

FUEL CELL TECHNOLOGY

H A N D B O O K

Edited by

Gregor Hoogers



CRC PRESS

Boca Raton London New York Washington, D.C.

TABLE 1.1 Currently Developed Types of Fuel Cells and Their Characteristics and Applications

Fuel Cell Type	Electrolyte	Charge Carrier	Operating Temperature	Fuel	Electric Efficiency (System)	Power Range/ Application
Alkaline FC (AFC)	KOH	OH ⁻	60–120°C	Pure H ₂	35–55%	<5 kW, niche markets (military, space)
Proton exchange membrane FC (PEMFC) ^a	Solid polymer (such as Nafion)	H ⁺	50–100°C	Pure H ₂ (tolerates CO ₂)	35–45%	Automotive, CHP (5–250 kW), portable CHP (200 kW)
Phosphoric acid FC (PAFC)	Phosphoric acid	H ⁺	~220°C	Pure H ₂ (tolerates CO ₂ , approx. 1% CO)	40%	CHP (200 kW)
Molten carbonate FC (MCFC)	Lithium and potassium carbonate	CO ₃ ²⁻	~650°C	H ₂ , CO, CH ₄ , other hydrocarbons (tolerates CO ₂)	>50%	200 kW–MW range, CHP and stand-alone
Solid oxide FC (SOFC)	Solid oxide electrolyte (yttria, zirconia)	O ²⁻	~1000°C	H ₂ , CO, CH ₄ , other hydrocarbons (tolerates CO ₂)	>50%	2 kW–MW range, CHP and stand-alone

^a Also known as a solid polymer fuel cell (SPFC).

for the chlor-alkali industry by DuPont and have proved instrumental in combining all the key parts of a fuel cell, anode and cathode electrodes and the electrolyte, in a very compact unit. This membrane electrode assembly (MEA), not thicker than a few hundred microns, is the heart of a PEMFC and, when supplied with fuel and air, generates electric power at cell voltages up to 1 V and power densities of up to about 1 Wcm⁻².

The membrane relies on the presence of liquid water to be able to conduct protons effectively, and this limits the temperature up to which a PEMFC can be operated. Even when operated under pressure, operating temperatures are limited to below 100°C. Therefore, to achieve good performance, effective electrocatalyst technology (Chapter 6) is required. The catalysts form thin (several microns to several tens of microns) gas-porous electrode layers on either side of the membrane. Ionic contact with the membrane is often enhanced by coating the electrode layers using a liquid form of the membrane ionomer.

The MEA is typically located between a pair of current collector plates with machined flow fields for distributing fuel and oxidant to anode and cathode, respectively (compare Fig. 4.2 in Chapter 4). A water jacket for cooling may be inserted at the back of each reactant flow field followed by a metallic current collector plate. The cell can also contain a humidification section for the reactant gases, which helps to keep the membrane electrolyte in a hydrated, proton-conduction form. The technology is given a more thorough discussion in Chapter 4 (compare Section 10.2.3).

Having served as electric power supply in the *Gemini space program*, this type of fuel cell was brought back to life by the work of *Ballard Power Systems*. In the early 1990s, Ballard developed the Mark 5 fuel cell stack [Fig. 10.4(a)] generating 5 kW total power at a power density of 0.2 kW per liter of stack volume. With the Mark 900 stack [Fig. 10.4(b)] jointly developed by Ballard and DaimlerChrysler in late 1990s, the power density had increased more than fivefold to over 1 kW/l. At a total power output of 75 kW, this stack meets the performance targets for transportation (compare Section 10.2.3).

PEMFCs are also being developed for stationary applications. In the 250-kW range, *Ballard Generation Systems* is currently the only PEMFC-based developer. More recently, the *micro-CHP* range has been claimed by a wide range of developers. Here, high power density is not the most crucial issue. In a

(don
econ

1.4

Two high
consider
anionic
advanta
achieved
efficient
processing
ature pow
temperatur
only there
A full ac
in Chapter

1.5 Li

No doubt o
on a liquid
fuel cell (D
therefore d
anode cata
densities),
poisoning
generate u
conditions
estimated
stages. Th
in Chapte

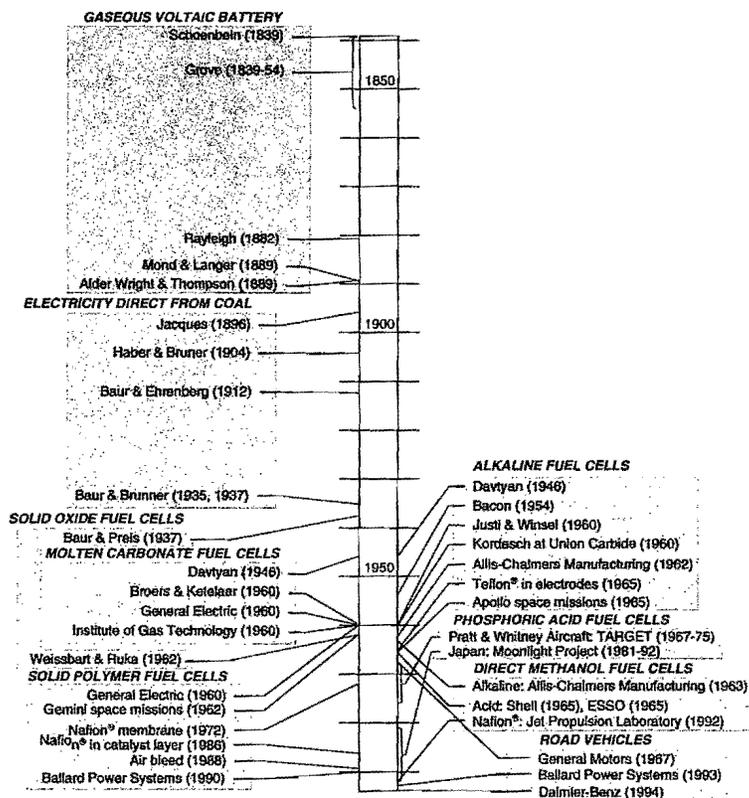


FIGURE 2.1 The achievements highlighted in this chapter are grouped into nine sections. The chronology is based on the year of publication by authors and companies. (Teflon® and Nafion® are registered trademarks of E.I. du Pont de Nemours and Company.)

In the early history of the fuel cell, researchers recognized — but struggled to achieve — the high theoretical efficiency of electrochemical energy conversion. Improvements were needed in the design of electrodes, the selection of suitable electrolytes, and the development of compatible hardware materials to support the reactions. This chapter retells the development of the main types of fuel cells, reviewing the progression that has led to the current state of the technology.

The timeline in Fig. 2.1 shows the nine sections of the chapter. The early period of development encompassed four of the types classified in terms of electrolyte: the “gaseous voltaic battery” used aqueous acid, and the “direct coal” fuel cells were tested with alkaline, carbonate, and solid oxide electrolytes. After the discussion of these beginnings, each type of fuel cell is addressed in a separate section with highlights of the major achievements ordered by chronology. After the sections about types, the final section about road vehicles includes the three types of fuel cells that have been used in vehicle propulsion systems. The conclusion summarizes the lineage of the main types of fuel cells and offers references to other significant work that could not be accommodated in this chapter.

2.1 The “Gaseous Voltaic Battery”

Before it went by the name “fuel cell” (Rideal and Evans, 1922), it was first known as the “gaseous voltaic battery” (Grove, 1842). The gaseous voltaic battery of Grove used platinum electrodes and sulfuric acid electrolyte, with hydrogen and oxygen as reactants. At that time, platinum was already known to be a catalyst for the reaction between hydrogen and oxygen, and the first published experimental results of Grove were “an important illustration” of that principle (Grove, 1839). Schoenbein

had referred to the experiment as a scientific curiosity. An instance of Grove's (1839) of the attention to the matter. Among other things, Grove (1839) and Rayleigh, and the efforts to

2.1.1 W

In 1839, when Grove, 1842 of the gaseous voltaic battery into a beaker containing hydrogen and oxygen gases displaced the water. Grove's galvanometer showed a deflection, and the electrolysis

Because of the dependence on the layer of liquid on the surface of a solid platinum electrode, the goal of an electrolytic cell version of a different gas mixture had dissolved

had referred to this principle in 1838, using it to explain the electrical current that he measured in experiments on platinum electrodes, but it was necessary for him to bring this to the attention of the scientific community after the demonstration of Grove's battery of cells (Schoenbein, 1843). Another instance of researchers claiming precedent occurred after the demonstration by Mond and Langer (1889) of their gas battery, which was more practical; Alder Wright and Thompson (1889) brought attention to their "aeration plate" electrodes that also acted as a matrix to contain the electrolyte. Among other, less controversial papers about improvements to the gas battery was one from Lord Rayleigh (1882), reporting the use of platinum gauze as electrodes with higher surface area. Also, Rayleigh, and later Mond and Langer, used as fuel impure hydrogen derived from coal, which preceded the efforts to develop a "direct coal" fuel cell.

2.1.1 William R. Grove (1839, 1842, 1843, 1845, 1854)

In 1839, when the fuel cell was invented by William R. Grove, it was called a "gaseous voltaic battery" (Grove, 1842). Grove performed this first experiment in Swansea, Wales, and included a description of the gaseous battery as a postscript to an article describing experiments with electrode materials for galvanic batteries. In the experimental set-up, two platinum electrodes were halfway submerged into a beaker of aqueous sulfuric acid, and tubes were inverted over each of the electrodes, one containing hydrogen gas and the other containing oxygen gas. When the tubes were lowered, the gases displaced the electrolyte, leaving only a thin coating of the acid solution on the electrode; a galvanometer deflected to indicate a flow of electrons between the two electrodes. After the initial deflection, the current decreased in magnitude, but the reaction rate could be restored by renewing the electrolyte layer.

Because of the importance of this coating layer, Grove later realized that the reaction was dependent on the "surface of action" (Grove, 1842), an area of contact between the gas reactant and a layer of liquid electrolyte thin enough to allow the gas to diffuse to the solid electrode. To increase the surface of action, Grove used platinized platinum electrodes (platinum particles deposited on a solid platinum electrode), and with 26 cells connected in electrical series was able to achieve his goal of electrolyzing water by the products of electrolysis — hydrogen and oxygen. A smaller, four-cell version of Grove's gas battery is shown in Fig. 2.2. In further experiments, Grove substituted different gases in the tubes to see what effects he would observe, and he found that with a combination of hydrogen and nitrogen, there was a slight effect; he understood that oxygen from the air had dissolved in the solution.

