrates the large reduction in cell performance due to internal cell resistance (17).

Concentration polarization becomes a problem at high current densities. This is of particular importance in high temperature fuel cells operating on hydrocarbon or carbon monoxide fuels because of the formation of carbon dioxide at the fuel electrode. To reduce this, high fuel circulation rates must be used resulting in decreased fuel conversion efficiency (18). The effects of concentration polarization have been greatly reduced by adding water vapor to the fuel to promote hydrogen formation but is still a factor at high current densities. Figure 24 illustrates the effect of adding water vapor to carbon monoxide feed of a fuel cell (17).

A more serious problem of high temperature fuel cells is the short operational life (57). The cell life of high temperature fuel cells is currently limited to about six months primarily because of corrosion and electrolyte degradation (17, 57).

Corrosion is a problem because of the extreme corrosive conditions encountered at high temperatures with molten electrolytes. The molten electrolytes are very reactive substances and at high temperatures deteriorate all known gasket materials (2).

Electrolyte deterioration occurs gradually because of direct vaporization of carbon dioxide, lithium oxide, sodium oxide, and potassium oxide (17). Also, the reactions of the electrolyte with the gasket material and cell components change the electrolyte composition.

All of these effects combine to reduce the cell performance during continuous operation. As a result of corrosion and electrolyte loss, gas leaks occur, and electrode-electrolyte contact is reduced until the cell fails (2, 17, 20, 57). Figure 23 shows the increase in internal cell resistance of an experimental fuel cell as a function of time (18).

Figures 24, 25, and 26 show performance data of several fuels. Table XIV lists the general operating characteristics of the high temperature cell of the Consolidation Coal Company which is representative of most high temperature fuel cells (57).

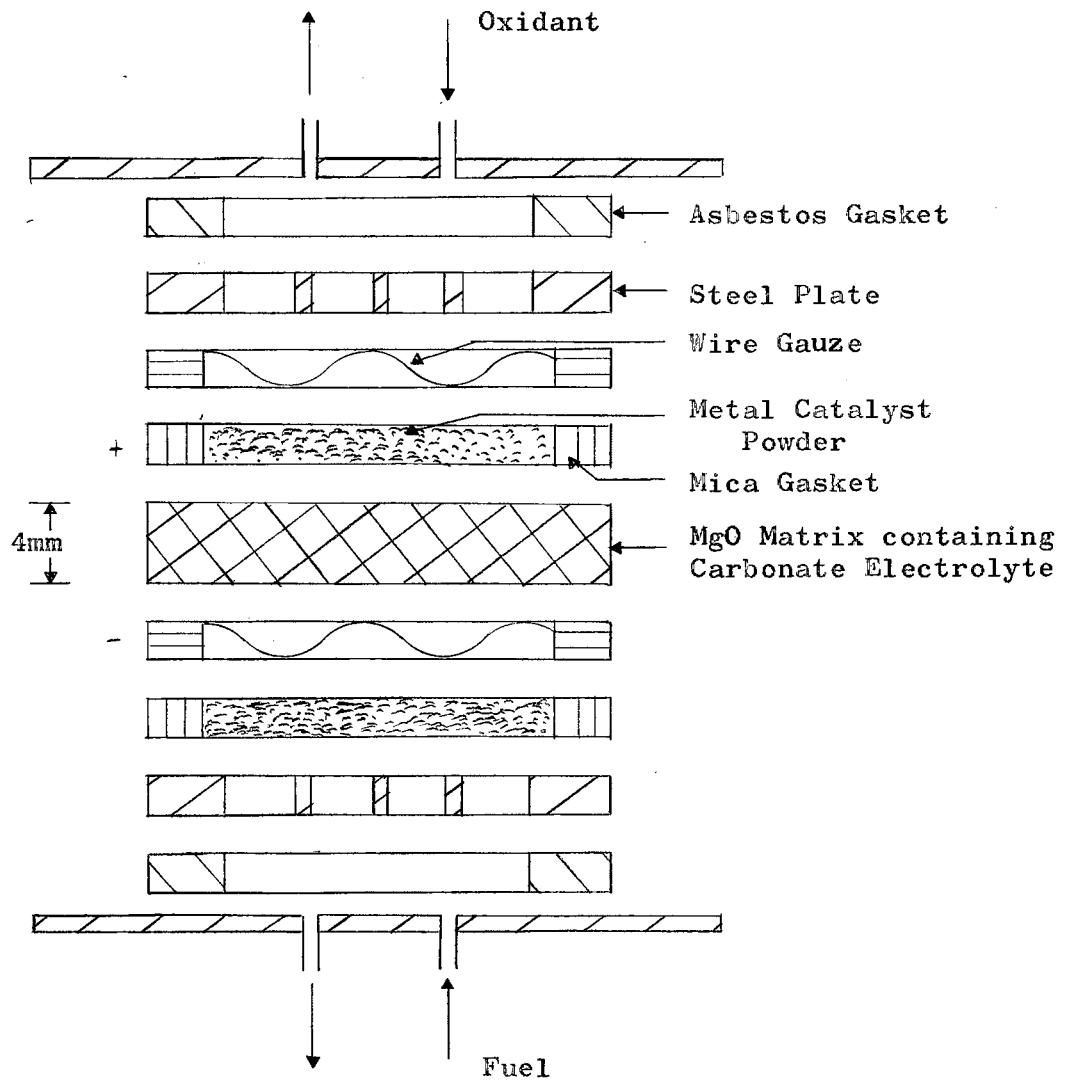


Figure 22

High Temperature Fuel Cell

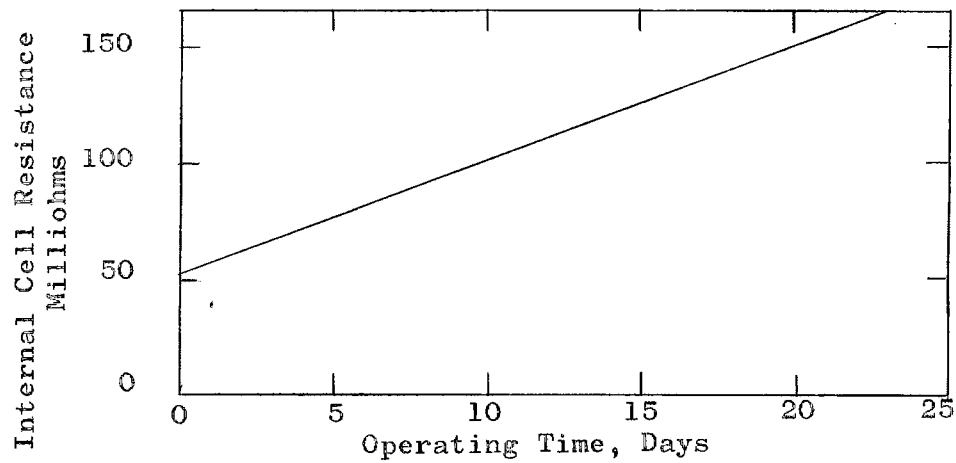


Figure 23

Increase in Internal Cell Resistance with Time

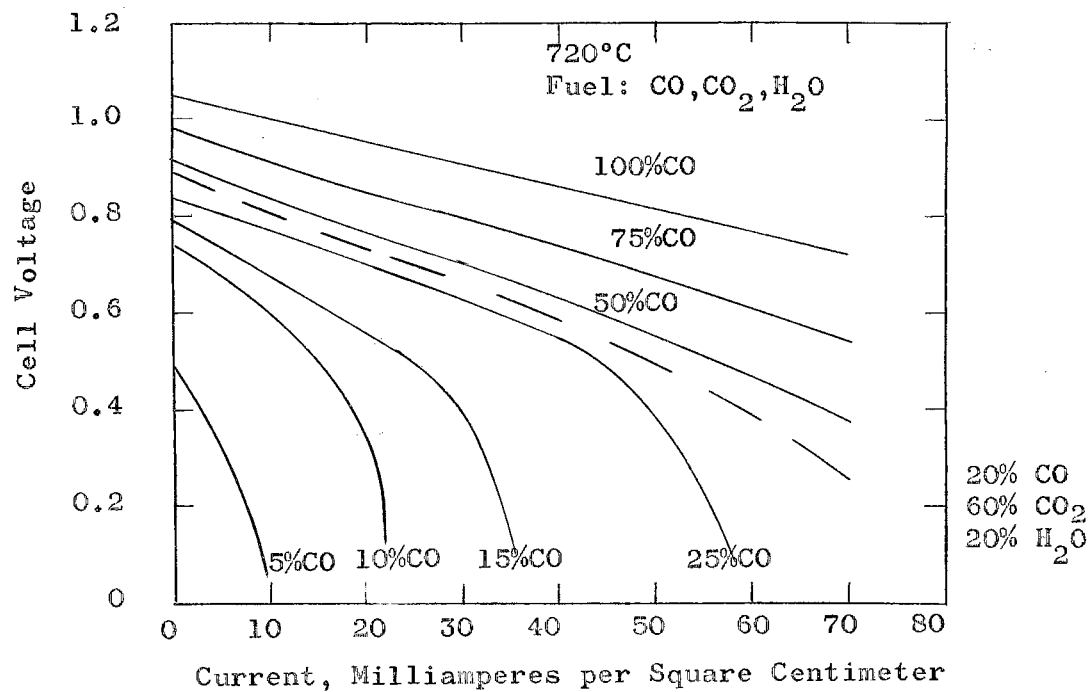


Figure 24

Effect of Adding Steam to Carbon Monoxide Fuel

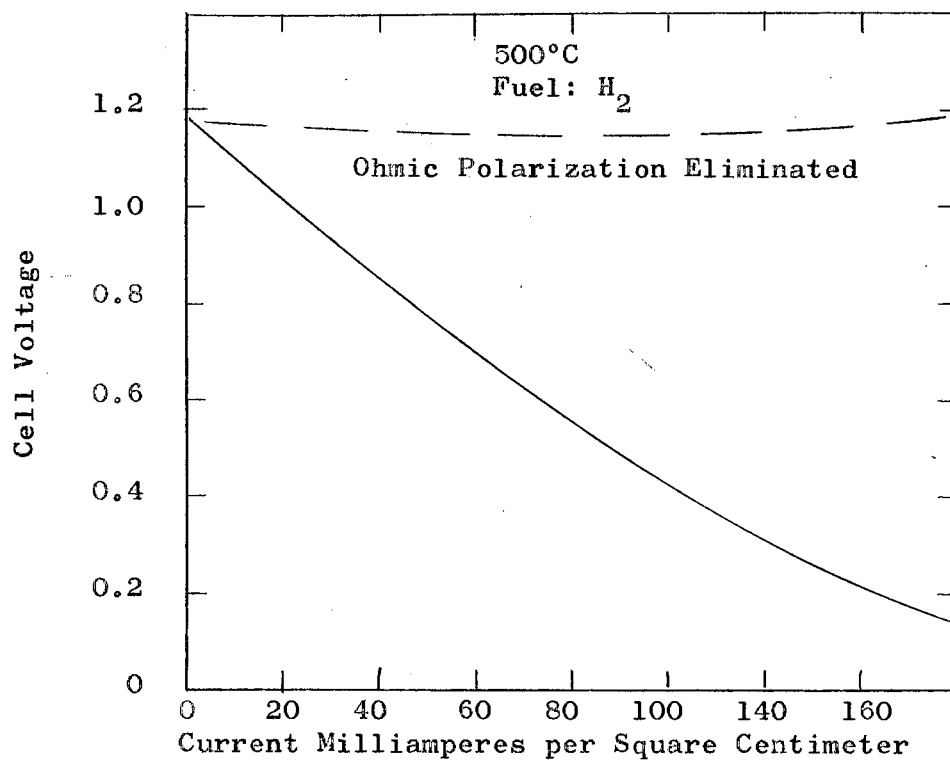


Figure 25

Ohmic Polarization in High Temperature Fuel Cells

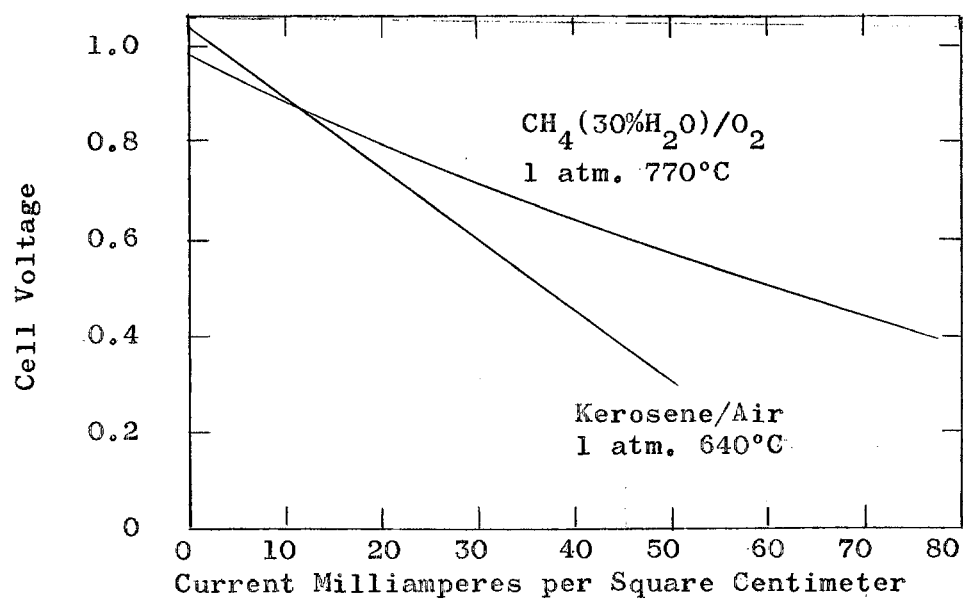


Figure 26

Methane and Kerosene Fuels in High Temperature Fuel Cells

TABLE XIV
 OPERATING CHARACTERISTICS
 CONSOLIDATION COAL COMPANY HIGH TEMPERATURE
 FUEL CELL

Anode Material	Porous Nickel
Cathode Material	Porous Nickel Oxide
Fuel	Carbon, Hydrocarbons
Oxidant	Oxygen or Air
Electrolyte	Lithium-Sodium Carbonates in Magnesium Oxide Matrix
Operating Temperature (°C)	700-800°C
Operating Pressure (atm.)	1
Open Circuit Voltage (Volts)	1.24
Operating Voltage (Volts)	0.96 - 0.54
Current Density (amperes/ft ²)	30-100
Power to Weight Ratio (Watts/Lb)	--
Power to Volume Ratio (Watts/ft ³)	100 - 200
Operational Life	Several Hours
Energy Efficiency (Per Cent)	to 65
Starting Time	Long

Power Costs

The cost of electrical power that can be produced by fuel cells is uncertain. Fuel cells have not been developed to the point where this cost can be reliably estimated (55). However, Adams (2) has compiled a thorough cost analysis for fuel cell systems. This cost analysis though thorough, is at best an estimate, based on several assumptions regarding future fuel cell developments. The cost figures presented by Adams represent fuel cell performances that are not attainable at the present time. Although this cost analysis is an estimate, it does provide an indication of what power costs can be expected from fuel cells in the future assuming the cells are developed.

The only cost factor that can be estimated reliably are the theoretical minimum energy costs, and even these are uncertain because purity has such a large effect on fuel prices. Also, whether high purity oxygen or air is used as the oxidant can effect power cost by several magnitudes.

Table XV lists several fuel costs for potential fuels. Table XVI shows a comparison of the theoretical minimum energy costs of these fuels. Tables XVII and XVIII list some expected cell costs, based on large scale manufacturing (2).

Discussion

The fuel cells described in this section represent the various development stages of the major current fuel cells. As is evident from the review of these cells, many problems remain

to be solved before fuel cells are to become competitive with conventional power sources. None of the current cells satisfy all of the desirable characteristics outlined in Chapter II. The major problem facing fuel cells today is obtaining a satisfactory cell life at practical or desired power outputs, operating with an economic fuel and air.

Low temperature cells have reached the most advanced development stage with respect to cell lives and power rating. However, they operate only on high purity, high cost hydrogen and oxygen. The chemical regenerative and ion-exchange cells fail if the membrane fails (57). The aqueous alkaline electrolyte cells are unsuited for carbon-containing fuels, and catalysts are not available to permit the use of an acidic electrolyte with the oxygen electrode. The consumable electrode cells have short lives and use moderately priced fuels. The dissolved fuel fuel cells show promise of using low priced fuels, but are undeveloped at the present time.

The moderate temperature high pressure alkaline cell has attained high power performances for short periods but must use high purity hydrogen and oxygen, and requires complex pressure control equipment.

The moderate temperature low pressure cells offer good possibilities, but too little data is available for comparison.

The high temperature cells are capable of using the low cost fuels, but corrosion problems presently limit cell lives to about six months.

The present cost of electrical power in the United States is approximately 0.01 \$/KWhr (2). For fuel cells to compete in the commercial market with the more conventional power sources, natural gas, coal gas, or petroleum fuels, with air will have to be used (85). Present day hydrogen oxygen cells even with an assumed cell life of 10 years are less economical than conventional power generation methods (2).

There are two basic approaches for developing cells to utilize carbonaceous fuels (2). These are: 1) to raise the temperature so that special catalysts will not be required, and 2) to develop catalysts and electrolytes which will allow the reactions to take place at low temperature and pressure.

There are many organizations currently engaged in research on low temperature cells (2, 85). The probability that a low temperature cell operated on a hydrocarbon fuel with an efficiency greater than that of conventional means will be developed at an early date is high (57).

The success of high temperature cells depends upon the development of corrosion resistant materials and stable electrolytes.

In all fuel cells, there is the need for better electrodes and catalysts. Electrode development, though subject to the scientific approach is still regarded as a "black art" (71). This operation has been and will probably continue to be, an experimental trial and error procedure in which an electrode is fabricated, tested, and the effects of catalysts and method of construction are evaluated (2, 57, 71).

A large area of fuel cell applications that should not be overlooked is that area where cost is a minor factor. There are many special uses existing for fuel cells operating on expensive fuels and oxidizers (71, 72). Specialized military equipment that have power requirements far removed from normal requirements, indicate that a need exists for specialized power generating devices at all levels of power output (57). The possibility also exists that a short life, high power output device may be more economical using fuel cells rather than conventional rotating power equipment (57).

A large potential use of fuel cells exists in areas now served by batteries where power per unit weight is a very important factor. Table XIX presents a power density comparison between several fuel cells and storage batteries (72).

To study fuel cell performances, three parameters that should be available are cell potential, current density, and time of operation. Very few literature sources include relations showing time of operation. For this reason, much of the data available relating current density and cell voltage were omitted.

No attempt was made to include all current cells in this work. A major problem in reviewing this subject is the limited amount of current data available.

TABLE XV

FUEL COST

Fuel	Cost Range			Cost used in Table XVI	
Hydrogen	2.68	-	0.05 \$/Lb	0.45	\$/Lb
Carbon	0.003	-	0.001 \$/Lb	0.002	\$/Lb
Methane	0.025	-	0.005 \$/Lb	0.01	\$/Lb
Ethane	0.02	-	0.01 \$/Lb	0.02	\$/Lb
Propane	0.05	-	0.02 \$/Lb	0.03	\$/Lb
Butane	0.05	-	0.02 \$/Lb	0.03	\$/Lb
Pentane	0.05	-	0.02 \$/Lb	0.03	\$/Lb
Methanol	0.08	-	0.04 \$/Lb	0.06	\$/Lb
Ammonia	0.1	-	0.042 \$/Lb	0.042	\$/Lb
Sodium	0.3	-	0.17 \$/Lb	0.23	\$/Lb
Oxygen	0.184	-	0.04 \$/Lb	0.04	\$/Lb

TABLE XVI

MINIMUM FUEL COST OF FUEL CELLS

Fuel	Temperature °K	Energy Density Btu/Lb	Fuel Cost ¢ /Kwhr	Fuel and Oxygen Cost ¢ /Kwhr
Hydrogen	298	48780	3.15	5.48
Carbon	1000	14121	0.05	2.75
Methane	1000	21466	0.159	2.619
Ethane	1000	21160	0.322	2.84
Propane	1000	20960	0.489	2.98
Butane	1000	19546	0.525	3.15
Pentane	1000	20753	0.443	2.88
Methanol	500	9386	2.184	4.48
Ammonia	298	7110	2.01	3.04
Sodium	298	5622	12.0	16.0

Based on 100% Fuel Conversion

TABLE XVII

INITIAL FUEL CELL COSTS (2)*

<u>Cell Type</u>	<u>Electrode Material</u>	<u>Cost</u> (\$/2 ft ² electrode surface)
Low temperature and pressure H ₂ - O ₂ cell	Porous carbon	2-5
Ion - exchange	Coated resin membrane	30-40
Low temperature and pressure hydrocarbon cell	Porous nickel	3-7.5
Intermediate tempera- ture and high pressure H ₂ -O ₂ cell	Dual porous nickel	4-12.5
Sodium amalgam	Steel plate porous carbon	25-65
Dissolved methanol	Platinum coated plates	1-5

* Based on large scale production

TABLE XVIII

ESTIMATED ELECTRODE COST (2)*

Electrode	Cost (\$/ft ²)
Porous carbon	0.5-2
Porous nickel	0.7-3
Bacon type nickel	1.0-5
Porous stainless steel	0.5-1
Non-porous platinum coated plates	0.4-2

* Based on large scale production

TABLE XIX

POWER DENSITY COMPARISON:

FUEL CELLS AND STORAGE BATTERIES (150 HR. OPERATION)

<u>Power Source</u>	<u>Watt Hours/Lb.</u>
Fuel Cell, Tank H ₂ & O ₂	125
Fuel Cell, Tank H ₂ & Air	200
Fuel Cell, Chemical Regeneration of Fuel	500
Lead Acid Battery	10
Leblanche Cell	30
Silver Zinc Cell	50

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Fuel cell development has only begun. Even the most advanced fuel cells are still in an experimental stage of development. Fuel cells are not in commercial use at the present time and their use will be limited until the development of better cells with longer operational lives allows the use of inexpensive fuels and air.

The possible applications for fuel cell power seems unlimited. Fuel cells show promise for applications ranging from small vehicles to large stationary power plants.

Fuel cells have two major factors in their favor; the high energy efficiency possible, and the fact that fuel cell systems may be arranged to produce any amount of desired power.

Fuel cell research is currently being applied in two main areas; in developing fuel cells for commercial and for specialized purposes.

The commercial success of fuel cells depends upon future progress made to allow the use of inexpensive fuels and air. The success for special purpose fuel cells depends upon the development of dependable cells with high power outputs and cell lives corresponding to the particular need.

What is most needed for fuel cells is basic research in the

areas of catalysts, electrolytes, high temperature materials, electrode design, and techniques of cell fabrication. A better fundamental understanding of the relations between the polarization losses of operating fuel cells is needed.

A SELECTED BIBLIOGRAPHY

1. Adams, A. M., Chem. Proc. Eng., 199 (January, 1949).
2. Adams, D. R., et. al., Fuel Cells, Fuel Cell Research Associates, Cambridge 38, Mass., (1960).
3. Austin, L. G., Scientific American, 72 (October, 1959).
4. Austin, L. G., Fuel Cells, Reinhold Publishing Co., Inc., New York (1960), p. 34.
5. Bacon, F. T., Fuel Cells, Reinhold Publishing Co., Inc., New York (1960), p. 51.
6. Bacon, F. T., Beama Journal 61, 6 (1954).
7. Bacon, F. T., U. S. Patent 2716670, (August 30, 1955).
8. Baur, E. and J. Tobler, Z. Electrochem. 39, 169 (1933).
9. Baur, E. and H.Z. Pries, Z. Electrochem. 43, 727 (1937).
10. Baur, E. and H. Z. Pries, Z. Electrochem. 44, 695 (1938).
11. Berl, W. G., Trans. Electrochem. Soc. J. 83 253 (1943).
12. Bockris, J. O'M., Modern Aspects of Electrochemistry, Butterworths Scientific Pub., London, (1954).
13. Bockris, J. O'M. and G. Kortum, Electrochemistry, Elsevier Pub. Co., Inc., New York, (1954).
14. Bockris, J. O'M. Chem. Review 43, 525 (1948).
15. Broers, G. H. J., Ph. D. Thesis, University of Amsterdam, (1958).
16. Broers, G. H. J. and J. A. A. Ketelaar, Fundamental Criteria in Fuel Cell Design, Laboratory for Electrochemistry Report, University of Amsterdam, (1959).
17. Broers, G. H. J. and J. A. A. Ketelaar, Fuel Cells, Reinhold Pub. Co., Inc., New York, (1960) p.78.