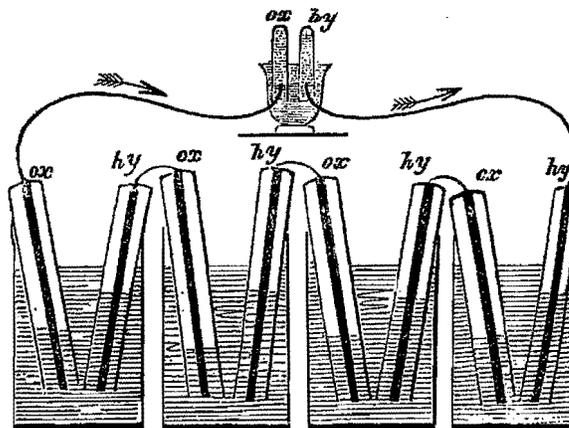


FIGURE 2.2 Grove (1842) built a gas battery with 50 cells and found that 26 cells were the minimum needed to electrolyze water. In this figure, four cells are shown. (With permission from The Taylor and Francis Group, <http://www.tandf.co.uk>.)

960)
(1962)

LS
(1967-75)
?)
CELLS
facturing (1963)
35)
atory (1992)

67)
ams (1993)
4)

ms. The chronology is based
d trademarks of E.I. du Pont

l to achieve — the high
e needed in the design of
atible hardware materials
es of fuel cells, reviewing

7 period of development
aic battery" used aqueous
l solid oxide electrolytes.
1 a separate section with
ms about types, the final
used in vehicle propulsion
s and offers references to

: known as the "gaseous
platinum electrodes and
e, platinum was already
he first published exper-
rove, 1839). Schoenbein

Controversy existed about the operating principle of the gaseous battery, and Grove (1843) strove to prove his opinion that it was oxygen that contributed to the chemical reaction. He tested fourteen combinations of gases on the anode and cathode and concluded that chlorine and oxygen, fed to one of the electrodes, and hydrogen and carbon monoxide, fed to the other, "are the only gases which are decidedly capable of electro-synthetically combining so as to produce a voltaic current." Because of the selectivity of the gaseous battery to oxygen rather than nitrogen in the air, he proposed a practical use for the fuel cell — as a eudiometer, an instrument to determine the volumetric composition of a gas mixture, used especially for determining the purity of air.

In 1845, Grove presented to the Royal Society of London the results of additional experiments and introduced the gas voltaic battery as an instrument to test for vaporization. He used phosphorus and iodine in the solid form, which are non-conducting, and suspended them in nitrogen in the tubes of a gas battery, and the cell gave a continuous voltaic current. He also tested "other volatile electro-positive bodies, such as camphor, essential oils, ether and alcohol," placing them in nitrogen on the anode side and associating them with oxygen, and he found that those cells gave a continuous voltaic current. He then described a "new form of gas battery" that could accommodate an indefinite number of cells, using hydrogen from zinc and oxygen from the air.

In 1854, in a commentary on a paper (Matteucci, 1854), Grove proposed a farther-reaching application of the gas battery as a source of electricity derived from conventional fuels:

It has often occurred to me, that if, instead of using zinc and acids, which are manufactured, and comparatively expensive materials, for the production of electricity, we could realize the electricity developed by the combustion in atmospheric air, of common coal, wood, fat, or other raw material, we should have at once a fair prospect of the commercial application of electricity.

This application stemmed from his "conviction ... that every chemical synthetic action may, by a proper disposition of the constituents, be made to produce a voltaic current."

2.1.2 Christian Friedrich Schoenbein (1838, 1839, 1843)

After reading about the experiments of Grove, Schoenbein (1843) drew attention to experiments of his own, published in 1841 and 1842, that were similar in subject and had results "closely connected" to those of Grove. Schoenbein (1838) had been trying to prove that currents were not the result of two substances coming into "mere contact" with each other, but were caused by a "chemical action." In a letter published in 1839 (written in December 1838), Schoenbein reported a conclusion based on experiments on platina wire and how it could become polarized or depolarized depending on the atmosphere in which it was placed. He tested fluids, separated by a membrane, with different gases dissolved in each compartment. One of the tests used platina wires to bridge one compartment having dilute sulfuric acid in which hydrogen was dissolved with another compartment that had dilute sulfuric acid in which no hydrogen was dissolved, but which was exposed to air. The compartment with hydrogen had a negative polarity compared to the one without hydrogen. With gold and silver wires, no current was present. In one of his conclusions, he recognized that the combination of hydrogen and oxygen was caused by platinum:

The chemical combination of oxygen and hydrogen in acidulated (or common) water is brought about by the presence of platina in the same manner as that metal determines the chemical union of gaseous oxygen and hydrogen.

In his conclusion to this letter, Schoenbein used the results from this test to demonstrate that it was not "mere contact" but it was "chemical action" that caused the current, for if it had been the contact, the gold and silver wires would have produced the same effect. But because platinum was known to catalyze the combination of hydrogen and oxygen (and gold and silver were not), the current was determined to have been caused by the "combination of hydrogen with [the] oxygen [contained dissolved in water] and not by contact."

2.1.3 L

In 1882, "a the efficient the gas, and of platinar electrode o and the hy used coal g

2.1.4 M

The "new : improvem contributi sulfuric ac

[Grove] the con for gas therefor

The ma

... such acid or and wit

In con developin resistance

The pl being : conduc

Figure 2. Mond and they data, sho Mond 0.97 V i

FIGURE sulfuric : chamber

2.1.3 Lord Rayleigh (1882)

In 1882, "a new form of gas battery" was developed by Lord Rayleigh and was an attempt to improve the efficiency of the platinum electrode by increasing the surface of action between the solid electrode, the gas, and the liquid, "or at any rate meets the liquid and is very near the gas." Rayleigh used two pieces of platinum gauze with an area of about 20 in² (instead of the usual platinum foil), placing the air electrode on the surface of the liquid electrolyte so that the "upper surface is damp but not immersed" and the hydrogen electrode on the surface but in an enclosed chamber. Besides using hydrogen, he also used coal gas as fuel, and the gas battery produced "an inferior, but still considerable, current."

2.1.4 Mond and Langer (1889)

The "new form of gas battery" described by Ludwig Mond and Carl Langer in 1889 was more than an improvement; it was the prototype for the practical fuel cell. These researchers considered their main contribution as being a solution to the problem of electrode flooding, caused by a liquid electrolyte. The sulfuric acid could be held in place by using a matrix:

[Grove], as well as later investigators, overlook one important point, viz., the necessity of maintaining the condensing power of the absorbent unimpaired ... platinum black, the most suitable absorbent for gas batteries, loses its condensing power almost completely as soon as it gets wet, and that it is therefore necessary for our purpose to keep it comparatively dry.

The matrix, also called diaphragm, was a porous, non-conducting solid:

... such as plaster of Paris, earthenware, asbestos, pasteboard, &c., is impregnated by dilute sulphuric acid or another electrolyte, and is covered on both sides with thin perforated leaf of platinum or gold and with a thin film of platinum black.

In continuing to describe their first of two designs, Mond and Langer showed their insight into developing practical hardware to sustain the fuel cell reaction. They realized that internal electrical resistance would reduce the voltage from across the two electrodes:

The platinum or gold leaf, which serves as conductor for the generated electricity (the platinum black being a very bad conductor), is placed in contact at small intervals with strips of lead or other good conductor in order to reduce the internal resistance of the battery to a minimum.

Figure 2.3 shows one of Mond and Langer's designs for a gas battery.

Mond and Langer were concerned about a lower electromotive force (EMF) or open circuit cell voltage, and they realized that it was related to the method used to prepare the platinum black catalyst. Their data, showing the performance of one catalyst, are presented in Fig. 2.4.

Mond and Langer investigated the cause of the lower open circuit voltage, which they reported to be 0.97 V instead of the expected 1.47 V. (The maximum cell voltage that was expected, according to

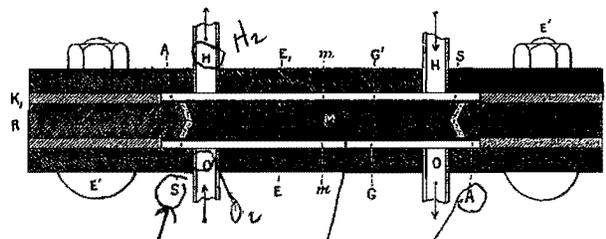


FIGURE 2.3 One design of the gas batteries of Mond and Langer (1889), which used a diaphragm to contain the sulfuric acid electrolyte. The lettering in the diagram denotes (A): conducting strips, E: ebonite plates, G: gastight chambers, H: hydrogen, K: rubber frames, O: oxygen, M: earthenware plate, R: ebonite frame, S: electrode.

2-6

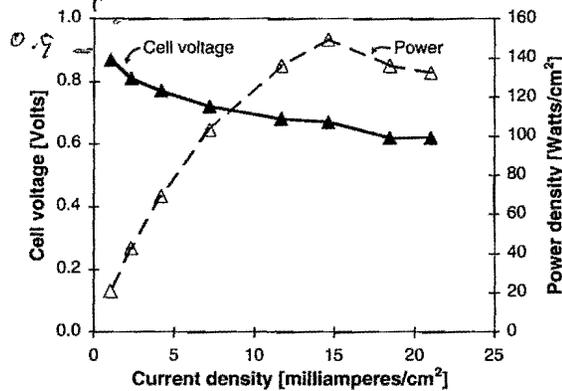


FIGURE 2.4 The performance of a gas battery of Mond and Langer (1889). It is unclear whether these data are based on the cathode reactant being pure oxygen or oxygen from the air because Mond and Langer fed their cells with both gases. The electrode area was 42 cm².

Liebhaftsky and Cairns (1968), was based on the "Thomsen-Berthelot Fallacy" that the heat released in a chemical reaction was a measure of the chemical affinity of the reactants; in other words, the change in enthalpy was thought to be equal to the change in Gibbs energy. By substituting different electrode materials for both anode and cathode, they identified it to be the PtO as the electrode that caused the loss. These data would be confirmed by Alder Wright and Thompson in a paper (see Section 2.1.5) meant to dispute the originality of Mond and Langer's work.

Mond and Langer calculated that the efficiency of the battery was nearly 50% (based on the expected 1.47 V) and realized that the wasted energy was converted to heat within the cell. To maintain the temperature constant at 40°C, they passed through excess air, which simultaneously removed the water formed at the cathode.

With a useful effect of 50 per cent, one-half of the heat produced by the combination of the H with the O is set free in the battery, and raises its temperature. By passing through the battery a sufficient excess of air, we can keep the temperature of the battery constant at about 40°C, and at the same time carry off the whole of the water formed in the battery by means of the gases issuing from it, so that the platinum black is kept sufficiently dry, and the porous plate in nearly the same state of humidity.

The battery performance degraded by 4 to 10% in a period of an hour. Mond and Langer identified the concentration gradient of the acid, being stronger at the anode than the cathode, as the cause: "Probably this difference of concentration of the acid sets up a counter-current." To reduce the concentration polarization, they switched the gases at the electrodes and therefore the direction of ion flow through the diaphragm once per hour, to return the acid to the weak side.