18. Broers, G. H. J. and M. Schenke, High Temperature Galvanic Fuel Cells, Final Report, Central Technical Institute TNO, The Hague, Netherlands, (1959).
19. Cairns, E. J., D. L. Douglas and L. W. Niedrach, Performance of Fractional Watt Ion Exchange Membrane Fuel Cell, Research Report, General Elec. Res. Lab., Schenectady, New York (1959).
20. Chambers, H. H. and A. D. S. Tantrum, Fuel Cells, Reinhold Pub. Co., Inc., New York, (1960) p. 94.
21. Ciarlariello, T. A. and R. C. Werner, Fuel Cells Based on Nuclear Reactors, A.I.Ch.E. Symposium Report on Fuel Cells, Washington, D. C., December, (1960).
22. Ciarlariello, T. A. and R. C. Werner, Chem. Eng. Prog. 57, 42 (1961).
23. Davy, H., Ann. Physics 8, 301 (1801).
24. Davy, H., Nicholsons J. Nat. Sci. Phil., 144 (1802).
25. Davydan, O. K., Izvest. Akad.Nauk. S.S.S.R., Otdel. Tekh. Nauk., No. 1 and 2 (1946). Translations 60H9R and 61H9R, Assoc. Tech. Services, East Orange, New Jersey, (1946).
26. DeZubay, E. A., High Temperature Fuel Cells, Presented at SAE National Aeronautics Meeting, New York (April, 1960).
27. Douglas, D. L., Fuel Cells, Reinhold Pub. Co., Inc., New York, (1960), p. 129.
28. Douglas, D. L., Elec. Eng. 78, 906 (1959).
29. Douglas, D. L. and H. A. Liebhafsky, Physics Today 13, 26 (1960).
30. Douglas, D. L. and H. A. Liebhafsky, Mech. Eng. 81, 64 (1959).
31. Eisenberg, M., SAE Journal 69, No. 3 28 (1959).
32. Elmore, G. V. and H. A. Tanner, J. Electrochem Soc. 108, No. 7, 669 (1961).
33. Evans, G. E., Fuels for Fuel Cells, Presented at the National A.I.Ch.E. Meeting, Washington D. C., (December 4, 1960).
34. Fredersdorf, C. G., Chem. Eng. News 39, No. 38, 86 (1961).

35. Glasstone, S., Introduction to Electrochemistry, D. Van Nostrand Co., Inc., New York (1962).
36. Gorin, E., U. S. Patents 2570543 (October 9, 1951), 2581650 (January 8, 1952), 2581651 (January 8, 1952).
37. Gorin, E. and H. L. Recht, Fuel Cells, Reinhold Pub. Co., Inc. New York (1960), p. 109.
38. Gorin, E. and H. L. Recht, U. S. Patent 2914596 (November 6, 1959).
39. Gorin, E. and H. L. Recht, Mech. Eng. 81, No. 3, 63 (1959).
40. Grove, W. R., Phil. Mag. 3, No. 14, 139 (1839).
41. Grove, W. R., Phil. Mag. 21, 417 (1842).
42. Grubb, W. T., U. S. Patent 2913511, (1957).
43. Grubb, W. T. and L. W. Niedrach, J. Electrochem. Soc. 107, 131 (1960).
44. Ihrig, H. K., Agri. Eng. 41, 232 (1960).
45. Jones, et.al., Janaf Interim Thermochemical Tables I, II, (1960).
46. Justi, E., High Drain Hydrogen Diffusion Electrode Operating at Ambient Temperature and Low Pressure, Akademie der Wissenschaften and der Literature, Mainz, Abhandlungen der Mathematical - Natur - Wissenschaftlichen Klasse, No. 8 (1959). Translated by: T. E. Burton, Research Info. Services, Div. Personnel Int. Corp., 40 E. 23 st., New York 10, New York.
47. Justi, E., U. S. Patent 2830109, (April 8, 1958).
48. Kirkland, T. G., Proc. Am. Power Conf. XXII, 465 (1960).
49. Kordesch, K., Fuel Cells, Reinhold Pub. Co., Inc., New York (1960), p. 11.
50. Kordesch, K., Electrochemical Cell Power Systems, Research Report, Union Carbide Consumer Products Co., (1960).
51. Kordesch, K. and A. Moroko, U. S. Patents 2615932 (October 28, 1952), 2669598 (February 16, 1954).
52. Kornfiel, F., Galvanic Fuel Cells, Presented at the A.I.E.E., Signal Corps. Eng. Lab. Ft. Monmouth, New Jersey (1956).

53. Kortum, G. and J. O'M Bockris, Electrochemistry, Elsevier Pub. Co., Inc., New York (1951).
54. Liebhafsky, H. A., J. Electrochem Soc. 106, 1068 (1956).
55. Liebhafsky, H. A. and D. L. Douglas, Fuel Cells, Reinhold Pub. Co., Inc., New York (1960), p. 1.
56. McKee, J. H. and A. M. Adams, Fuel 28, No. 1, 61 (1949).
57. McCormick, J. E., Fuel Cell Systems, PB161972, U. S. Dept. of Commerce, Office Tech. Services, (1960).
58. Miller, K. D., Chem. Eng. Prog. 57, No. 2, 140 (1961).
59. Mond, L. and C. Langer, Proc. Royal Soc. 46, 296 (1889).
60. Niedrach, L. W., The Ion Exchange Membrane Fuel Cell, Power Sources Conf., Atlantic City, (April, 1959).
61. Ostwald, W., Z. Electrochem. 1, 122 (1894).
62. Porter, R. W., Elect. Eng. 79, 801 (1960).
63. Posner, A. M., Fuel 34, 330 (1955).
64. Potter, E. C., Electrochemistry, Cleaver-Hume Press Ltd., London, (1956).
65. Prutton, C. F. and S. H. Maron, Principles of Physical Chemistry, The Macmillan Co., New York (1958).
66. Rideal, E. K., Trans. Faraday Soc. 17, 466 (1921).
67. Rossini, F. D., Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds, Carnegie Inst. of Technology, Pittsburgh (1953).
68. Schmid, A., Stuttgart F. Enke., (1923).
69. Sherman, G. W., Forecasts For Space Flight Vehicle Power, SAE International Congress, Detroit, Michigan (January, 1961).
70. Skelcher, B. W., M.S. Thesis, University of Birmingham, England (1956).
71. Stien, B. R., Status Report on Fuel Cells, PB151804, ARO Report No. 1, U.S. Dept. of Commerce, Office Tech. Ser., (1959).

72. Sweeney, W. J. and C. E. Heath, The Fuel Cell: Its Promise and Problems, Presented at the 26th Midyear Meeting, A.P.I., Houston, (May, 1961).
73. Trapnell, B. M. W., Chemisorption, Butterworths Sci. Pub., London (1955).
74. Treybal, R. E., Mass-Transfer Operations, McGraw-Hill Book Co., Inc., New York (1955).
75. Wiessbart, J., J. Chem. Ed. 38, No. 5, 267 (1961).
76. Yeager, E. W., The Oxygen Electrode in Aqueous Fuel Cells, Tech. Report 12, Electrochemistry Res. Lab., Western Reserve University.
77. Young, G. J. and R. B. Rozelle, Fuel Cells, Reinhold Pub. Co., Inc., New York (1960).
78. Young, G. J. and Rozelle, J. Chem. Ed. 36, 68 (1959).
79. _____, Proceedings, 12th, 13th and 14th Annual Battery Research and Development Conf., Power Sources Division, U. S. Army Signal Res. and Dev. Lab., Ft. Monmouth, New Jersey (May, 1958, April, 1959, and May, 1960).
80. _____, Proceedings, 139th and 140th Meeting of The American Chemical Society, Division of Gas and Fuel Chemistry, (1960, 1961).
81. _____, Chem. Eng. 64, No. 12, 154 (1957).
82. _____, Oil and Gas J. 58, No. 15, 26 (1960).
83. _____, Chem. and Eng. News 38, No. 49 56 (1960).
84. _____, Power Eng. 65, No. 1 67 (1961).
85. _____, Chem. Eng. 68, No. 9, 34 (1961).
86. _____, Chem. Eng. 68, No. 20, 40 (1961).

APPENDIX A

NOMENCLATURE

- A_o = effective electrode area per unit geometrical area.
- a = activity
- B = (D_{eff}/r) , effective diffusion coefficient, current/pressure.
- D = ionic diffusion coefficient, area/time.
- D_{eff} = effective gas diffusion coefficient, area/time.
- E = potential, volts.
- E_a = actual cell potential, volts.
- E_c = potential with current drain, volts.
- E_{ocv} = potential at zero current, volts.
- E_{rev} = reversible potential.
- e = electron.
- F = Faraday constant, coulombs/gram-equivalent.
- f = fugacity, force/area.
- G = $U + PV - TS$, free energy, energy
- H = $U + PV$, enthalpy, energy
- I = current, coulombs/time.
- I' = current in either forward or reverse direction at zero net current, current/area of active electrode surface.
- I_a = actual electrode net current, current/area of active electrode surface.
- i = net current/unit of geometrical electrode area.
- i_e = limiting current for ionic concentration polarization.
- i_L = limiting current for gas concentration polarization.

- K = constant in equation 50.
 k = reaction rate constant for forward direction.
 k' = reaction rate constant for reverse direction.
 L = distance
 l = distance
 N_s = active electrode site area/area of effective electrode area.
 P = pressure, force/area.
 p = partial pressure, force/area.
 Q = quantity of electrical charge, coulombs.
 q = heat absorbed by system, energy.
 r = pore diameter, length.
 r = electrical resistance, ohms.
 r_{eff} = effective ohmic resistance of cell, ohms.
 S = entropy, energy.
 T = absolute temperature, degrees.
 T_o = absolute temperature of heat sink, degrees.
 t_i = ionic transport number.
 U = internal energy, energy.
 V = volume.
 v = reaction rate, equivalents/time.
 v_r = reverse reaction rate, equivalents/time.
 v_f = forward reaction rate, equivalents/time.
 v_{net} = $v_f - v_r$, net forward reaction rate, equivalents/time.
 W = work done by system, energy.
 W' = reversible work done by system other than PV work.
 W_m = maximum work available from a heat engine, energy.

Z = electrochemical equivalents.

Superscripts

° = standard state.

* = activation.

Abbreviations

act = activation.

exp = exponential, i.e., $\exp(x) = e^x$.

ln = logarithm to the base e.

ocv = open circuit voltage.

wh/lb = watt hours per pound

APPENDIX B

A COMPREHENSIVE BIBLIOGRAPHY

ON FUEL CELLS

This bibliography on Fuel Cells was compiled by Mr. A. M. Adams of Central Electricity Research Laboratories, Leatherhead, England, and is reproduced through his courtesy.

The bibliography originally included the period from 1801 to 1950. The work has been expanded to include 1960.

<u>Author</u>	<u>Date</u>	<u>Appendix Section</u>	*
Adams, D. R., et. al. Fuel Cells, Fuel Cell Research Assoc., Cambridge, Mass.	1960	4.2, 5.1. 5.2.	
Allemond, A.J. and Ellingham, H.J.T. Principles of Applied Electrochemistry London: Longmans, Green & Co., Ltd.	1924	5.3.	
Anon Zeits. Electrochem. <u>3</u> , p. 192 German Patent No. 88327	1895	3.3.	
Anon Electrical Eng., <u>21</u> , pp. 261, 497	1896	1.3.2.	
Anon Zeits. Electrochem. <u>4</u> pp.124-136, 165-167	1897	1.3.2.	
Andrews, E. V. Fodor	1895	2.1.2. 2.1.3.	

* See Page 146

<u>Author</u>	<u>Date</u>	<u>Appendix Section</u>
Archercau, H.A. British Patent No. 1,037/A.D. 1883	1888	1.3.2.
Arsonval, A. d' French Patent No. 152,348	1882	2.1.5.
Atkinson, A.B. and Treharne, F.G. British Patent No. 8,906/A.D. 1896	1896	2.1.5.
Averbach, F. Zeits, Electrochem. <u>25</u> , p. 82	1919	2.1.1.
Bacon, F. T. Beama Journal <u>61</u> , p. 61	1954	3.1. 3.3. 4.1.
Bacon, F. T. Fuel Cells, Reinhold Pub. Co. Inc., New York	1960	3.1. 3.3. 4.1.
Bacon, F. T. U. S. Patent 2716670	1955	3.1. 3.3. 4.1.
Baillod, Dissertation, Basle	1927	3.3.
Basset, L. P. British Patent No. 7375/A.D. 1906, 16905/A.D. 1906	1906	2.1.3.
Basset, L. P. British Patent No. 21,475/A.D. 1907 22,236/A.D. 1907	1907a	2.1.3.
Basset, L. P. German Patent No. 202,369	1907b	2.1.3.
Baur, E. and Glaessner, A. Zeits. Electrochem. <u>9</u> , pp. 534-539	1903	2.1.1. 2.2.2.
Baur, E. Zeits. Electrochem. <u>16</u> , pp. 330-302	1910	1.2. 1.3.2. 2.1.3 2.2.2.
Baur, E. and Ehrenburgh Zeits. Electrochem. <u>18</u> , pp. 1002-1011	1912	1.3.3. 2.1.5.

<u>Author</u>	<u>Date</u>	<u>Appendix Section</u>
Baur, E., Petersen A., and Fullemann, G. Zeits. Electrochem. <u>22</u> , pp. 409-414	1916a	1.3.3.
Baur, E. and Treadwell, W. D. German Patent Nos. 325,683; 325,783 British Patent No. 126,766	1916a 1918	1.3.2. 1.4. 1.3.2.
Baur, E. Zeits. Electrochem. <u>27</u> , pp. 194-199	1921a	2.2.1.
Baur, E., Treadwell, W. D., and Trumpler Zeits. Electrochem. <u>27</u> , p. 199	1921b	1.3.2. 2.1.5.
Baur, E. Helv. Chem. Acta <u>4</u> , pp. 325-333	1921c	2.1.5.
Baur, E. German Patent No. 357,290	1921d	2.1.5.
Baur, E. Brennstoff Chem. <u>2</u> , p. 147	1921e	5.2.
Baur, E. Zeits. Electrochem. <u>36</u> , pp. 410-414	1930	3.1.
Baur, E. and Tobler, J. Zeits. Electrochem. <u>39</u> , pp. 169-180	1933	2.1.2. 5.1
Baur, E. and Brunner, R. Zeits. Electrochem. <u>41</u> , p. 794	1935	1.3.2.
Baur, E. and Brunner, R. Zeits. Electrochem. <u>43</u> , pp. 725-27	1937a	1.3.2. 3.1
Baur, E. and Preis, H. Zeits. Electrochem. <u>43</u> , pp. 727-732	1937b	1.4 2.1.6. 2.2.2.
Baur, E. and Preis, H. Zeits. Electrochem. <u>44</u> , pp. 695-698	1938	1.4 2.1.6. 2.2.2.
Baur, E. Brennstoffchem. <u>20</u> , p. 385	1939	2.1.6. 5.2
Baur, E. German Patent No. 713,570	1941	2.1.6. 2.2.2.
Bechterew, P. Zeits. Electrochem., <u>17</u> , pp. 851-77 v.a. Sacher and Lorenz	1911	5.1.

<u>Author</u>	<u>Date</u>	<u>Appendix Section</u>
Becquerel, A.C. "Treatise on Electricity" (In French) Paris: Firmin Didot Freres Vol. 1	1855	1.3.1.
Bernstein German Patent Nos. 32,822 V 32,988; 34,097	1895	2.1.1. 2.1.2.
Bernstein Zeits. Electrochem. <u>6</u> , p. 156	1897	2.1.1. 2.1.2.
Berthier, A. "Electrical Energy of Tomorrow" (In French) Paris: Desforges, Girardot and Cie.	1929	5.1
Beutner Zeits. Electrochem. <u>17</u> , pp. 91-93	1911	2.1.5. 3.3
Blanchard, V. W. British Patent No. 5695/A.D. 1882	1882	2.1.2.
Blanke, M. German Patent No. 730, 247	1942	2.1.5. 2.2.2. 3.3.
Borchers, W. J. Chemical Industr. (London) <u>17</u> , p. 502	1894	2.1.1. 2.2.2.
Boudouard Ann. chem. phys. (VII) <u>24</u> , p. 5	1904	5.3.
Bradley v. Anon 1897	1888	1.3.2.
Brandt, R. German Patent No. 408,435	1925	2.2.1
Brard Compte. rend. Paris. <u>95</u> , pp. 890-892 pp. 1158-1160	1882	1.3.1.
Braun, G. and Schneider, F. British Patent No. 25,879/A.D. 1910	1910	2.1.1. 6.
British Electrical and Allied Industries Research Association Translation of Davtyan 1947 (q.v.)	1949a	5.1

<u>Author</u>	<u>Date</u>	<u>Appendix Section</u>
British Electrical and Allied Industries Research Association Technical Report Z/T76	1949b	5.1.
British Electrical and Allied Industries Research Association Annual Report 1949	1950	2.1.2. 4.1
Britzke, O. German Patent No. 131,893 British Patent No. 23,675/A.D. 1900	1900	2.1.5. 6.
Broers, G.H.J. Thesis, University of Amsterdam	1958	2.1.5. 2.3.2. 3.3.
Broers, G.H.J. and J. A. A. Ketelaar Fuel Cells, Reinhold Pub. Co. New York	1960	2.1.5. 2.3.2. 3.3.
Brooks, E. E. Electrical Review. <u>35</u> , p. 190	1894a	1.3.1.
Brooks, E.E. Electrotech. Zeits. <u>15</u> , p. 550	1894b	1.3.1.
Bucherer, A.H. German Patent No. 88327	1896a	2.1.5.
Bucherer, A.H. Zeits. Electrochem. <u>3</u> , pp. 192-6	1896b	2.1.1. 2.1.5.
" Bührer, C. Dissertation, Basle.	1929	2.1.4. 3.3.
Bull, H.C. British Patent No. 11,712/A.D. 1891	1891	1.3.2.
Byrnes, E.A. Trans. Amer. Electrochem. Soc. <u>2</u> , pp. 113-119	1902	1.3.2.
Cailletet, L. and Collardeau, E. Compt. rend. Paris <u>119</u> , pp. 830-834	1894	2.1.2. 3.1 4.1
Carbone Soc, Anon. German Patent No. 392,688	1923	3.2

<u>Author</u>	<u>Date</u>	<u>Appendix Section</u>
Cairns, E.J., D. L. Douglas and L.W. Niedroch Research Report, General Electric Research Lab., New York	1959	2.1.2.
Case, W.E. v. Berthier 1929	1887	1.1.
Case, W. E. British Patent Nos. 12,171/A.D. 1899 12,172/A.D. 1899	1899	1.1.
Ciarlarello, T.A. and R. C. Werner A.I.Ch.E. Symposium, Washington, D.C.	1960	2.2
Chipman, J. and Murphy, D.W. Ind. Eng. Chem. <u>25</u> pp. 319-327	1933	5.3.
Citovich, E. British Patent No. 303, 027	1929	4.1. 2.1.2.
Clark, A.M. v. Fodor	1883	1.3.1.
Coehn, A. Zeits. Electrochem. <u>2</u> , p. 541	1896	1.1.
Coehn, A. Zeits. Electrochem. <u>3</u> p. 424	1897	1.1.
Crossley, C. E. British Patent No. 220,422	1923	1.5. 6.
Davies, J. H. v. Fodor	1882	1.3.1.
Davtyan, O. K. Bull. Acad. Soc. U.S.S.R. Dept. Sci. Tech. (No. 1) p. 107 (No. 2) pp. 215-218	1946	2.1.2. 2.1.6. 5.1.
Davtyan, O. K. "Direct Conversion of Chemical Energy of Fuel into Electrical Energy", Moscow: Academy of Sciences: E.R.A. Translation 1949.	1947	2.1.2. 2.1.4. 2.1.6. 3.1. 3.2. 3.3. 3.4. 4.2. 5.1.

<u>Author</u>	<u>Date</u>	<u>Appendix Section</u>
Davy, H. Ann. Phys. <u>8</u> , p. 301	1801	2.2.1.
Davy, H. Nicholson's Journal Nat. Phil. p. 144	1802	1.1.
DeZubay, E.A. SAE Nat. Aero. Meeting	1960	2.1.5. 2.3.2.
Dobell, J. L. J. Soc, Chem. Ind. London <u>14</u> , p. 974	1895	1.3.1.
Dobell, J. L. British Patent Nos. 2,272/A.D. 1897 4,442/A.D. 1897	1897a	1.3.3. 2.1.5.
Dobell, J. L. British Patent No. 10,484/A.D. 1897	1897b	1.3.3. 2.1.5.
Douglas D. L. Fuel Cells, Reinhold Pub. Co., New York	1960	2.1.5. 2.3.2.
Doyle, J.D. and Doyle. M. K. British Patent No. 428,933	1934	2.1.2.
Ellingham, H.J.T. J. Soc. Chem. Ind. London. <u>63</u> p. 125	1944	5.3.
Ellingham, H.J.T. British Association Lecture 5:9:50	1950	5.2.
Elmore, G. V. and H. A. Tanner J. Electrochem. Soc. <u>108</u> , p. 669.	1961	2.3.3.
Eltenberg, A. S. von, and Lach, H. British Patent No. 24,307/A.D. 1907	1907	4.2.
Fabingi and Farkas Compt. rend. Paris. <u>106</u> p. 1597	1888	1.3.2.
Faure, C. A. German Patent No. 37,336	1891	2.2.1.
Fery, C. La Nature. <u>90</u> p. 224; v.a. Ind. Engng. Chem. <u>10</u> p. 744	1918	3.1.
Fery, C. Comptes rend. Paris, <u>192</u> p. 881	1930	3.1.

<u>Author</u>	<u>Date</u>	<u>Appendix Section</u>
Fischer, F. and Kronig, W. "Ges. Abhandl Kenntis Kohle. <u>7</u> pp. 213-30	1922	1.2. 2.1.2. 4.1.
Fischer, F. and Kronig, W. "Zeits. anorg.u.allg.Chem. <u>153</u> p. 169	1924	1.2. 2.1.2. 4.1.
Fischer, F. and Lepsius, R. Ber.d.Deutch. Chem. Ges. <u>45</u> p. 2312	1912	1.3.2. 2.1.5.
Fleischmann and Forster "Zeits.anorg. u. allg. Chem. <u>51</u> pp. 249-289	1906	2.1.6.
Fodor, E.de "Electricity Direct from Coal" (In German) Vienna. Vol. 46 of Harleben's "Elektrotechnischer Bibliothek"	1897	5.1. v.a.1.3.1. 2.1.1. 2.1.3.
"Forster, F. and Diethelm Zeits. phys. Chem. <u>62</u> p. 138	1908	2.1.2. 2.2.2. 3.1.
"Forster, F. Zeits. phys. Chem. <u>69</u> p. 236	1909	2.1.2. 3.1.
"Forster, F. "Electro Chemistry of Acqueous Solutions" (in German)	1915	3.1. 3.3.
"Forster, F. Zeits. Electrochem. <u>29</u> p. 64	1923	2.1.2. 2.1.4. 3.3.
Gaiser, C. German Patent No. 346,771	1918	2.1.2.
Gordon, K. J. Inst. Fuel <u>20</u> pp. 42-58	1946	5.2.
Gore Phil. Mag. (4) <u>27</u> p. 641	1864	1.3.2.
Gorin, E. U. S. Patents 2570543 2581650 2581651	1951 1952 1952	2.1.5. 2.1.5. 2.1.5.