Ludwig Mond had begun developing this gas battery with the hope of it using more efficiently his "Mond Gas," the product of the reaction of air and steam passed through glowing coal (Cohen, 1956). Originally, Mond had intended to synthesize ammonia with this reaction, but the results showed that no fixation of nitrogen occurred. Instead, the reaction product was rich in hydrogen, and this "smokeless fuel" could be used for power generation and for heating furnaces and kilns. Mond knew that its chemical energy would be more efficiently used by a gas battery to produce electricity, and in 1889, he and Carl Langer reported that the performance of a gas battery was sustainable when fed with Mond Gas containing 30 to 40% H₂.

2.1.5 Alder Wright and Thompson (1889)

One day after seeing the demonstration of Mond and Langer at a meeting of the Royal Society of London, Alder Wright and Thompson (1889) reintroduced a device that they had used in experiments performed in 1887, intending to prove that their work had been performed first. Their electrodes were called "aeration

FIGURE 2.5 (1889) brought

plates." The "to the surface of the electrolyte (on one side of the cell) oxidizable fuel gas, a form of

With charcoal was called "cell one chamber voltage reaction Wright and Thompson plate cells" la a high cell voltage appliance" w

Alder Wright powerful current (zinc or alumin

As yet we had and such like that such a

Alder Wright the same performance EMF, and the

2.2 "Electro

At a time when engine, Ostwald process. Ostwald between the battery was lost. Instead that converted was to produce item would be

150 w/cm²!
↑
mw?

1889!

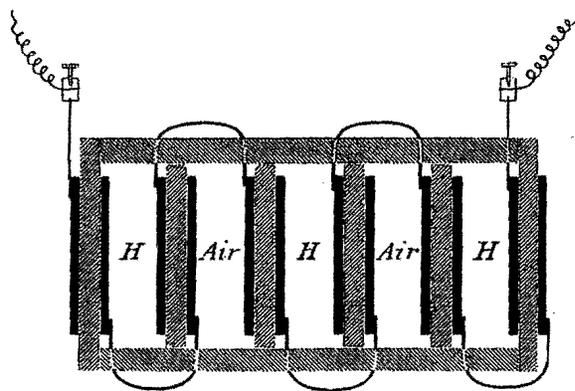


FIGURE 2.5 In response to the demonstration of Mond and Langer's gas battery, Alder Wright and Thompson (1889) brought attention to their "double aeration plate cells," which had been developed earlier.

plates." The material for the aeration plate (platinum black giving the highest performance) was applied "to the surface of unglazed earthenware, or other similar porous non-conducting material," and the electrolyte (sulfuric acid or caustic soda solution) was absorbed in the porous material. On the opposite side of the earthenware was a plate of oxidizable metal or of non-oxidizable material immersed in an oxidizable fluid: "By employing two aeration plates, one in contact with the air and one with the oxidizable gas, a form of gas battery was obtained." Figure 2.5 shows Alder Wright and Thompson's apparatus.

With chambers alternating between hydrogen (closed) and air (open to the atmosphere), the device was called "double aeration plate cells." Sealing the chambers was difficult, and the leakage of gases from one chamber to another resulted in an open circuit voltage of less than 1 volt per cell. The maximum voltage reached 0.6 to 0.7 volts per cell with measurable current. Despite this poor performance, Alder Wright and Thompson concluded that technically it would be possible to construct "double aeration plate cells" large enough to yield currents with a small current density required by each cell to maintain a high cell voltage. However, they also concluded that the economic possibility of developing a "large appliance" with sufficient power for commercial purposes was poor.

Alder Wright and Thompson also foresaw the use of liquid fuels as the sources of energy. To produce powerful currents with atmospheric air and large aeration plates, the source of energy could be metal (zinc or aluminum) or a fluid, such as solution of sodium hydrosulfite or ammoniacal cuprous oxide:

As yet we have not succeeded in effecting the direct oxidation in this way of alcohol, petroleum, coal, and such like forms of comparatively cheap sources of energy, but we are far from being convinced that such actions are impracticable.

Alder Wright and Thompson tested different combinations of materials for the aeration plate, recording the same performance as Mond and Langer had two years later when investigating the lower open circuit EME, and they found that platinum black gave the highest voltage.

2.2 "Electricity Direct from Coal"

At a time when only 10% of the chemical energy in coal was converted into mechanical energy in a steam engine, Ostwald (1894) perceived electrochemistry as the solution to the inefficient energy conversion process. Ostwald was dismayed that the only energy that could be harnessed in a steam engine was between the boiler and the condenser, and that the energy of burning the coal to raise the temperature was lost. Instead of losing this amount, he proposed that using electrochemistry was a better way — one that converted energy without heat — so that the entire energy content of coal could be won. His hope was to produce electricity from coal by electrochemical processes, but it was uncertain how the galvanic item would be created. Ostwald did refer to an attempt by Jablockhoff (1877 in Ostwald, 1894), who

used saltpeter (potassium nitrate) in an attempt to produce electricity directly from coal. Ostwald also recommended the search for a different electrolyte, one that would not be consumed in the reaction.

Jacques (1896) built fuel cells that produced electricity from coal, but Haber and Bruner (1904) determined the electrochemical reaction to have been first between the coal and the electrolyte and then with the electrode; therefore, instead of the direct oxidation of coal, the Jacques cell was "indirect." Baur and Ehrenberg (1912) tested several types of electrolytes, including hydroxide, carbonate, silicate, and borate. A mixture of alkali metal carbonates was used by Baur and Brunner (1935), who found that CO₂ supplied to the cathode improved the performance of the fuel cell. Because the molten electrolyte flooded the electrodes, Baur and Brunner (1937) concluded that a solid electrolyte was more suitable and began investigating ceramic materials.

2.2.1 William Jacques (1896)

In 1896, William W. Jacques reported on his experiments to produce "electricity direct from coal." He had "often dreamed of converting the stored-up energy of the coal into some form of energy even more useful to man than heat," which would be in the form of electricity, but the production of electricity was complicated and inefficient. After experiments in which he tried to convert the energy of coal more directly into electricity, such as harnessing the lightning from his "miniature thunder-storms," he figured he could convert the stored-up energy of coal directly into electricity ...

... if the oxygen of the air could be made to combine with the coal under such circumstances that the production of heat could be prevented, and at the same time a conducting path could be provided in which a current of electricity might develop, the chemical affinity of the coal for the oxygen would necessarily be converted into electricity and not into heat.

To do this, Jacques submerged coal in a liquid to prevent the oxygen of the air from making direct contact with the coal. He intended for the oxygen to temporarily enter into chemical union with the liquid and then be crowded out by a further supply of oxygen and forced to combine with the coal." His coffee-cup-sized experimental reactor proved that the concept worked. A small platinum crucible was partially filled with common potash (potassium hydroxide) and was held over a gas flame to keep the potash electrolyte in the molten state. A peanut-sized lump of ordinary coke was held in the potash by a platinum wire, and air was blown into the molten electrolyte through a platinum tube. The wire holding the coal acted as the negative electrode, and the crucible was the positive electrode:

Attaching these wires to a small electric motor, I found that when air was blown into the potash the motor started, and moved more rapidly as air was blown in; when the current of air was interrupted, the motor stopped. From this minute apparatus a current of several amperes was obtained. The electromotive force was a little over one volt.

This design was built on a larger scale, and what had been a platinum crucible became an iron barrel for the sake of lower expense. Jacques called the cell of the "carbon electric generator" a "pot," and each pot contained potassium hydroxide surrounding six sticks of carbon, 3 inches in diameter and 18 inches long. Each pot produced about 0.75 amperes per square inch of carbon surface (116 mA/cm²), had a voltage a bit higher than 1 V, and produced a little more than one electrical horsepower (1 hp = 745.7 W). The cell current was increased when the air distribution in the electrolyte was improved by using an air supply pipe with a rose nozzle to divide the gas into fine sprays.

Jacques realized that the disadvantage of using potassium hydroxide as the electrolyte was the absorption of carbonic acid (carbon dioxide dissolved in a liquid), which in the base would be converted to carbonate. Eventually, the contaminated electrolyte would have to be cleansed. Jacques also realized that using a molten electrolyte required a heat source, and the energy consumed in the heating amounted to 60% of the amount of coal used to produce 1336 W × hr, as shown in Table 2.1. From a 1-lb mass of coal, 0.4 lb was consumed in the pots and 0.6 lb was burned on the grate to supply heat, and 1336 W × hr was produced, which is 32% of the theoretical amount (higher heating value of carbon).

Jacques sp would bring range and electricity fo

2.2.2 Ha

Haber and B. tivating the e first reacted v that caustic s grade iron alk from the air (or the water) To prove thei

Hydrogen CO₃Na₂ + 4H of 300°C. An 2NaOH = CC Haber and would be con

Das Jacques: verschwind einschliesst Wasserstoff

Translation: problems. I degradator and hydrog

2.2.3 Bau

Baur and Ehr selecting molt With one elect having to be n itself or, for ga less expensive

The electrol a mixture of tl potassium fluo temperature w

← still our dream!

1st or

> 1A @ > 1V

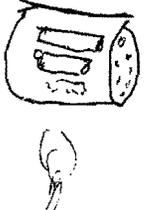


TABLE 2.1 The Performance of the "Carbon Electric Generator" of Jacques (1896)

Electrical power generated	2.16 hp (1611 W)
Electrical power consumed by the air pump	0.11 hp (82 W)
Net electrical power generated	2.05 hp (1529 W)
Carbon consumed in pots	0.223 lb/hp/hr
Coal consumed on grate (for heating)	0.336 lb/hp/hr
Total fuel consumed	0.559 lb/hp/hr

Jacques speculated at the improvements the more efficient and cleaner use of coal to produce electricity would bring about: railway trains with higher speeds and lower pollution; transatlantic liners with farther range and quieter motors; lighting, heating, and cooking for homes by cleaner electricity; cheaper electricity for metallurgical reduction of ores; and cleaner air in large cities.

*speculation
application*

2.2.2 Haber and Bruner (1904)

Haber and Bruner (1904) worked on direct coal fuel cells, which were called the "Jacques element," investigating the electrical potential of iron electrodes in molten alkaline electrolytes and finding that the coal first reacted with the electrolyte, which made it an "indirect" coal fuel cell. Haber and Bruner pointed out that caustic soda (sodium hydroxide, NaOH) contained manganese as an impurity, and even technical-grade iron also contained manganese. This manganese would become oxidized in the presence of oxygen from the air to form permanganate (MnO₄⁻), which would act as the vehicle for the oxygen from the air (or the water) to the immersed iron. The iron, coated with an oxide layer, "was a splendid oxygen electrode" To prove their theory, Haber and Bruner substituted the iron with bright platinum, which also worked.