<u>Author</u>	<u>Date</u>	<u>Appendix Section</u>
Greger, H. H. Proc. World Engineering Congr. Tokyo 1929 <u>32</u> pp. 192-205	1931	2.1.5. 5.1. 5.2.
Greger, H. H. German Patent No. 570,600	1933	2.1.5. 4.2. 5.1.
Greger, H. H. U. S. Patent No. 1,963,550	1934	2.1.5. 4.2. 5.1.
Greger, H. H. U. S. Patent No. 2,175,523	1939	2.1.5. 4.2.
Greger, H. H. U. S. Patent No. 2,276,188	1942	2.1.5. 4.2.
Gazel v. Tommasi 1889	1886	1.1.
Grove, W. R. Phil. Mag. (3) <u>14</u> p. 139	1839	2.1.2. 3.1.
Grubb, W.T. U.S. Patent 2913511	1957	2.1.2.
Grubb, W. T. and L. W. Niedrach J. Electrochem Soc. <u>107</u> , p. 131	1960	2.1.2.
Grube, G. Zeits. Electrochem. <u>16</u> p. 621	1910	2.1.2. 2.2.2.
Grube, G. "Fundamentals of Electrochemistry" (In German)	1932	5.3.
Haber, F. Zeits. anorg.u.allg. Chem. <u>51</u> p. 356	1906	2.1.5.
Haber, F. Zeits. anorg.u.allg. Chem. ? pp. 91-93	1911?	2.1.6.
Haber, F. and Bruner, L. Zeits. Electrochem. <u>10</u> p. 697	1904	1.3.2.
Haber, F. and Moser, A. Zeits. Electrochem. <u>11</u> pp. 593-609	1905	2.1.6.
Habicht, F. P. British Patent No. 143,532	1919	1.3.2. 2.2.1.

<u>Author</u>	<u>Date</u>	<u>Appendix Section</u>
Hamer, W. J. and Schrodtt, J. P. J. Amer. Chem. Soc. <u>71</u> pp. 2347-52	1949	2.2.1.
Heise, G. W. and Schumacher, E. A. Trans. Amer. Electrochem. Soc. <u>62</u> pp. 383-391	1932	3.1.
Hering, K. and Dobrowolsky Electr. World. <u>25</u> p. 220	1895	2.1.1.
Hoffmann, A. G. German Patent No. 369,829	1920b	2.1.5.
Hoffmann, F. German Patent No. 437,009	1920c	2.1.5.
Hofmann, K.A. Ber. d. Deutsch. chem. Ges. <u>51</u> pp. 1526-37	1918a	2.1.1.
Hofmann, K.A. German Patent No. 310,782	1918b	2.1.1.
Hofmann, K. A. Ber. d. Deutsch. chem. Ges. <u>53</u> pp. 914-921	1920a	2.1.1.
Hofmann, K.A. and Ritter, K. Ber. d. Deutsch. chem. Ges <u>47</u> pp. 2233-44	1914	1.1.
Hofmann, K. A. and Wurthmann, B. Ber. d. Deutsch. chem. Ges <u>52</u> pp. 1185-1194	1919	2.1.1.
Hofmann, K.A. Ber. d. Deutsch. chem. Ges <u>56</u> p. 1456	1923	3.1. 3.3.
Howard, H.C. "Chemistry of Coal Utilization" ed. H.H. Lowry, <u>2</u> pp. 1568-1585 New York: Wiley, 1945.	1945	5.1.
Hughes, G. British Patent No. 369,920	1930	2.1.5.
Ivanov and Kobezev Zhurn. Fiz. Khim. <u>10</u> p.1	1937	3.1.

<u>Author</u>	<u>Date</u>	<u>Appendix Section</u>
Jablochkoff, P. Comp. rend. Paris <u>85</u> p. 1052; German Patent No. 6123	1877	1.3.1.
Jacques, W. W. British Patent No. 4,788/A.D. 1896; v.a. Anon 1896	1896	1.3.2.
Jacques, W. W. Harper's Magazine. <u>94</u> pp. 144-50	1896-7	1.3.2.
Jacques, W. W. Zeits. Electrochem. <u>4</u> p. 286	1898	1.3.2.
Jedlicka, H. Naturforsch. <u>3a</u> pp. 669-70	1948	2.1.4. 2.2.1.
Jedlicka, H. Naturforsch. <u>4a</u> pp. 301-302	1949	2.1.4. 2.2.1.
Jone, H. U. S. Patent No. 764,595	1904	2.2.1.
Jungner, E. W. British Patent No. 15,727/A.D. 1906	1906	1.1. 2.1.3.
Jungner, E. W. German Patent No. 199,250 Zeits. Electrochem. <u>14</u> p. 357 British Patent Nos. 5214/A.D. 1908 5223/A.D. 1908	1908a; b;c	1.2. 2.1.3.
Jungner, E. W. German Patent Nos. 206,108 and 206,273 Zeits. Electrochem. <u>15</u> pp. 347-351	1909a; b	1.2. 2.1.3.
Justi, E. U. S. Patent 2830109	1958	3.1. 3.3. 3.4.
Justi, E. Aleadomi der Wissenschaften and der literature Mainz. Germany (In German) Translation, Res. Info. Services, New York	1959	2.1.2. 3.1. 3.3. 3.4. 5.3.
Kendall v. Berthier, p. 184	1884	3.3.
Kendall, J. A. and Gore, R. E. British Patent No. 271,581; 273,095	1926	2.1.5.

<u>Author</u>	<u>Date</u>	<u>Appendix Section</u>
" Keyser, H. J. British Patent No. 3,913/A.D. 1904	1904	2.1.1. 2.2.2. 3.3.
Kirkland, T. G. Proc. Am. Power Conf. XXII, p. 465	1960	2.3.1.
" Konig, A. Zeits. angew. Chem. <u>44</u> p. 461; <u>45</u> p. 436	1931	2.1.5. 3.3.
" Konig, A. and Zohner, K. Siebert-Festschr. pp. 179-92; Chem. Abs. <u>26</u> 4259 (1932)	1931	2.1.5. 3.3.
Korda, D. Electrotech. Zeits. <u>16</u> p. 273	1895	1.3.2.
Kordesch, K. and A. Morko U. S. Patent 2615932 U. S. Patent 2669598	1952 1954	3.1. 3.1.
Kordesch, K. Fuel Cells, Reinhold Pub. Co. New York	1960	2.1.2. 3.2. 3.3. 3.4.
Kordesch, K. Research Report, Union Carbide Consumers Products Co.	1960	2.1.2. 3.2. 3.3. 3.4.
Lamb, A. B. and Elder, R. W. J. Amer. Chem. Soc. <u>53</u> pp. 137-163	1931	2.2.1. 2.2.2. 3.1.
Langhaus, R. German Patent No. 34,425	1886	1.3.2.
Langhaus, R. British Patent No. 430/A.D. 1901	1901	3.4.
Lavison, H.E. d R. de British Patent No. 9803/A.D. 1897	1897	4.2.
Liebenow, C. and Strasser, L. Zeits. Electrochem. <u>3</u> , p. 353	1897	1.3.2.
McCormick Fuel Cell Systems, PB161972 U. S. Department of Commerce	1960	5.1 5.2

<u>Author</u>	<u>Date</u>	<u>Appendix Section</u>
McKee, J. H, and Adams, A. M. Fuel. <u>28</u> pp. 1-6	1949	1.3.3. 1.4. 5.1.
Miller, K. D. Chem. Eng. Prog. <u>57</u>	1961	2.2.1.
Mond, L. and Langer, C. Proc. Roy. Soc. London <u>46</u> pp. 296-308	1889	2.1.1. 3.1.
Mond, L. and Langer, C. Zeits. Electrochem. <u>4</u> p. 131	1897	2.1.2. 3.1.
Mugdan Chem. Ztg. <u>26</u> p. 1156	1902	2.1.5.
" Muller, W. A. and Wallmann, J. F. German Patent No. 99,544	1898	2.1.2.
" Muller, W. A. Zeits. phys. Chem. <u>40</u> p. 158	1902	2.1.4.
Nasarischwily, A. Zeits. Electrochem. <u>29</u> pp. 320-323	1923	3.1.
Nelson, J. B. and McKee, J. H. Nature, London. <u>158</u> p. 753	1946	6.
Nernst, W. German Patent Nos. 259,241 259,500 265,424 264,026	1911a) 1911b) 1912a) 1912b)	2.1.1. 2.1.4. 2.2.2.
Nernst, W. and Wartenburg, von Zeits. phys. Chem. <u>56</u> p. 548	1906	5.3.
Niedrach, L.W. Proc. Power Sources Conf. Atlantic City	1959	2.1.2.
Nobis Dissertation, Dresden	1909	2.1.4.
Noble and Anderson U. S. Patent No. 759, 740	1903	1.1.
Ostwald, W. Zeits. Electrochem. 1 p. 122	1894	5.2.

<u>Author</u>	<u>Date</u>	<u>Appendix Section</u>
Polyani, M. and Hevesy, G. von German Patent No. 306,153	1916	2.1.4.
Posner, A. M. Fuel, <u>34</u> p. 330	1955	2.1.5. 2.2.2.
Rasch, E. German Patent No. 143,423	1900	2.1.6. 6.
Rawson, W. S. British Patent No. 24,570/A.D. 1898	1898	2.1.5.
Reed, A. Trans. Amer. Electrochem. Soc. <u>33</u> p. 189	1918	1.3.3.
Reed, C. J. Electrical World. <u>28</u> pp. 44-5, 74-5 98-100, 134-5	1898	1.3. 2.2.1.
Regensburger Dissertation, Karlsruhe	1929	2.1.2. 3.3.
Reid, J. H. British Patent No. 1670/A.D. 1903 German Patent No. 181,814 U.S. Patent Nos. 730,016 and 730,017 Swedish Patent No. 16936	1903 1904	2.1.2. 2.1.5. 3.3.
Rhorer, L. von Zeits. Electrochem. <u>29</u> p. 478 German Patent No. 367,151	1923	1.3.1.
Ribbe, P. German Patent No. 142,470	1902	3.3.
Rideal, E. K. and Evans, U. R. Trans. Faraday Soc. <u>17</u> pp. 466-482	1921	2.1.2. 2.1.5. 2.2.1. 2.2.2. 3.1. 5.1.
Rodgers U. S. Patent No. 487,644	1888	2.1.5.
Ruzicka, C. British Patent No. 18,931/A.D. 1905	1905	1.1. 4.1.

<u>Author</u>	<u>Date</u>	<u>Appendix Section</u>
Sacher and Lorenz v. Bechterew 1911	?	1.3.2.
Scharf, P. German Patent No. 48, 466	1888	2.1.1. 2.1.2. 2.1.4. 3.2. 3.3.
Schmid, A. "Diffusion Gas Electrodes" (In German) Stuttgart: F. Enke.	1923	2.1.4. 3.3.
Schmid, A. Helv. Chem. Acta. <u>7</u> , p. 370	1924	2.1.4. 3.3.
Schmitz, G. Electrotech. Zeit. <u>16</u> p. 145	1895	1.3.1.
Schoop, P. "Primary Elements" (In German) Halle	1895	1.3.3.
Sconzo, A. Ann. chim. applicata. <u>22</u> pp. 794-802	1932	1.3.1.
Seton, A. D. and Dobell, J. British Patent No. 15,903/A.D. 1897	1897	1.3.3. 2.1.5.
Short, R. U. S. Patent No. 569, 591	1896	1.3.1.
Shrewsbury, C. P.; Marshall, F. L. ; Cooper, J. and Dobell, J. L. Jour. Soc, Chem. Ind. <u>14</u> p. 874; German Patent No. 88,704; British Patent No. 12,483/A.D. 1894	1894	1.3.1.
Shurmovsky, N. and Burns, L. Zhurn, Fiz. Khim. <u>14</u> Nos. 9-10 p. 1183	1940	6.
Siegel, K. Electrotech. Zeits. <u>34</u> p. 1317	1913	2.1.2. 3.1.
Siemens Schuckertwerke German Patent No. 284,821	1913	2.1.3.
Sims British Patent No. 315,209	1929	2.1.2.