Hydrogen was formed by the coal in the molten caustic soda by the reaction: $C + H_2O + 2NaOH = CO_3Na_2 + 4H_2$. The water needed for the reaction is present in molten caustic soda even at temperatures of 300°C. Another reaction generating hydrogen involved carbon monoxide and caustic soda: $CO + 2NaOH = CO_3Na_2 + H_2$.

Haber and Bruner concluded that the prospects of the Jacques coal cell were poor because the electrolyte would be consumed for the sake of producing hydrogen:

Das Jacquessche Kohle-Element wird nun wohl allmaehlich aus dem Kreise der technischen Probleme verschwinden. Denn wer wollte Hoffnungen an eine Zelle knuepfen, deren Arbeit die Notwendigkeit einschliesst, das teure Aetznatron zu der billigen Soda zu verschlechtern, um dafuer eine geringe Wasserstoffentwicklung und Wasserstoffwirkung einzutauschen?

Translation: The Jacques coal element will now probably disappear gradually from the circle of technical problems. Because who would want to attach hopes to a cell that, in order to work, requires the degradation of expensive caustic soda into cheap soda in order to obtain a small amount of hydrogen and hydrogen effect?

*negative
conclusion*

2.2.3 Baur and Ehrenberg (1912)

Baur and Ehrenberg (1912) followed the work of Taitelbaum (1910, in Baur and Ehrenberg, 1912), selecting molten silver as the cathode for a coal cell because of its good oxygen-dissolving properties. With one electrode having been selected, they investigated different electrolytes, which they identified as having to be melts in order to maintain the temperature. The anode material could be either the carbon itself (or) for gaseous fuels such as hydrogen and carbon monoxide, a metal but, specifically, one that was less expensive than platinum, such as iron or copper.

The electrolytes that were tested were soda (sodium hydroxide) and potash (potassium hydroxide) or a mixture of the two; potassium sodium carbonate (KNaCO₃); potassium silicate (K₂SiO₃) with added potassium fluoride; cryolite (Na₃AlF₆) with alumina (Al₂O₃); and borax (sodium borate, NaB₄O₇). The temperature was 1000°C, and the researchers reported obtaining a performance of 100 A/m² at 1 V.

Iron, nickel, and copper were used as the anode electrode for testing with hydrogen and carbon monoxide, and molten silver was the oxygen electrode exposed to the air. Sodium borate was the electrolyte. With hydrogen as fuel, the iron and nickel proved to be better suited for the reaction than copper, which could not dissolve as much hydrogen and which also formed an oxide layer that would dissolve in the borate. With carbon monoxide, the highest performance of 0.80 V was achieved by the nickel, but Baur and Ehrenberg considered that value unsatisfactory.

2.2.4 Baur and Brunner (1935, 1937)

Baur and Brunner (1935) returned to the problem of the "direct coal air chain" despite the problems associated with it (high temperatures, ash formation, dilution of the fuel gases by carbon dioxide and water vapor), focusing their efforts on carbonate electrolytes. The electrolyte was a mixture of salts containing eight parts of K_2CO_3 , seven parts of Na_2CO_3 , and six parts of $NaCl$ with some borates.

With carbon as the anode electrode and platinum the cathode, they operated the cell at 500 to 600°C and found that the performance worsened rapidly when current was drawn from the electrodes. But when they fed the cathode with the exhaled air from their breath, the performance improved in a remarkable way (see Fig. 2.6). They showed that the improvement was caused by carbon dioxide. It was thought that at the cathode, oxides formed Na_2O , which blocked the carbon dioxide from dissolving in the electrolyte. They stated that it was insufficient for the carbon dioxide that formed at the anode to dissolve in the electrolyte, and therefore an external source was required.

In 1937, Baur and Brunner reported on their testing of iron cathodes that they had mentioned in their paper of 1935, and they also pointed to a new design. Beginning with a description of previous work by Ehrenberg, Treadwell-Trümppler, Brunner, and Barta, they gave an account of the reasons for the progression (see Fig. 2.7). The Treadwell-Trümppler cell used a porous diaphragm made of magnesia (MgO) to keep the iron electrode dry, but that increased the internal resistance. Therefore, efforts returned to

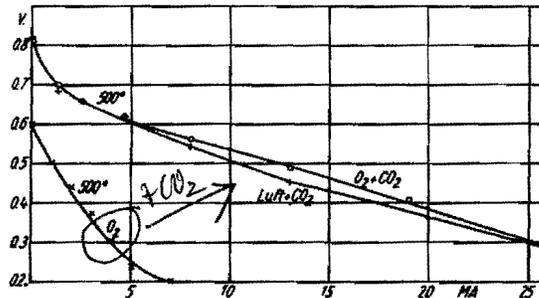


FIGURE 2.6 With CO_2 fed to the cathode, performance improved in a carbonate fuel cell (Baur and Brunner, 1935). The cathode was platinum.

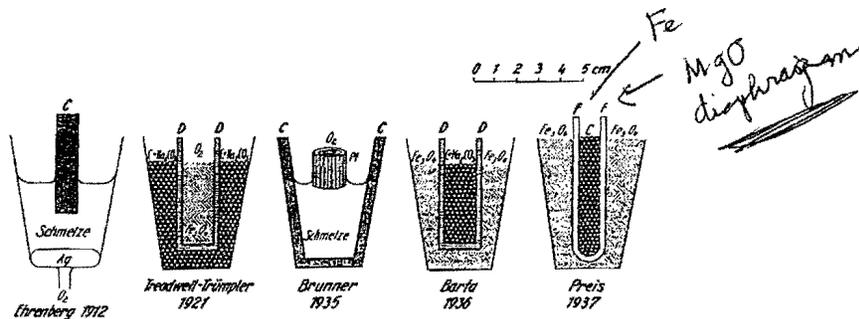


FIGURE 2.7 The progression of cell designs used for the direct coal fuel cell (Baur and Brunner, 1937). C: coal, D: diaphragm, and F: Festleitern (solid state conductor).

His

imp
plati
a po
faile
was
unflc
it wa

Tr
ad
dia

Ins
at the
fragile
of 50!
the sai

2.3

Baur a:
compa
Nernst
Westin

Nerr
time, in
carbon
temper:
resistan
emit rac
Nern:
conduct
electroly
In partic
4 siemer.

Nerns
but when
no effect
bodies fr
pure whi
began er

2.3.1

Baur and
on invest:
earlier, in
chains wo
decided th
Preis inve:
1050 and
but all of

drogen and carbon
um borate was the
or the reaction than
ide layer that would
was achieved by the

despite the problems
carbon dioxide and
as a mixture of salts
h some borates.

e cell at 500 to 600°C
n the electrodes. But
nance improved in a
arbon dioxide. It was
de from dissolving in
rmed at the anode to

ad mentioned in their
n of previous work by
e reasons for the pro-
le of magnesia (MgO)
re, efforts returned to

after a ↑ with diaphragm

flooded = ---

improving Ehrenberg's design and the result was Brunner's design (cell in 1935 paper), which used platinum or silver gauze, but the electrodes were flooded by the electrolyte. Baur and Brunner tried using a porous iron oxide (magnetite, Fe_3O_4) tube closed at one end, submerged into the carbonate melt. This failed to work on the Brunner cell, so then they tried it on Ehrenberg's and Barta's cells. Because magnetite was the only practical material for the electrode, and because of the difficulties with maintaining an unflooded electrode unless a diaphragm was used (which would then increase the internal resistance), it was concluded that the molten alkali carbonate electrolyte was unsuitable for the direct coal application:

Translation: For the building of coal-air chains, melts of alkali carbonate are to be rejected In addition, the magnetite air electrode, which is the only efficient one for practical use, requires a diaphragm. This however, under all circumstances, would fall to destruction by the soda melt.

Instead, Baur and Brunner proposed using a solid electrolyte in the cell because of its simplicity but at the same time acknowledged the difficulty of reducing the internal resistance. Glass was deemed too fragile but porcelain looked promising. A thin porcelain pipe with 0.1-cm wall thickness had a resistance of 50 Ω at 1000°C. Baur and Brunner identified as their task the development of a ceramic material with the same moldability and durability, but with a resistance one magnitude lower.

2.3 The Solid Oxide Fuel Cell

Baur and Preis (1937) developed the solid oxide fuel cell out of a need for a more manageable electrolyte compared to the molten electrolytes. They used a solid compound that had been developed by Wilhelm Nernst in 1899. A similar zirconia-based electrolyte was used by Weissbart and Ruka in 1962 at the Westinghouse Electric Corporation.

Nernst (1899) had investigated solid conductors at high temperatures for use as lamps because, at that time, incandescent lamps had just been developed and used filaments with high melting points, especially carbon and also osmium and tantalum. (Carbon had a short life span because it would vaporize at high temperatures in the vacuum chamber; not until 1906 was tungsten used as filament.) For metals, because resistance increases as temperature increases, the filament could not reach the temperatures necessary to emit radiation in the visible spectrum.

Nernst realized that, compared to metals, melted salts behaved in the opposite way, improving their conductivity at high temperatures. He was trying to develop an electrical lamp ("glow body") by using solid electrolytes and found that the conductivities of mixed oxides were surprisingly high at high temperatures. In particular, mixtures of Mg, Si, Zr, and rare earth elements gave extraordinary conductivities—beyond 4 siemens, which was much higher than the most conductive sulfuric acid (0.74 at 18°C).

Nernst first used alternating current to avoid possible decomposition of the electrolyte by electrolysis, but when he tried direct current the conductors continued to emit light for hundreds of hours, showing no effect of decomposition as was initially feared. Nernst and Wild (1900) prepared electrolytic glow bodies from the oxides of zirconium, thorium, yttrium, and the rare earth elements, which emitted nearly pure white light compared to the "strongly reddish light of the normal lamps." They found that the pins began emitting light between 500 and 700°C depending on their composition.

2.3.1 Baur and Preis (1937)

Baur and Preis (1937), in the article immediately following that of Baur and Brunner (1937), reported on investigations into suitable solid electrolytes and a design of a cell. (According to Baur and Preis, earlier, in 1916, Baur and Treadwell had applied for a patent, but it seemed at the time that coal chains would work only with molten electrolytes. After the investigation by Baur and Brunner, it was decided that solid conductors deserved serious developments to lower their resistance, and Baur and Preis investigated the internal resistance at different temperatures.) Ceramic materials were tested at 1050 and 1100°C in the form of tubes made out of brickyard clay and two types of unglazed porcelain, but all of the materials were deemed to be useless because of high resistances (ranging from 20 to

2/19/99

source?

l cell (Baur and Brunner,

runner, 1937). C: coal, D:

TABLE 2.2 Comparison of Solid Electrolytes Used by Baur and Preis (1937)

No.	Composition	Resistance at 1050°C (Ω)	Behavior
1	ZrO ₂	90	Current consumption increases resistance; no noticeable polarization
2	ZrO ₂ + 10% MgO	60	Like No. 1
3	CeO ₂ + 50% clay	200	Polarization; no noticeable resistance increase
4	"Electron-Mass"	< 40	Like No. 3
5	"Nernst-Mass" 85% ZrO ₂ + 15% Y ₂ O ₃	1-4	Current consumption increases resistance to 15 ohms; no polarization.

Note: Samples were tested as tubes of similar dimensions.

600 Ω, respectively). (The hard porcelain had the lowest resistance, but, when current was passed through, it developed a non-conductive layer because the cations moved away, leaving a non-conductive silicate lattice.) Then they tried tube crucibles from Degussa: commercially available zirconia (ZrO₂), a mixture of 90% ZrO₂ + 10% MgO, CeO₂ + 50% clay, a compound with good conductivity at low temperatures (500 to 600°C) called "electron-mass," and "Nernst-Mass" (85% ZrO₂ + 15% Y₂O₃). The results of their tests are shown in Table 2.2.

The "Nernst-Mass" had the best performance. However, its resistance rose from 1-4 to 15 ohms when current was drawn, behaving in a similar manner as the ceramics behaved with the electrolytic shift (cations moving away), which was proven by reversing the polarity of the cell. Baur and Preis built a battery with a volume of 250 cm³ holding eight tubes to test the "Nernst-Mass" on a larger scale. The tubes were filled with coke and immersed in a magnetite bath. With the tubes in parallel, the battery gave a steady-state 0.83 V, which was 0.2 V below the desired performance that was attained in the tests of single cells. The voltage dropped to 0.65 V when a 0.070-A current was drawn, and the power of the cell was therefore 0.045 W/250 cm³ or 0.18 W/l. The resistance of the tubes was 12 to 15 Ω, and for the cells in parallel the resistance was about 2 Ω. Baur and Preis projected that the resistance could be halved by reducing the thickness of the tubes by half, and that the battery size could be made more compact by half, which would give 0.8 W/l, but this value was still one order of magnitude too low. Because of this, they looked to improve the "Nernst-Mass."

They tried to make ceramics and turned to cerium dioxide and clay. They found that conductivity came at the expense of hardness, which was necessary for temperature resistance. With lithium silicate, they improved the conductivity and temperature resistance of clay and porcelain, but still the resistance was too high (10 Ω at 1100° for 60% porcelain, 15% cement, 15% lithium silicate). Therefore, they returned to the "Nernst-Mass" and were able to reach 2 Ω at 1050°C for 70% "Nernst-Mass," 10% sintered magnesia (as reinforcement), and 20% lithium silicate. In another mixture that was better than the one with lithium silicate (higher conductivity at lower temperatures), a combination of 60% "Nernst-Mass," 10% clay (to escape the harmful Li-Si-Al eutectic point), and 30% lithium zirconate, the performance was acceptable, leading Baur and Preis to conclude that this compound would meet the requirements. Unfortunately, it would be too expensive for practical use.

With this new electrolyte, Baur and Preis calculated the performance of a small battery, shown in Fig. 2.8, that could produce 10 W/l with tubes 6 cm in length, with 0.1-cm wall thickness. The tubes would be filled with granulated iron (1 mm, Fe₃O₄), and the gaps in between would be filled with iron (Fe). Another tube would be inserted in the electrolytic tubes to deliver air, and Baur and Preis stated that it was essential that the air be used to recover heat. When scaled up, this battery could meet the demands of power production with a power density of 10 W/l (or 10 kW/m³). However, the power density was still one magnitude lower than that deemed necessary by Schottky (1935, in Baur and Preis, 1937), who projected that a fuel cell power station using solid electrolytes at high temperatures had to have a power density of 100 kW/m³ in order to compete with steam power plants. Baur and Preis, however, pointed to the proposed "power station west" in Berlin, which had a lower goal of 1 kW/m³. Although the volumetric power density was competitive, economic considerations were less optimistic unless less expensive materials were used in place of zirconia and yttria. The targeted cost of power production of

$$\frac{0.83}{0.2} = 2.03$$

FIGURE 2. to be 10 kv

the "power estimated could meet

2.3.2

Weissbart 85% ZrO₂ of 2.5 cm² was low (see Fig. 2. flowed over hydrogen;

The cell hydrogen at 20° and curves; and at 1094°C

Other to hydrogen, tested as the rate too far of the met. the H₂/O₂ steam refo: anode invo within the

0.2 W/l
later
10 W/l

100 W/l
about 70
by perimeter

want
100 W/l

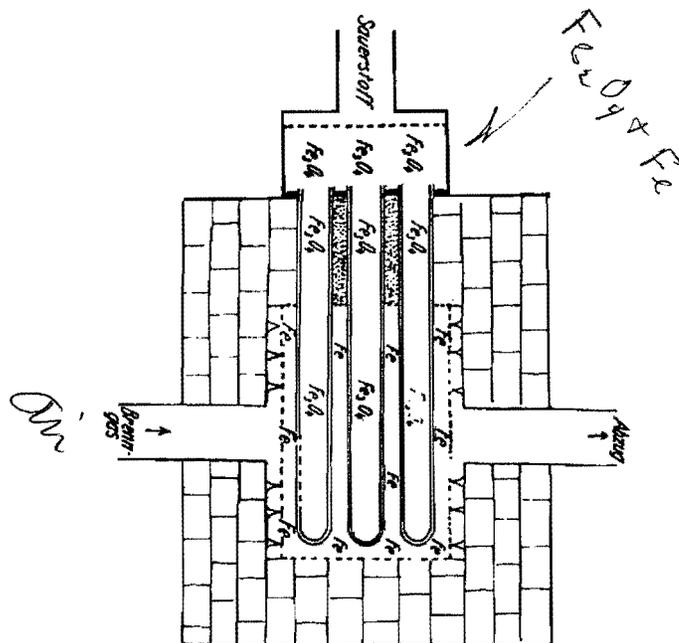


FIGURE 2.8 Baur and Preis (1937) sketched this concept of a fuel cell and estimated the volumetric power density to be 10 kW/m^3 , a level competitive with the 1 kW/m^3 of steam power plants.

the "power station west" in Berlin was 234 Marks/kW, but with the solid electrolyte Baur and Preis estimated it to be 1000 Marks/kW. They concluded that practical solid electrolytes could be built and could meet the space requirements of power production.

2.3.2 Weissbart and Ruka at Westinghouse Electric Corporation (1962)

Weissbart and Ruka (1962) at the Westinghouse Electric Corporation constructed a fuel cell that used $85\% \text{ ZrO}_2$ and $15\% \text{ CaO}$ as the electrolyte and porous platinum as the electrodes. The cell had an area of 2.5 cm^2 and 0.15-cm thickness (each electrode was less than 0.00254 cm or 0.001 inches thick) and was located at the closed end of a tube made of the same material as the electrolyte $(\text{ZrO}_2)_{0.85}(\text{CaO})_{0.15}$ (see Fig. 2.9). Pure oxygen at ambient pressure flowed over the cathode, and either hydrogen or methane flowed over the anode after first flowing through a water bubbler. The effect of water content in the hydrogen gas on the open-circuit voltage was found to be near the theoretical performance at 1015°C .

The cell had been proven in earlier experiments as an oxygen concentration cell. As a fuel cell, with hydrogen at the anode, the cell performed as expected with the cathode half-cell reaction being $\text{O}_2 + 4e^- \rightleftharpoons 2\text{O}^{2-}$ and not a peroxide reaction. The cell was tested between 800 and 1100°C to generate current-voltage curves; an example of the performance at 0.7 V is a current density of 10 mA/cm^2 at 810°C and 76 mA/cm^2 at 1094°C with pure O_2 and H_2 (with $3 \text{ mol}\% \text{ H}_2\text{O}$) at pressures slightly above ambient ($730 \text{ mm H}_2\text{O}$ gauge).

Other tests were done to determine the resistance characteristics with 3% and $46 \text{ mol}\%$ water in hydrogen, showing that the increased water content had no effect on the resistance. Methane was then tested as the anode fuel in a mixture of 3.8% methane, 2.1% water, and 94.1% nitrogen, but at a flow rate too fast for the steam reforming reaction to reach equilibrium. Under these conditions, about 20% of the methane was consumed, giving an open circuit voltage of 0.945 V , a value within 5 mV of that of the H_2/O_2 reaction and 50 mV lower than that of the CO/O_2 reaction. Slower flow rates allowed more steam reforming, and the open circuit potential increased, reflecting that the reactions occurring at the anode involved the H_2 and CO from the reforming reaction rather than from CH_4 itself. Carbon formation within the cell was found in other experiments with similar $\text{H}_2\text{O}/\text{CH}_4$ ratios.

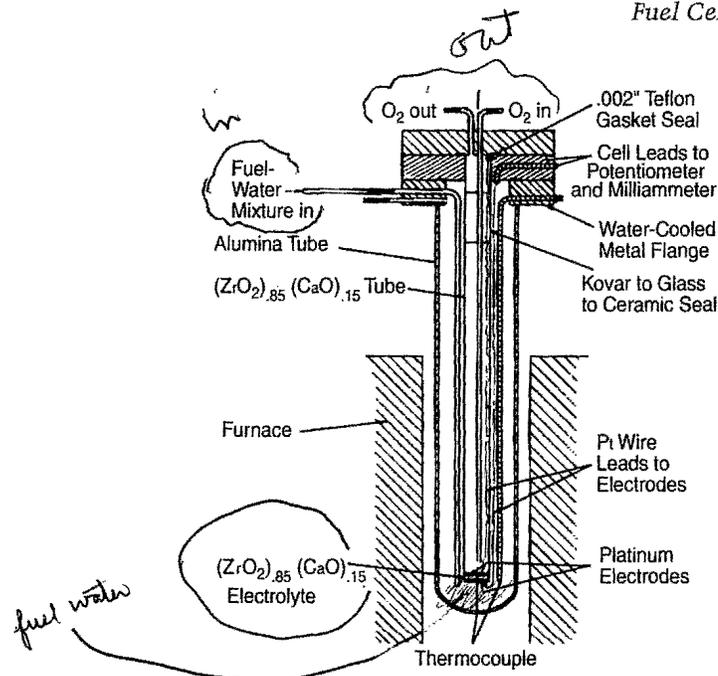


FIGURE 2.9 The fuel cell at Westinghouse Electric Corporation using a solid oxide electrolyte (Weissbart and Ruka, 1962). An advantage of the tubular design was that the reactant gases were separated. (Reproduced by permission of The Electrochemical Society, Inc.)