<u>Author</u>	<u>Date</u>	<u>Appendix Section</u>
Spiliotopol British Patent No. 18, 115/A.D. 1908	1908	2.2.1.
Spiridonov Nauk. i. zhizn (Acad. Sci. U.S.S.R.) No. 6, p. 22	1941	2.1.2.
" Starke German Patent No. 421,167	1925	3.2.
Stien, B. R. Fuel Cell, PB161972 U. S. Department of Commerce	1959	5.1. 5.2.
" Sussmann, R. and Sussmanns, G. German Patent No. 359,305	1916	2.2.2. 4.1.
Swan, J. W. Electrician <u>33</u> p. 127	1894	2.1.4.
Sweeney, W. J. and C. E. Heath 26th Midyear Meeting of A.P.I.	1961	2.3.
Szabo, St. von Naray Zeits. Electrochem. <u>33</u> p. 15	1927	3.1.
Taitelbaum, I. Zeits. Electrochem. <u>16</u> pp. 286-300	1910	1.2. 1.3.2. 2.1.1. 2.1.3. 2.2.2.
Tamaru, S. and Kamada, M. Zeits. Electrochem. <u>41</u> pp. 93-96	1935a	1.3.2.
Tamaru, S. and Kamada, M. J. Chem. Soc. Japan. <u>56</u> pp. 92-103	1935b	1.3.2.
Tatlow, W. Electrician <u>34</u> p. 344	1895	2.1.1. 2.2.2.
Thiel, A. Zeits. Electrochem. <u>21</u> p. 325	1915	1.1.
Tobler, J. Zeits. Electrochem. <u>39</u> pp. 148-167	1933	2.1.2. 3.1.
Tommasi "Treatise on Electric Cells" (In French) Paris	1889 (Grezel 1886)	1.1.

<u>Author</u>	<u>Date</u>	<u>Appendix Section</u>
Tommasi, D. and Radiguet v. Fodor	1884	1.1.
Tourneur, H. French Patent No. 332,982	1903	2.1.3. 2.2.2.
Treeby Electrician. <u>28</u> p. 206	1889	2.1.2.
" Union Electrization Gesellschaft German Patent No. 42,227	1902	2.1.1.
Waldburger, E. Dissertation, Basle	1930	2.1.2. 2.1.4. 3.1.
Welsbach, A. von Chem. Ztschr. <u>1</u> p. 690	1903	2.2.2.
Westphal, C. German Patent	1880	2.1.2. 3.1. 3.3. 4.2.
Winand, P. and Coullery Electrotech. Zeits. <u>16</u> p. 35-36	1895	2.1.1. 2.2.2.
Wright, A. and Thomson, C. Proc. Royal Soc. (London) <u>46</u> p.372-6	1889	2.1.2. 3.1.
Yeager, E. W. Tech. Rept 12, Western Res. Univ.	1954	5.3.
Young, G. J. and R. B. Rozelle J. Chem. Ed., <u>36</u> p. 68	1959	3.1.
Zettel, T. Zeits. Electrochem. <u>2</u> p. 543	1896	2.1.2.
" Zopke, C. German Patent No. 131,596	1902	2.1.2.
_____, Proc. 12th, 13th, 14th Annual Battery R. and D. Conf. Ft. Monmouth, New Jersey	1958 1959 1960	5.1. 5.2. 5.3.
_____, Proc. 139th, 140th Nat. ACS Meeting, Division Gas and Fuel Chemistry	1960 1961	5.1. 5.2. 5.3.

Classification of cells referred to in Bibliography

1. Direct cells operating on solid carbonaceous fuels.
 - 1.1. Aqueous electrolytes at temperatures below 100°C
 - 1.2. Aqueous electrolytes above 100°C
 - 1.3. Molten electrolytes (high temperature)
 - 1.3.1. Nitrate
 - 1.3.2. Carbonate or hydroxide
 - 1.3.3. Borax, etc.
 - 1.4. Solid electrolytes (high temperature)
 - 1.5. Ionized gas electrolytes (high temperature)
2. Indirect Cells.
 - 2.1. Cells operating on gaseous reaction products of carbon
 - 2.1.1. Low-temperature carbon monoxide cells
 - 2.1.2. Low-temperature hydrogen cells
 - 2.1.3. Low-temperature cells using other gases; e.g. SO₂
 - 2.1.4. Cells using halogens
 - 2.1.5. High-temperature hydrogen and carbon monoxide cells with molten electrolytes
 - 2.1.6. High-temperature hydrogen and carbon monoxide cells with solid electrolytes
 - 2.2. Cells operating on solid or liquid reaction products of carbon.
 - 2.2.1. Cells using metals as fuel
 - 2.2.2. Oxidation-reduction cells
 - 2.3. Cells operating on hydrocarbon fuels
 - 2.3.1. Low-temperature and pressure hydrocarbon cells
 - 2.3.2. High-temperature hydrocarbon cells
 - 2.3.3. Moderate-temperature low pressure cells

3. Electrodes.
 - 3.1. Activation of electrodes
 - 3.2. Liquid proofing
 - 3.3. Diffusion electrodes
 - 3.4. Methods of preparation of electrodes
4. Cell Construction.
 - 4.1. High-pressure cells
 - 4.2. Mechanical arrangements
5. Reviews and General Principles.
 - 5.1. Literature reviews
 - 5.2. General articles, economics, and applications
 - 5.3. Theoretical
6. Miscellaneous.

N.B.: When the electrolyte is shown enclosed by a broken line, it is retained in a porous material. The symbol \parallel is used to indicate the presence of a diaphragm.

1. Direct Solid Fuel Cells

1.1. Using aqueous electrolytes below 100°C

Davy	1802	$C/H_2O \parallel HNO_3/(C)O_2$
Tommasi and Radiguet	1884	$C/NaCl \parallel Pb/O_2/(C)O_2$
Grezel 1886 (v. Tommasi 1889)		$C/Acid \parallel (NH_4)_2CO_3/(C)O_2$
Case 1887 (v. Berthier 1929)		$C/H_2SO_4 \parallel KCl O_3/(Pt)O_2$
Case	1889	$C(Pt) \left[\begin{array}{c} FeCl_3 \parallel FeCl_3 \\ H_2O \parallel HCl \end{array} \right] (Pt)O_2$
Coehn	1896, 1897	$C/H_2SO_4/(PbO_2)O_2$
Nobel and Anderson	1903	$C/HNO_3/(Al)O_2$
Ruzicka	1905 (v.a. 4.1)	$C/KOH/(NiO)O_2$ and (non aqueous) $C/liquid Cl_2 Al$

Jungner 1906;1908a,b;1909a,b (v.a. 2.1.3) $C, SO_2 \left| H_2SO_4 \begin{array}{c} \parallel \\ \parallel \\ \parallel \end{array} \begin{array}{c} \text{Nitrosyl} \\ H_2SO_4 \end{array} \right| (C)O_2$

Hofmann and Ritter 1914 (v.a. Thiel 1915) $C/NaOH_{aq} \begin{array}{c} \parallel \\ \parallel \end{array} NaCl O_3 / (Pt)O_2$

Thiel 1915 theory of Case's cell

1.2. Using aqueous electrolytes above 100°C

Taitelbaum 1910) Baur 1910) $C \left| H_2SO_4 + V, Tl, \text{ sulphates} \right| \begin{array}{c} (Au) O_2 \\ (C) \\ (Pt) \end{array}$
250°C

Fischer and Kronig 1922, 1924 $C(Fe) \left| Aq. \text{ alkali} \right| (Fe) O_2$
200°C 30 Atm.

1.3. Direct cells operating at high temperature with molten electrolyte.

1.3.1. Nitrate Electrolytes e.g. C/molten sodium nitrate/ (metal)O₂

Becquerel	1855	Platinum cathode
Jablochkoff	1877	Iron cathode
Brard	1882	
Davies	1882 (v. Fodor 1897)	
Clark	1882 (" " ")	
Brooks	1894a;b	KHSO ₄ added to electrolyte, CuS cathode
Shrewsbury	1894	
<u>et.al.</u>		
Dobell	1895	Iron cathode
Schmitz	1895	
Sconzo	1930	C/Ag NO ₃ / (Ag, Pt, Pd, etc.) O ₂

1.3.2. Carbonate or hydroxide electrolytes.

Gore	1864	$C \left Na_2CO_3, CaO \text{ glass} \right (Fe)O_2$
Archereau	1883	$C \left \text{Alkali carbonate or hydroxide} \right (metal)O_2$
Langhaus	1886	"
Fabinghi and Farkas	1888	"
Bradley	1888	"
	(v. Anon. 1897)	
Bull	1891	"

Korda	1895	C K ₂ CO ₃ (CuO) O ₂
Anon.	1896;1897)	
Jacques	1896;1897)	C/NaOH/(Fe) O ₂
	1898 (v.a. Haber and Bruner 1904)	
Liebenow & Strasser	1897	Modifications of Jacques cell
Reed	1898	" " " "
Sacher and Lorenz		
	(v.Bechterew 1911)	" " " "
Byrnes	1902	" " " "
Haber and Bruner	1904	Addition of sodium manganate to NaOH
	(v.a. 2.1.2.)	
Baur	1910)	C + carbonaceous NaOH + (Fe)O ₂
Taitelbaum	1910)	material MnO ₂
Bechterew	1911	C NaOH + selenates, tellurates, etc. (FeO) O ₂
Fischer and Lepsius	1912	C NaOH (Fe ₂ O ₄)O ₂
	(v.a. 2.1.5.)	
Baur and Treadwell	1916b; C	salt (Fe ₃ O ₄)O ₂
	1918	
Baur <u>et.al.</u>	1921b	C carbonates in porous Mgo (Fe ₃ O ₄)O ₂
Habicht	1919	C,CO,Na (Pb, Sn) NaOH (Ag) molten O ₂
Rhorer, von	1923	Alkali + Barium carbonates and alumina, etc. Pt or Ag cathodes.
Tamaru and Kamada	1935a	Carbonates; Pt, Au, Ag cathodes
	b	
Baur and Brunner	1935	C/carbonate/(Ag Pt)O ₂
" " "	1937a	C/carbonates (Fe ₃ O ₄)O ₂

1.3.3. Borax and other electrolytes.

Schoop	1895	C/lead oxides/(Fe)O ₂
Short	1896	C/lead oxides/(Pt)O ₂
Dobell	1897a	C(molten Pb) lead oxides/ (Fe)O ₂
	1897b	C or CO(molten chromates 8 (Fe) Pb) hydroxides O ₂
Seton and Dobell	1897	C or CO(molten arsenates (Fe) Pb,Bi,etc.) chromates O ₂ vanadates etc.

Baur and Ehrenberg	1912	C/borax/(molten Ag) O ₂
Baur <u>et.al.</u>	1916a	C/borax/(CuO) O ₂
Reed	1918	C/borax + MnO ₂ /(Au) O ₂
McKee and Adams	1949	C $\left \begin{array}{c} \overline{\text{CeO}_2} + \overline{\text{WO}_3} \text{ in} \\ \text{porous Al}_2\text{O}_3 \end{array} \right \left(\begin{array}{c} \text{Pt} \\ (\text{Fe}_3\text{O}_4) \end{array} \right) \text{O}_2$

1.4. Direct cells operating at high temperatures with solid electrolyte.

Baur and Treadwell	1916b)	"Nernst mass" or
Baur and Preis	1937b;1938)	CeO ₂ + WO ₃ + clay
McKee and Adams	1949	CeO ₂ + WO ₃ + clay

1.5. Direct cells operating at high temperatures and using ionized gas or electrolyte.

Crossley	1923 (v.a. 4.2.)	C(Fe)/heated ionized gas/ (metal)O ₂
----------	------------------	--

2. Indirect cells.

2.1. Gas cells.

2.1.1. Low temperature carbon monoxide cells.

Winand and Coullery	1887	CO(Cu?) $\left \text{Cu}_2\text{Cl}_2 \right\ \left\ \text{CuCl}_2 \right \text{O}_2$
	(v. 1895)	
Scharf	1888	
	(v.a. 2.1.2.)	CO/electrolyte/air
	2.1.4.	

3.3.

Borchers	1894	CO(Cu) $\left \text{Cu}_2\text{Cl}_2 \right\ \left\ \text{CuCl}_2\text{HCL} \right (\text{Cu})\text{O}_2$
	(v.a. Fodor 1897)	
Hering & Dobrowolsky	1895	CO(C-Pt) $\left \text{H}_2\text{SO}_4 \right (\text{Pt})\text{O}_2$
Bernstein	1895;1897	CO + H ₂ $\left[\text{H}_2\text{SO}_4 \text{ aq} \right] (\text{C})\text{O}_2$
Tatlow	1895	$\left(\begin{array}{c} \text{water gas} \\ \text{coal gas} \\ \text{water gas} \end{array} \right) \left (\text{C})\text{Cu}_2\text{Cl}_2 \right\ \left\ \text{CuCl}_2 \right (\text{C})\text{O}_2$
Bucherer	1896b	Discussion of Borchers' cell
Union Elektr.Gesell	1902	Use of acetylene instead of CO
Baur and Glaessner	1903	CO, H ₂ etc $\left(\begin{array}{c} \text{Ni} \\ \text{Pt} \end{array} \right) \left \text{Ce}^{3+} : \text{NaOH aq} : \text{Ce}^{4+} \right \dots$
		$\left(\begin{array}{c} \text{Pt} \\ \text{C} \end{array} \right) \text{O}_2$
"Keyser	1904	CO, etc $\left \text{KOH}, \text{K}_2\text{CO}_3, \text{FeCl}_2 \right (\text{Fe})\text{O}_2$
		Boiling

Braun and Schneider	1910	CO(metal) H ₂ SO ₄ (metal)O ₂
	(v.a. 6)	
Baur)	Tl ³⁺ V ⁴⁺ H ₂ SO ₄ Tl ³⁺ V ⁵⁺ ...
	(v.a. 2.2.2.)	
Taitelbaum	1910)	
		(Pt)
		... (Au)O ₂
		(C)
Nernst	1911;1912	Use of Ti and Ce instead of Tl, V
	(v.a. 2.2.2.)	
Hofmann	1918a;b;1920a)	Co(Cu) NaOH aq., (Cu) lye soln, etc. (Cu)O ₂
Hofmann	Wurthmann 1919)	
Auerbach	1919)	

2.1.2. Low temperature hydrogen cells.

Grove	1839	H ₂ (Pt)/H ₂ SO ₄ /(Pt)O ₂		
Westphal	1880	H ₂ (Pt)/Acid/(Pt)O ₂		
Blanchard	1882	H ₂ (Pb)/H ₂ SO ₄ /(PbO)O ₂		
Scharf	1888	H ₂ /electrolyte/air		
	(v.a. 2.1.1.;2.1.4.)			
Treeby	1889)	H ₂ (Pt.blk) <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>H₂SO₄ ...</td></tr><tr><td>porous material</td></tr></table>	H ₂ SO ₄ ...	porous material
H ₂ SO ₄ ...				
porous material				
Mond and Langer	1889;1897)			
Wright and Thompson	1889)			
		...(Pt.blk)O ₂		
Cailletet Collardeau	1894)	H ₂ (Pt)/H ₂ SO ₄ /(Pt)O ₂		
	(v.a. 4.1.)	high pressure		
Andreas	1895			
Bernstein	1895;1897	v. 2.1.1.		
Zettel	1896	H ₂ (Ag) H ₂ SO ₄ (Ag)O ₂		
"				
Muller and Wallmann	1898)	Hydrogen/oxygen cell		
Zopke	1902)			
Reid	1903;1904	H ₂ , CO ₂ (porous C)/NaOH aq/ (Fe)O ₂		
"				
Forster and Dithelm	1908	H ₂ (Pt)Ti sulphates/(Pt)O ₂		
"				
Forster	1909	H ₂ /H ₂ SO ₄ /O ₂		
Grube	1910;1932	H ₂ /H ₂ SO ₄ :Fe ³⁺ or NO/O ₂		
Siegel	1913	Platinised C anodes in H ₂ -O ₂ cell		

Gaiser	1918	$H_2(Pt) \left \begin{array}{c} H_2SO_4 + \text{colloidal} \\ Pt \text{ or } Ag \end{array} \right (Pt)O_2$
Rideal and Evans	1921	$H_2(Ni, Pt, blk) \left \begin{array}{c} NaOHaq \\ NaOH + MnO_2 \end{array} \right (C)O_2$
Fischer & Kronig	1922; 1924	$H_2(Pt) \left H_2SO_4, NO \right (Pt)O_2$
Hofmann	1923	$H_2(Pt) \left \text{lye soln} \right (Pt)O_2$
	(v.a. 3.1.)	
Forster	1923	v. 2.1.4.
Regensburger	1929	$H_2(Pd) / H_2SO_4 \left \begin{array}{c} NaOH \\ (Pt, C) \end{array} \right O_2$
Sims	1929	$H_2(C) / ? / (C)O_2$
Citovich	1929	H_2-O_2 cell with Cu anode (v.a. 4.1.)
Waldburger	1930	$H_2(C-Pt) \left HCl \right (C)Br_2$
Baur and Tobler	1933	$H_2(C-Pt) \left \begin{array}{c} NaOH \\ (Ag) \\ (C) \\ (Cu) \end{array} \right O_2$
Tobler	1933	v. 3.1.
Doyle and Doyle	1934	$H_2 \left \text{acid or alk.} \right (PbO)O_2$
Spiridinov	1941	$H_2 \left \begin{array}{c} (C, Ni) \text{ electrolyte} \\ (Active C) \end{array} \right O_2$
Davtyan	1946; 1947	$H_2(C, Ag) / KOH_{aq} / (C, Ni)O_2$
Brit. E.R.A.	1950	$H_2(Ni) \left KOH_{aq} \right (Ni)O_2$ (high pressure)
Grubb	1959)	$H_2(Pt, Pd) \left \begin{array}{c} ion \\ Exchange \end{array} \right (Pd, Pt)O_2$
	1960)	
Justi	1958)	$H_2(Ni) \left KOH \right (Ag) O_2$
	1959)	
Kordesch	1960	$H_2 \left(\begin{array}{c} Ni \\ porous C \end{array} \right) \left (KOH_{aq}) \right \dots$ $\dots \begin{array}{c} Ag \\ porous C \end{array} O_2$

2.1.3. Low temperature gas cells other than H_2 , CO, and halogen cells.

Andreas	1895	$SO_2(C) \left \begin{array}{c} Cu_2Cl_2 \\ CuCl_2 \end{array} \right (C)Cl_2$
	(v. Fodor 1897)	
Tourneur	1903	$SO_2(C) \left HNO_3 \right (C)O_2$

Basset	1906;1907a;b	$\text{SO}_2, \text{H}_2\text{S}, \text{HI},$ etc (porous C)	$\left \begin{array}{l} \text{H}_2\text{SO}_4 \text{ aq} + \\ \text{Br}_2, \text{NO} \end{array} \right $	(Graphite) O_2
Jungner	1906;1908;1909	SO_2 (Coke)	$\left \begin{array}{l} \text{H}_2\text{SO}_4 \text{ Nitrosyl} \\ \text{H}_2\text{SO}_4 \end{array} \right $	(C) O_2
Taitelbaum	1910)	SO_2 (C)	$\left \begin{array}{l} \text{H}_2\text{SO}_4 + \text{Tl}, \text{V}, \\ \text{sulphates} \end{array} \right $	(Pt) (Au) (C) O_2
Baur	1910)	(v.a. 1.2.)		
Siemens	1913	HI (C)	$\left \begin{array}{l} \text{H}_2\text{SO}_4 \text{ HNO}_3 \end{array} \right $	(C) O_2
Schuckertwerke				

2.1.4. Halogen Cells.

Scharf	1888	$\text{H}_2, \text{CO}/\text{electrolyte}/\text{Cl}_2, \text{F}_2$		
	(v.a. 2.1.1;2.1.2;3.3)			
Swan	1894	? KCl, NaCl or PbCl ₂		Cl_2
"				
Muller	1902	$\text{H}_2 - \text{Cl}_2$ cell		
Nobis	1909	$\text{H}_2 \text{HCl aq } 60^\circ $		Cl_2
Nernst	1911	$\text{H}_2 - \text{Cl}_2$ cell with regenera- tion of Cl_2		
Polyani & v.Hevesy	1916	? alkaline electrolyte		$\text{NO},$ Cl_2 (metal oxide)
"				
Forster	1923	$\text{H}_2(\text{Pt})/\text{HCl}/(\text{C})$		Cl_2
Schmid	1923;1924)			
"	(v.a. 3.3.)	$\text{H}_2(\text{Pt}, \text{C})/\text{HCl}/(\text{C})$		Cl_2
Buhrer	1929)			
Waldburger	1930	$\text{H}_2(\text{Pt}, \text{C}) \text{ HCl}/(\text{C})$		Br_2
Davtyan	1947	$\text{H}_2(\text{Fe}, \text{Si})/\text{HCl}/(\text{C})$		Cl_2
Jedlicka	1948;1949	$\text{Na}(\text{Hg})/\text{NaCl aq}/(\text{C})$		Cl_2

2.1.5. High Temperature gas cells with molten electrolyte.

Arsonval, d'	1882	H_2 etc (Sb, Pb, etc)	$\left \begin{array}{l} \text{Sb}_2\text{O}_3 \text{ Sb}_2\text{O}_5 \\ \text{(Sb) O}_2 \end{array} \right $	
Rodgers	1888	$\text{H}_2/\text{metal oxide}/$		O_2
Atkinson & Treharn	1896	$\text{H}_2/\text{molten Pb}/\text{PbO}/(\text{Ag})$		O_2
Bucherer	1896a;b	$\text{CO}, \text{H}_2(\text{Fe})/\text{carbonate}/(\text{Pt})$		O_2

Jacques	1896	v. 1.3.2. (Haber & Bruner 1904)
Dobell	1897a;b)	
Seton & Dobell	1897)	v. 1.3.3.
Rawson	1898	CO(molten Pb)/Metal Salt/(?)O ₂
Britzke	1900	CO(Cu) $\overline{\overline{\text{PbO}}}$ (Cu)O ₂
Magdon	1902	H ₂ (Pb) Na ₂ CO ₃ NaOH Feritte (Fe)O ₂ CO
Reid	1903	CO(C) NaOH (Metal) O ₂
Haber & Bruner (v.a. 1.3.2.)	1904	H ₂ (C) NaOH, Na ₂ MnO ₄ (Fe)O ₂
Haber	1906	CO, H ₂ /Carbonates/(Metal) O ₂
Beutner (v.a. 3.3.)	1911	CO, H ₂ (Ni, Pt)/halides/(Metal) O ₂
Baur & Ehrenburg (v.a. 1.3.3.)	1912	CO, H ₂ (Pt, Fe, Ni, Cu) /Borax/... ... (molten Ag) O ₂
Fischer & Lepsius (v.a. 1.3.2.)	1912	H ₂ (C)/NaOH/(Pt)O ₂
Hoffman, A. G.	1920b	CO(C)/molten Cu/(CuO)O ₂
Hofmann, F	1920c	CO(Cu)/ - /(CuO)O ₂
Bauer, <u>et.al.</u>	1921b	H ₂ , (Fe) $\overline{\overline{\text{NaKCO}_3}}$ (Fe ₃ O ₄)O ₂ in MgO
Baur	1921c 1921d	H ₂ , CO, (Fe)/(NaOH)/(Fe)O ₂
Rideal & Evans	1921	CO, H ₂ (Pt)/UO ₂ Posphate GlassNa ₂ Mn ₄ /(Fe)O ₂ Sn may replace Pt & a carbonate the UO ₂ -Glass
Kendall & Gore Hughes	1926) 1930)	H ₂ , CO $\overline{\overline{\text{carbonates}}}$ (Ag, etc)O ₂ borates (Ag) (Ni) (Cu)
Greger	1931;1933 1934 1939 1942	CO, H ₂ (Metal) $\overline{\overline{\text{carbonates +}}}$... halides (Ni, Fe) ... (Ferrite)O ₂ (etc.)