2.4 Molten Carbonate Fuel Cell

Alkali metal carbonates were among the many compounds used during the development of the "direct coal" fuel cell, but they emerged from the other salts because of their compatibility with the products of the oxidized fuel. The work was influenced by Baur and Preis (1937) in Switzerland, Davtayan (beginning in 1946) in Russia, Broers and Ketelaar (1960) in the Netherlands, Baker et al. (beginning in 1960) at the Institute of Gas Technology, and Douglas (1960) at General Electric Company.

2.4.1 Davtayan (1946)

With the goal of using coal gas as fuel, Davtayan (1946, in Ketelaar, 1993) chose to develop a high-temperature cell that would operate at 700°C with a solid ionic conductor as electrolyte. According to Broers and Ketelaar (1960), who studied the works of Davtayan, this solid electrolyte was influenced by the work of Baur and Preis (1937). Just as Baur and Preis investigated (mixtures of rare earths) (oxides of rare earth metals), specifically "Nernst-Mass" (85% ZrO_2 + 15% Y_2O_3) and added clay and lithium silicates (and other compounds), so also did Davytan mix compounds, developing an electrolyte consisting of monazite sand, sodium carbonate, tungsten trioxide, and soda (soda-lime) glass. These compounds improved the conductivity and mechanical strength of the electrolyte (Broers and Ketelaar, 1960a). Monazite sand is a phosphate mineral, containing cerium, lanthanum, yttria, and thorium; it was baked with sodium carbonate and then baked with tungsten trioxide, with the excess sodium carbonate forming sodium wolframate (Na_2WO_4). The electrolyte composition was "calcinated Na_2CO_3 , 27% monazite, 20% WO_3 and 10% soda glass." After baking, the product consisted of Na_3PO_4 , Na_2CO_3 , Na_2O_4 , Na_2SiO_3 , and oxides CeO_2 , La_2O_3 , and ThO_2 (Broers and Ketelaar, 1960a).

Broers and Ketelaar (1960a and 1960b) prepared electrolyte mixtures based on the work of Davtayan and concluded that the electrolyte was not completely solid but instead had a liquid phase immobilized within a solid matrix. They determined this state by testing different mixtures at different temperatures, finding that the resistivity of the electrolyte depended on its temperature, which was between 650 and 750°C. From their measurements and analyses, they determined that the matrix was formed from the monazite ore, with

the oxides of lanthanum, cerium, and thorium forming from the phosphate salts upon baking. The liquid phase was a mixture of phosphates, wolframates, silicates of sodium, and sodium carbonate.

The electrolytes had resistivities of 13.6 Ωcm at 700°C and 1.3 Ωcm at 900°C. Davtayan formed this electrolyte into a disk (4 mm thick) and sandwiched it with porous electrodes; the anode was made of 20% iron powder, 20% clay, and 60% Fe₂O₃, and the cathode was made of 20% magnetite (Fe₃O₄), 20% clay, and 60% Fe₂O₃. With generator gas as fuel, the cell performance at 700°C was 0.79 V when a current of 20 mA/cm² was drawn.

2.4.2 Broers and Ketelaar (1960)

Testing the electrolyte formulations of Davtayan was the starting point for Broers and Ketelaar (1960) in their work on molten carbonate fuel cells at the University of Amsterdam. The conclusion of their investigation (begun in 1951) was that the state of the electrolyte, which was supposed by Davtayan to have been solid, was actually two phases: a molten phase consisting of carbonates, phosphates, tungstates, and silicates (a eutectic salt mixture) and a solid phase of rare earth oxides. The solid phase was formed by the Ce-La-Th oxides (which have high melting points) and acted as a porous frame to hold the molten electrolyte. Fuel cells that used this electrolyte with town gas as fuel and air as oxidant were unable to sustain stable performance beyond 72 hours, with some degrading within 24 hours. In tests at 650 to 800°C, the tungstate was chemically reduced, the cathode was oxidized, the anode was reduced, and components of the cells cracked.

Broers and Ketelaar settled on using carbonates as electrolyte after having considered using other electrolytes. Salts such as phosphates, chlorides, sulfates, and nitrates were converted into carbonates (which would therefore require replenishment), and borates and silicates, though more resistant to conversion into carbonates, would be too polarized when current was drawn. By using carbonate salts, Broers and Ketelaar eliminated the problem of decomposition by CO₂, and they were able to reduce the concentration polarization by adding CO₂ to the cathode (as Baur and Brunner had shown in 1937).

The fuel cell design had the molten carbonate electrolyte held in a matrix. The electrolyte mixture of alkali carbonates (lithium, sodium, and/or potassium carbonate) was impregnated into a porous sintered disk of magnesium oxide (MgO). The commercially available MgO was sintered at 1200°C, and the volume porosity was 40–50%. After impregnating the electrolyte into the disk, which gave an electrolyte content of 40% by weight, the electrode materials were applied to both sides of the disk as powders with thicknesses of 1 mm. The cathode was always silver (an ideal O₂ + CO₂ electrode with no polarization at 150 mA/cm² and 500°C), and the best anode electrodes for hydrogen were platinum and nickel. The most active electrodes for the oxidation of carbon monoxide were platinum, platinumized iron or nickel, iron, and nickel. When methane was used as fuel, steam was added to the feed, and the nickel electrode catalyzed the internal steam reforming into synthesis gas and also oxidized the hydrogen and carbon monoxide for the fuel cell reaction.

The cells (10 cm²) were tested between 550 and 700°C on air and fuels such as town gas, hydrogen, carbon monoxide, and natural gas, lasting several months under continuous operation. One cell operated for 6 months on town gas as fuel and air and CO₂ as the cathode feed, but its open-circuit voltage degraded from 1.1 V down to 0.90 V in that time because of a loss in the electrolyte, which increased the cell resistance from 0.3 to 1.5 ohm. The loss of electrolyte was caused by vaporization of CO₂, Li₂O, Na₂O, and K₂O and by chemical reactions with gasket materials; more of the reactant gases leaked through the MgO disk and lowered the efficiency and performance of the electrodes.

2.4.3 Institute of Gas Technology (1963, 1965)

Beginning in 1960, work on molten carbonate fuel cells began at the Institute of Gas Technology, basing the designs on the concepts of Broers in his thesis submitted in 1958. The electrolyte paste was sandwiched by a silver cathode 10 μm thick and a porous nickel fiber anode. The molten carbonate fuel cell was chosen over the higher temperature solid oxide fuel cell (SOFC) because it was seen that noble metals

e (Weissbart and Ruka, reproduced by permission

ment of the "direct with the products of Davtayan (beginning in 1960) at the

to develop a high-olyte. According to e was influenced by re earths (oxides of and lithium silicates rolyte consisting of

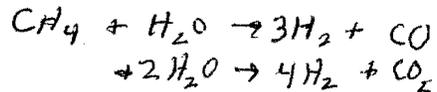
These compounds id Ketelaar, 1960a). orium; it was baked 1 carbonate forming 27% monazite, 20% Na₂O₄, Na₂SiO₃, and

ork of Davtayan and immobilized within mperatures, finding 50 and 750°C. From : monazite ore, with



Added CO₂

added op₂



were required for the sake of stability at high temperatures (Baker et al., 1965). Shultz et al. (1963) suggested that methane could be used "directly" (chemically rather than electrochemically) in a high-temperature fuel cell, where it would be reformed with steam on the anode surface to produce hydrogen, which would be oxidized electrochemically. The endothermic internal reforming reaction would act to cool the fuel cells, and heat that usually would be wasted could serve a useful purpose.

Baker et al. (1965) reported on work being done to improve the interface between the electrode and electrolyte. The electrolyte was formed by hot-pressing the electrolyte powder into disks at 8000 psi and 950°F. Macroscopic flooding had been occurring during periods of long operation, but when the electrode material was changed to a high surface area metal oxide, no flooding occurred. The porosity of the fiber nickel electrodes was varied to determine its effect on the fuel cell performance. Electrodes with low porosities (57 and 38% nickel) had higher polarizations and reached limiting currents (mass transport), but those with low porosities (85, 80, 67%) had lower polarizations.

2.4.4 General Electric Company (1960)

Douglas (1960) at General Electric used a porous electrode to contain the electrolyte instead of using a matrix. The fuel cell that was constructed was a laboratory cell with a reference electrode to investigate the performance of the diffusion electrodes. The electrodes were porous metal bodies shaped as short tubes with one closed end; the silver cathode electrodes were made by sintering powders in graphite molds at about 700°C. The electrodes were attached to the ends of alumina tubes. The porosities of the nickel electrodes were 34 and 40% (10–50 and 10–30 μm); of the silver, 42 and 50% (1–50 and 1–20 μm). Reactant gases were fed to the electrodes through the tubes at pressures (2 psig up to 5 psig) below that which would cause bubbles to escape from the electrode into the electrolyte. The cathode, especially silver, was corroded when dissimilar metals (used for joining the electrode with the alumina) were in contact with the electrolyte and oxygen. When nickel was used as both anode and cathode, the open circuit voltage was low. Also, when CO₂ and He were fed to the cathode, a current was still produced. The reason for these performances was that the oxygen used in the reaction was supplied by nickel oxide, which was formed by the melt oxidizing the nickel electrode. Douglas predicted that a molten carbonate fuel cell (MCFC) with free electrolyte and porous gas diffusion electrodes would be able to obtain higher current densities than the matrix type (operating at higher temperatures) because the electrode spacing could be reduced. For similar spacings, the free electrolyte type would have lower internal resistance.

2.5 Alkaline Fuel Cell

During the effort to develop a fuel cell that could use coal, alkaline electrolytes were deemed unsuitable because of chemical reactions that would lead to their degradation (see Section 2.2). However, if the fuel were hydrogen, an alkaline electrolyte would be very suitable. One advantage of using an alkaline electrolyte was that electrode materials besides noble metals (platinum) could be used with less risk of corrosion, especially compared to acid electrolytes. With a selection of different electrode materials, researchers still had to develop electrode structures to contain the electrolyte, preventing it from flooding the electrode. Davtayan used paraffin, Bacon developed an electrode with layers of two different pore sizes, Justi and Winsel (1961) chose pore sizes in the DSK electrodes, and Kordesch (1968) and Niedrach and Alford (1965) used Teflon®. Another method of preventing the flooding of electrodes was to retain the electrolyte in a matrix of asbestos, which was done in the fuel cells of the Apollo space missions, at Allis Chalmers Manufacturing Company, and for the Orbiter fuel cell (space shuttle).

2.5.1 Davtayan (1946) also see 2.4.1

As well as developing a high-temperature fuel cell (Section 2.4.1), Davtayan also experimented with a low-temperature fuel cell that used an alkaline electrolyte and operated at atmospheric temperature and

pressure (Davit (35%), the hydrogen reduction catalyst sheet of perfluoropolymer waterproof, performance of the cell

2.5.2 Bacon

In 1932, when Bacon had the idea to that of a reversible cell (Bacon, 1969). He was at Newcastle-upon-Tyne on the edge of his support after hearing especially to research an engineering and practical application of potassium hydroxide and nickel gauze for 48 minutes (Bacon, 1969). He found acids, only not dissolved in the electrolyte.

Bacon resumed that year, he could produce were produced a cell which he had because of the

Between 1932 and 1933, work at the University of Cambridge associates developed a "layer" electrode sintered in a matrix. The pore size was pressure difference from entering through the cell reached hydroxide, thousands of performance

Bacon and his colleagues had caused a problem took more than an electrode with coating, although colleagues were creating a per-lithium hydroxide

flooding
phenomena

O₂ source

Amalium /
GE = ?

no ppt

pressure (Davtyan, 1946, in Bacon, 1954). The electrolyte was an aqueous solution of potassium hydroxide (35%), the hydrogen oxidation catalyst was activated carbon impregnated with silver, and the oxygen reduction catalyst was activated carbon impregnated with nickel. The catalyst was bound by rubber onto a sheet of perforated steel plated with nickel, and the electrode was coated with paraffin wax to make it waterproof, repelling water from entering the pores of the electrodes to prevent flooding. The performance of the cell at 25 to 35 mA/cm² was 0.80 to 0.75 V.

2.5.2 Bacon (1954, 1969, 1979)

reversible

In 1932, when reading an article about electrolysis, Francis T. "Tom" Bacon was inspired by a similar idea to that of William Grove — that the electrolysis of water could be reversible — and thought that if it were reversible the energy conversion process would be more efficient than that of the Carnot cycle (Bacon, 1969). The fuel cell intrigued him greatly, and as an engineer for C.A. Parsons & Co., Ltd., in Newcastle-upon-Tyne, England, Bacon began to construct a cell, attempting to do so without the knowledge of his supervisor. He sent a proposal to the directors of the company five years later in 1937 and, after hearing nothing in response, was encouraged by a scientist to continue the development and especially to repeat the experiments of Grove. In 1938, he built a small glass apparatus. In 1939, using an engineering approach to design a fuel cell with economically viable catalysts (non-precious metal) and practical high-pressure equipment and seals, he constructed a cell operating at 3000 psi that had potassium hydroxide (27%) as electrolyte, a pure asbestos cloth as a diaphragm (Bacon, 1979, p. 7C), and nickel gauze electrodes. The performance was 0.89 V at 13 mA/cm², which was sustainable for about 48 minutes (Bacon, 1979). The KOH electrolyte allowed the use of non-noble metals as electrodes; with acids, only noble metals could resist the corrosive environments on the oxygen electrode. The gas was dissolved in the electrolyte and fed to the electrodes.

*KOH
N₂(g)*

Bacon resumed his research in the summer of 1940 at King's College of the University of London. In that year, he constructed a two-cell system to achieve a more stable operation. The hydrogen and oxygen were produced in an electrolyzer and delivered to the electrodes in solution by the electrolyte. This battery was operated at 200°C and 600 psi (41 atm) but was unable to reach the goal of 100 mA/cm² at 0.8 V, which he had decided would give hope for a practical source of electricity. In 1941, the work was halted because of the war.

11

Between 1946 and 1955, with the support of the Electrical Research Association, Bacon began work at the University of Cambridge developing a complete fuel cell system. He and his research associates developed an electrode 4 mm thick with two sizes of pores, which was called a "double-layer" electrode. The electrodes were made from carbonyl nickel powder that was compressed and sintered in a reducing atmosphere. Two different grades of powder were used. On the gas side, the pore size was about 30 μm, and on the liquid side, much smaller pores of 16 μm diameter, so a pressure difference of about 2 psi was across each electrode. The pressure difference kept the liquid from entering the pores of the electrode and flooding it. Likewise, the gas was unable to bubble through the smaller pores on the liquid side because of the surface tension of the electrolyte. The cell reached 0.6 V at 1076 A/cm² at 240°C (Bacon, 1954). The electrolyte was 45 wt% potassium hydroxide, the operating temperature was standardized at 200°C to prolong the service life to many thousands of hours, and the pressure was reduced from 600 to 400 psi (41 to 27 atm). The performance was 230 mA/cm² at 0.8 V, 400 psi, and 200°C (Bacon, 1979).

*double layer
gas pores
→ liquid
bubble ↓*

Bacon and his research associates solved the problem of the oxidation of the oxygen electrode that had caused a gradual degradation in the performance of the fuel cell over a period of 25 to 30 hours. It took more than a year to develop the solution to the corrosion problem, which was to treat the nickel electrode with air at 700°C, thereby oxidizing it and allowing it to form a nickel oxide coating. This coating, although able to protect the electrode, prevented it from conducting electrons. Bacon and his colleagues were able to improve the conductivity of the nickel oxide, however, by doping it with lithium, creating a p-type semiconductor. The electrode, after having been sintered, was soaked in a solution of lithium hydroxide, dried, and then heated in air at 700°C for a few minutes.

*oxidation of O₂ electrode
→ corrosion ↓*

al. (1963)
in a high-
hydrogen,
uld act to

trode and
00 psi and
electrode
f the fiber
with low
ransport),

l of using
investigate
d as short
graphite
osities of
1-50 and
g up to 5
lyte. The
ode with
th anode
athode, a
e reaction
Douglas
diffusion
at higher
electrolyte

nsuitable
if the fuel
alkaline
ss risk of
materials,
flooding
ore sizes,
ranch and
retain the
s, at Allis

th a low-
ture and



FIGURE 2.10 Bacon with the 6-kW fuel cell stack, presented in 1959. (Copyright Hulton-Deutsch Collection/Corbis.)

In 1954, at an exhibition in London, Bacon demonstrated a six-cell battery that produced 150 W, operating at 15 bar (600 psi) and 200°C, and having electrodes 5 inches in diameter. Because of a lack of commercial interest in the technology, the work was discontinued in 1955.

In 1956, Bacon and his staff of 14 began development of a larger battery to show that a practical size of battery could be built. It would have 40 cells, based on the same design. The researchers received support from the National Research Development Corporation to do work at Marshall of Cambridge Ltd. (an industrial organization). The cells were 10 inches in diameter, and the battery had a control system. After three years, the battery, shown in Fig. 2.10, was completed. It produced 6 kW, which was used to power a fork-lift truck, welding equipment, and a circular saw. However, even after the successful demonstration, the work was ended because no commercial application could be foreseen.

As the work was progressing on the 6-kW fuel cell system, two licenses were taken out on the patents; in 1956, one was taken by Leeson Moos Laboratories, a research organization, and in 1959 Bacon learned that Pratt & Whitney Aircraft Division of United Technologies Corporation had taken a license on the patents.

A company was formed in 1961, called Energy Conversion Ltd., which began to develop fuel cells that could be produced commercially. In 1962, news reached him about the efforts of Pratt & Whitney to develop a fuel cell to supply power to the auxiliary units of the Apollo space module, and Bacon knew that was the turning point for the technology (Bacon, 1979).

2.5.3 Apollo Space Missions (1965)

Pratt & Whitney Aircraft began developing the fuel cell power plant for the Apollo Command and Service Module in March 1962 (Morrill, 1965). The fuel cell was model PC3A-2, and three were used to supply the electricity for life support, guidance, and communications for the module, as well as water for the crew throughout the two-week missions to the moon. The PC3A-2 had a mass of 109 kg (240 pounds), and the dimensions were approximately 57 cm (22.5 inches) in diameter and 112 cm (44 inches) in height. The fuel cells were jettisoned before re-entry into the atmosphere. Figure 2.11 shows the fuel cells being assembled.

The average power required during the mission was approximately 600 W (Ferguson, 1969). Each fuel cell was designed to operate within 27 to 31 V in the power range of 463 to 1420 W for a period of at least 400 hours; with this redundancy, one fuel cell module would be able to supply the electrical power to the spacecraft if two of the fuel cell modules were lost. The maximum power was 2295 W at a minimum voltage of 20.5 V (Morrill, 1965). At the maximum temperature of 260°C, the fuel cell produced 0.87 V

FIGURE 2.11 stack. (Courte

at a current c
at 0.72 V at 1

The fuel c
difference to
Bacon's desig
was maintain
Compared to
performance.
Prokopius, 19
the original I
oxide for the

Water and
heat transfer
system beyor
some of the
cryogenic ter
temperature
maintained b

The devel
vacuum envi
linear accel
humidity and
axes for 15 m
The storage
resistant to d

2.5.4 Jus

Justi and Wi
oxygen fuel c
electrodes we
the catalyst, c

50 cell
→ 2W

M

M

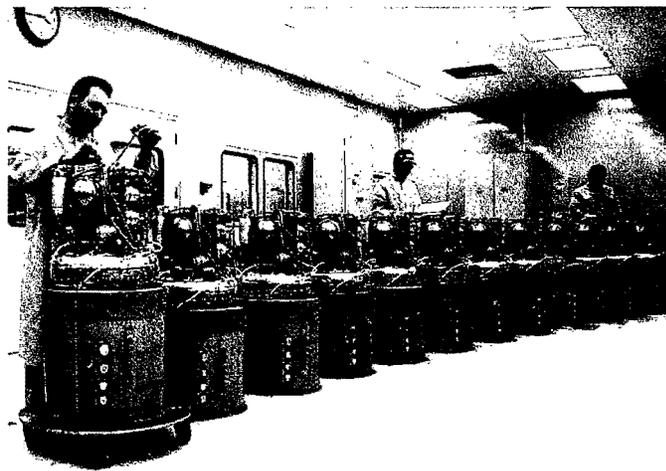


FIGURE 2.11 Apollo fuel cell systems being assembled by Pratt & Whitney Aircraft engineers. The lower half is the stack. (Courtesy of UTC Fuel Cells.)

at a current density of 160 mA/cm^2 ; and at the nominal temperature of 204°C , the fuel cell performed at 0.72 V at 160 mA/cm^2 (Warshay and Prokopius, 1990).

The fuel cells were based on the design of Bacon, using dual porosity electrodes and a pressure difference to control the interface between the gas reactant and the liquid electrolyte. A change from Bacon's design was the the elimination of electrolyte circulation. The potassium hydroxide electrolyte was maintained at a pressure of 50 psia, and the hydrogen and oxygen were fed at a pressure of 60 psia. Compared to the Bacon cell, the operating pressure of the PC3A-2 was lower, but to compensate for the performance, the potassium hydroxide concentration was higher, raised from 50 to 75% (Warshay and Prokopius, 1990). Also, the temperature was raised to 260°C . The electrode materials and structures of the original Bacon cell were kept: dual-porosity sintered nickel for the anode and lithium-doped nickel oxide for the cathode. Thirty-one cells were used in each fuel cell module.