Kohnig & Zohner	1931	$H_2(Pd)/KNO_2+NaNO_2/(Pd)O_2$
Blanke	1942	$H_2, CO, (C) \left \begin{array}{l} Na, Ba, etc, carbonates \\ + halides \end{array} \right \dots$ $\dots (C)O_2$

2.1.6. High temperature gas cells with solid electrolytes.

Rasch	1900	$CO, H_2, etc./Zircon-Yttria/$ Salt flame Glass/ O_2
Haber and Moser	1905)	$CO(Pt.blk)/Glass/(Pt.blk)O_2$
Haber	1906;1911)	
Fleischmann & Förster	1906	$H_2, CO/glass, porcelain/(?)O_2$
Baur and Preis	1937b, 1938)	
	(v.a. 1.4.)	$H_2, CO(Fe) \left \begin{array}{l} "Nernst mass" \\ CeO_2, WO_3, etc. \end{array} \right \dots$
Baur	1939)	
		$\dots (Fe_3O_4)O_2$
Baur	1941	Additions to electrolyte to reduce resistance, etc.

2.2. Indirect solid or liquid fuel cells.

2.2.1. Metal fuel.

Davy	1801	$Zn/FeCl_3/(C)O_2$
Faure	1891	$Fe/NaCl\ aq/(C)O_2$
Reed	1898	Discussion of metal fuels
Jone	1904	$Pb, Sn, Cd, Sb, etc/NaCl\ aq/O_2$
Spiliotopol	1908	$Sn, Al \left \begin{array}{l} Cr_2Cl_6; PbCl_2 \\ MnCl_2\ (fused) \end{array} \right (C)O_2$
Hahicht	1919	$Na(molten\ Pb, Sn) \left \begin{array}{l} molten \\ Na\ OH \end{array} \right (Ag)O_2$
Rideal and Evans	1921	$\left \begin{array}{l} Pb\ NaOH\ aq \text{ "Mn } O_2 \\ Na_2CO_3\ aq \text{ " } \end{array} \right (C)O_2$ $\left \begin{array}{l} Sn\ HCl \text{ "FeCl}_3 \\ HCl \end{array} \right (C)O_2$ $Sn \left \begin{array}{l} reduced \text{ "oxidized} \\ melt. \text{ " melt.} \end{array} \right (Fe)O_2$
Baur	1921a	$Na/NaOH/(Ag, Fe_2O_3, Fe_3O_4)O_2$
Brandt	1925	$NA/NaOH/(Passive\ metal)O_2$

Lamb and Elder	1931	$\text{Zn}/\text{H}_2\text{SO}_4/\text{FeCl}_3/(\text{Active C, Pt})\text{O}_2$
Hamer and Schrodtt	1949	$\text{Mg}/\text{molten or solid}/(\text{C})\text{MnO}_2\text{NaOH}$
Jedlicka	1948;1949 (v.a. 2.1.4.)	$\text{Na(Hg)}/\text{NaCl aq}/(\text{C})\text{Cl}_2$
Miller	1961	$\text{Na(Hg)}/\text{NaOHaq}/(\text{Ag})\text{O}_2$
Ciarlarello	1960	$\text{Li metal halogen (Fe)H}_2$

2.2.2. Oxidation-reduction cells using compounds of metals of variable valency, etc.

Tatlow	1894)	
Borchers	1894	$\text{Cu} + \rightleftharpoons \text{Cu}^{++}$
Windand and Coullery	1895)	(v.a. 2.1.1.)
Welsbach	1903)	$\text{Ce}^{3+} \rightleftharpoons \text{Ce}^{4+}$
Baur & Glaessner	1903)	(v.a. 2.1.1.)
Tourneur	1904	(a) C + Alkali sulphate - sulphide
		(b) Alkali Sulphide $\left \begin{array}{l} \text{K}_2\text{S} \\ \text{soln} \end{array} \right \begin{array}{l} \text{HNO}_3 \\ \text{KClO}_3 \end{array} \left \begin{array}{l} (\text{C}) \\ (\text{Pt}) \\ (\text{Fe-Si})\text{O}_2 \end{array} \right.$
Keyser	1904	Fe salts (v. 2.1.1.)
Junger	1906,1908	Mn,Cr,Fe,Cu,Hg salts (v. 1.1.;2.1.3.)
Forster & Dithelm	1908	Ti salts (v. 2.1.2.)
Taitelbaum	1910)	
Baur	1910)	v, Tl (V. 1.2.)
Grube	1910	Fe salts (v. 2.1.2.)
Nernst	1911;1912	Tl,Ti,Ce salts (v. 2.1.2.)
Sussmann and Sussmann	1916	Oxidation-reduction cells under pressure
Rideal and Evans	1921	Mn,U,V,Cr,Ce in glass (v. 2.1.5.)
Lamb and Elder	1931	Survey of various systems
Baur & Preis	1937b;1938)	Addition of Mn,Cr,V,Ti,U,etc.
Baur	1941)	to solid electrolyte (v.2.1.6.)
Blanke	1942	v. 2.1.5.

2.3.1.

Kirkland	1960	$\text{H}_2, \text{C}_3\text{H}_8/\text{electrolyte}/\text{O}_2$
Sweeney	1961	$\left \begin{array}{l} \text{C}_2\text{H}_6 \text{ Dissolved} \\ \text{in electrolyte} \end{array} \right \text{O}_2$

2.3.2. High Temperature Hydrocarbon Cells with Molten Electrolyte

Gorin	1952;1959	H_2, CO, CH_4	$\left[\begin{array}{c} K_2CO_3, Li_2CO_3, Na_2CO_3 \\ \text{in} \\ MgO \end{array} \right]$
Broers	1958;1959	C_2H_6, C_3H_8 (Ni)	
DeZubay	1960	Kerosene (Ag)	
Douglas	1960	etc	
		.. (Ag) Air, O_2	

2.3.3. Moderate Temperature Low Pressure Cells

Elmore & Tanner	1960	$H_2(Pt)/H_3PO_4-SiO_2/(Pt)O_2$
		$H_2(Pd) \left \begin{array}{c} KOH, NaOH \\ Ca(OH)_2 \end{array} \right (Ag)O_2$

3. Gas electrodes for fuel cells.

3.1. Activation.

Grove	1839)	Platinum for hydrogen
Westphal	1880)	
Mond and Langer	1889)	Platinum black for H_2
Wright & Thompson	1889)	
Caillet & Collardeau	1894	Pt, Pd, and Au
"Forster & Dithelm	1908)	Pt. electrodes for H_2 and O_2
Forster	1909;1915)	
Siegel	1913	Platinized carbon for H_2
Fery	1918;1930	Porous C electrodes for O_2
Rideal & Evans	1921	Platinized Ni for H_2
Hofmann	1923	Platinized clay for H_2
Nasarischwily	1923	Carbon electrodes for O_2
Szabo	1927	Platinized carbon electrodes
Baur	1930	"Hopcalite" for O_2
Waldburger	1930	Poisoning of Pt electrodes
Lamb & Elder	1931	Active carbon for O_2
Heise & Schumacher	1932	Porous C electrodes
Tobler	1933	Ni, Fe, C, Pt electrodes (plain or platinized) for H_2 and O_2

Ivanov & Kobozev	1937)	Fe ₃ O ₄ electrodes
Baur and Brunner	1937a)	
Davtyan	1947	Catalytic activation for H ₂ and O ₂
Bacon	1955	Ag for H ₂ , O ₂
Justi	1958;1959	Ni for H ₂ Ag for O ₂
Kordesch	1952;1954;1960	Ni for H ₂
Young	1960	Catalysts for fuel cells.

3.2. Non-wetting electrodes.

Scharf	1888	Wax coating
Carbone, S.A.) Stärke)		Gelatine coating
Davtyan	1947	Wax coating
Kordesch	1960	Surface active agents

3.3. Diffusion electrodes.

Westphal	1880	
Kendall	1884	
Scharf	1888	
Anon	1895	
Ribbe	1902	
Keyser	1904	
Reid	1903	CO diffusion through C
Beutner	1911	H ₂ diffusion through Pd
Forster	1915	
Schmid	1923;1924	
Förster	1923	
Hofmann	1923	
Baillod	1927	
Buhrer	1929	
Regensburger	1929	
König	1931;1932)	H ₂ diffusion through Pd
König & Zohner	1931)	
Blanke	1942	
Davtyan	1947	
Bacon	1955;1960	
Broers	1958	
Justi	1959	
Kordesch	1960	
Bacon	1960	

3.4. Methods of preparing active electrodes.

Langhaus	1901	Metallization of C
Davtyan	1947	Reduction of Ag,Ni,etc, on C

4. Special Construction of Cells

4.1. High Pressure Cells.

Cailleter & Collardeau	1894
Ruzicka	1905
Süssmann & Süssmann	1916
Fischer and Kronig	1922;1924
Citovich	1929
Brit. E.R.A.	1950

Bacon	1955
-------	------

4.2. Mechanical Details.

Westphal	1880	
Lavison	1897	Rotating electrodes
Eltenberg & Lach	1907	" "
Greger	1933;1934	
	1939;1942	
Davtyan	1947	
Adams	1960	

5. Reviews and General Principles

5.1. Literature reviews.

Fodor	1897
Bechterew	1911
Rideal & Evans	1921
Berthier	1929
Greger	1931
Baur & Tobler	1933
Howard	1945
Davtyan	1947
Brit. Elec. R.A.	1949a;b
McKee & Adams	1949
Ellingham	1950
Adams	1960
McCormick	1960
Stien	1959
Annual Battery R. and D.Conference	1958;1959;1960;1961
ACS Meeting, Division Gas & Fuel Chemistry	1960;1961

5.2. General articles, economics.

Ostwald	1894
Baur	1921e
Greger	1931
Baur	1939
Gordon	1946

5.3. Theoretical.

Boudouard	1904	
Nernst & Wartenburg	1906	
Allemand & Ellingham	1924	
Grube	1932	
Chipman & Murphy	1933	Free energies
Ellingham	1944	" "
Justi	1959	
Annual Battery R. and D. Conference	1958;1959;1960;1961	
ACS Meeting, Division Gas & Fuel Chemistry	1960;1961	

6. Miscellaneous

Britzke	1900)	
Rasch	1900)	Thermal ionization of CO
Braun & Schneider	1910)	Ionization of fuel gases
Crossley	1923)	by U.V. irradiation, etc.
Shurmovsky & Burns	1941	Mechanism of CO oxidation by Mn O ₂
Nelson & McKee	1946	Crystal structure of CeO ₂ : WO ₃ compounds

VITA

William Benson Lumpkin

Candidate for the Degree of

Master of Science

Thesis: FUEL CELL DEVELOPMENTS

Major Field: Chemical Engineering

Biographical:

Personal Data: Born in Muskogee, Oklahoma, January 17, 1935, the son of W. B. and Pearl E. Lumpkin. Married to Shirley F. Walker, Haskell, Oklahoma, in June, 1957.

Education: Attended grade school in Coweta, Oklahoma; graduated from Coweta High School in 1953, received the Bachelor of Science degree in Chemical Engineering from Oklahoma State University in 1960; completed requirements for the Master of Science degree in May, 1962.

Professional Experience: Employed as roustabout with Pan American Petroleum Company in the summers of 1956 and 1957. Employed as temporary process engineer with Callery Chemical Company in the summer of 1959. Employed as temporary engineer with Phillips Petroleum Company in the summer of 1960. Employed in the summer of 1961 as temporary research engineer with Jersey Production Research Company.