Water and heat were removed from the cell by the hydrogen gas stream, with the amount of mass and heat transfer controlled by the amount of excess gas flowing in the closed-loop hydrogen recirculation system beyond the requirement for electricity. The heat was removed in a condenser with glycol and some of the heat from the glycol was used to preheat the hydrogen and oxygen reactants from the cryogenic temperatures before reaching the fuel cell stack. Water content was controlled by the fixed temperature of the hydrogen gas exiting the condenser (Ferguson, 1969). The pH of the water was maintained between 6 and 8 so that the water would be drinkable.

The developmental modules passed the qualification tests of endurance, operating with load in a vacuum environment for 360 hours. The effects of environmental conditions were also tested: 7 g linear acceleration, soaking in low temperature at -20°F for 48 hours without load, soaking in 95% humidity and temperature up to 130°F for 240 hours without load, variable vibration loads on three axes for 15 minutes, and twelve start cycles; these series of tests had no adverse effect on the fuel cell. The storage life requirement of two years was met and exceeded, showing that the materials were resistant to degradation.

2.5.4 Justi and Winsel and the DSK Electrodes (1961)

Justi and Winsel (1961) started their research in 1943 and focused on the electrodes for hydrogen and oxygen fuel cells operating at temperatures below 100°C and pressures below 4 atm. Their gas diffusion electrodes were named "Doppelskelett-Katalysator" (Double Skeleton Katalyst, DSK) electrodes because the catalyst, considered a skeleton itself, was held by a skeleton that provided mechanical stability, form,

and electrical conductivity. The hydrogen electrode was developed before the oxygen electrode, and it used Raney nickel, an active hydrogenation catalyst that was insensitive to impurities in the gas feed. To prepare the catalyst, 50% aluminum (Al) and 50% nickel (Ni) were melted and then cooled. The cooled alloy was pulverized, and the Al was leached by KOH, giving these "microskeleton" grains of nickel catalyst large surface area and high activity because of lattice defects. The "macroskeleton" was a support skeleton made of carbonyl nickel powder, pressed and sintered into the shape of the electrode, providing mechanical stability and electrical conductivity for the "microskeleton" catalyst particles located in its pores.

The oxygen electrodes were more challenging to develop because of the ductility of Raney silver (Ag) alloy, which made it difficult to pulverize the metal. Friese (referenced by Justi and Winsel, 1960) developed a method to produce brittle Raney silver by melting 35% by weight Al under a protective coating of CaCl₂ in a graphite crucible, adding 65% Ag, and then mixing. The mixture was cooled and pulverized, and the Ag particles (diameter 50–100 μm) were combined with 1 part nickel particles of 5 to 10 μm and 0.5 part KCl particles sized 50 to 75 μm. To form a 40-mm electrode, 15 grams of the powder mixture were hot-pressed at 370°C and 10 tons (1 ton/cm²). A coating of nickel (2 grams) was applied onto the electrode to reduce the gas permeability through the electrode, forming a "double-layer electrode," and the electrode was leached in 10N KOH at 80°C. The final weight was 0.94 g/cm² and 0.05 g/cm² Ag (5.3% Ag by weight).

Dittmann et al. (1963) described another more advanced method of preparation in which 35% by weight Al was melted under a protective coating of CaCl₂ in a graphite crucible and then 65% Ag was added. The silver was in the ζ phase, and the aluminum was in the α phase; potassium hydroxide was added that attacked both phases, resulting mostly in Raney silver in the ζ phase. By melting above 800°C and quenching below 100°C, the metal became brittle and textured. The Raney silver catalyst was pulverized and mixed with nickel powder, and the mixture was hot-pressed between 300 and 500°C and 1 ton/cm² to form a nickel matrix supporting the catalyst in its pores. Potassium hydroxide was used to activate the electrode.

2.5.5 Electrolyte Matrix by the Allis-Chalmers Manufacturing Company (1962)

The fuel cells developed at the Allis-Chalmers Manufacturing Company used an "electrolyte vehicle," a porous matrix, to hold the alkaline electrolyte stationary (Wynveen and Kirkland, 1962). Fuel cell systems were made simpler with an immobilized electrolyte, which did away with the pumps and tubes of the circulation system. The matrix, made of sheet asbestos (as thin as 0.01 in or 254 μm), was filled with a controlled volume of the electrolyte before being sandwiched by the hydrogen and oxygen electrodes, both made of porous sintered nickel sheet (0.028 in thick) impregnated with a mixture of platinum and palladium. The pores of the electrodes were larger than those of the matrix, so because of the lower capillary potential associated with the larger pores, the electrolyte remained within the pores of the matrix. Also, making the electrodes wetproof was unnecessary because of the electrolyte vehicle. Therefore, this design used the electrolyte vehicle to contain the liquid instead of using the electrode as was done in Bacon's double-porosity electrodes and Justi and Winsel's double-skeleton and double-layer electrodes. The three layers together could have measured as thin as 0.066 in (0.17 cm), but the battery also included plates for gas distribution, support, and water transport membranes.

The pores of the asbestos sheet had a "high capillary potential," which means they required a high pressure to force a gas bubble through the largest pore in the matrix. With the matrix separating the hydrogen and oxygen electrodes, it required a pressure difference of 100 psi to force the gases through the pores of the asbestos to the opposite electrode. In simulations for space applications, the cells were tested with accelerations over ten times that of gravity, in zero gravity, and with shocks, tolerating these conditions and maintaining a constant performance because of the immobilized electrolyte. Water was removed from the cell by the hydrogen stream, and the removal rate could be adjusted by changing the gas flow; the oxygen was fed into a nearly dead-ended compartment. A battery of four cells, with total electrode area of 217 cm² (33.6 in²) could give an average of 0.8 V per cell at a current density of 108 mA/cm² (100 A/ft²) at 65 ± 3°C and 0 to 5 psig.

H₂ electrode
O₂ electrode

2.5.6

Karl V. Korde during the electrode research found the peroxide, current density of its product. Korde's company two were design both tube tube inside area it was of its mechanical length.

In 1960 assembly a component occur; the mechanical

The design (e.g., laminated and the carbon atmosphere and 100% by being composed waterp backing. The thickness of the cell electro was critical

2.5.7

At Georgetown "contaminated" temperature the electrode Teflon silver, catalytic The final

before the oxygen electrode, and it is due to impurities in the gas feed. To prevent this, the cooled "skeleton" grains of nickel catalyst "skeleton" was a support skeleton of the electrode, providing mechanical strength. The catalyst particles located in its pores. The ductility of Raney silver (Ag) by Just and Winsel, 1960) developed under a protective coating of CaCl₂, was cooled and pulverized, and the particles of 5 to 10 μm and 0.5 parts by weight of the powder mixture were hot-pressed. This mixture was applied onto the electrode as a "three-layer electrode," and the electrode was pressed at 0.05 g/cm² Ag (5.3% Ag by weight). The method of preparation in which 35% by weight of Raney silver was crucible and then 65% Ag was α phase; potassium hydroxide was the β phase. By melting above 800°C and pressing between 300 and 500°C and sintering. Potassium hydroxide was used to

Manufacturing

Many used an "electrolyte vehicle," and Kirkland, 1962). Fuel cell systems were developed with the pumps and tubes of the cell. The electrolyte, which was 0.01 in or 254 μm, was filled with a mixture of hydrogen and oxygen electrodes, and the matrix, so because of the lower resistance, remained within the pores of the electrolyte vehicle. Instead of using the electrode as was used in the double-skeleton and double-layer cell, the electrolyte was 0.066 in (0.17 cm), but the battery did not have membranes.

which means they required a high pressure matrix. With the matrix separating the cells, a pressure of 100 psi to force the gases through the cell, and with shocks, tolerating these cells with an immobilized electrolyte. Water was not used, but it could be adjusted by changing the electrolyte. A battery of four cells, with total voltage of 1.2 V per cell at a current density of 108

2.5.6 Kordesch at Union Carbide (1960)

Karl V. Kordesch (Kordesch, 1968) returned to using carbon, but instead of it being the fuel as it was during the early days of direct coal research, it was the electrode material. His interest in using carbon electrodes in alkaline fuel cells originated from his work at the University of Vienna, where he and Marko researched methods of catalyzing carbon with heavy metal oxides for use as oxygen electrodes. They found that the catalyst improved the activity of carbon and also promoted the decomposition of hydrogen peroxide, an intermediate reaction product in alkaline electrolytes, and could therefore produce high current densities in alkaline cells. The trouble with carbon was that its performance was unreliable because of its processing, which produced varying compositions and structures.

Kordesch, in 1955, joined the National Carbon Company (which merged with the Union Carbide Corporation in 1955) and began developing better carbon electrodes for fuel cells, benefiting from the company's technical expertise in carbon production. Four cell configurations were designed — the first two were based on tubular electrodes, and the last two used flat plate electrodes. The first tubular electrode design had hydrogen flowing through one tube and oxygen the other, with KOH electrolyte surrounding both tubes, and with electrical current collected at the ends of the tubes. The second design had one tube inserted into a larger tube to give a concentric cell, and because the outer tube had a larger surface area it was used as the air electrode. This concentric cell had a higher volumetric power density because of its more compact design, and it had a lower resistance polarization because current was collected along the length of the tube rather than at its ends.

In 1960, the tubes were superseded by plate electrodes, 6.35 mm (0.25 in) thick, that were easier to assemble into batteries in terms of current collection and gas manifolds. The final design (in 1963) used a composite electrode, 0.56 mm thick (22 mils), to obtain a "fixed-zone" where the reactions would occur; the porous carbon was the electrochemically active layer and a porous nickel plaque was the mechanical support and an electrical conductor (Kordesch, 1968, p. 401).

The all-carbon electrodes (used in the first three designs) were made from a mixture of base carbon (e.g., lampblack) and a binder (e.g., pitch or sugar), and the mixture was extruded to produce tubes or molded to produce plates. The electrodes were baked to remove the binder, which left a porous material, and then baked again in a CO₂ atmosphere for several hours to increase the internal surface area of the carbon. The electrodes were soaked in a solution of metal salts, dried in air, and heated again in a CO₂ atmosphere to 700 or 800°C. (For example, a salt made with 1.5 g cobalt nitrate, 3.5 g aluminum nitrate, and 100 ml water would form the spinel, cobalt aluminate, when heated.) The electrodes were wetproofed by being immersed in solutions of waxes or high molecular weight paraffins. To make the planar composite electrodes, the nickel plaque was sprayed with polytetrafluoroethylene (PTFE) to make it waterproof, a mixture of PTFE and inactive carbon powder was sprayed onto the nickel as an intermediate backing layer, and then polyethylene and active carbon were sprayed onto the intermediate backing layer. The three-layer electrode was pressed at 1000 psi between 130 and 140°C.

The performance of the tubular cells reached 0.8 V at 50 mA/cm². With the planar composite electrode, the cell performance was 0.8 V at 100 mA/cm² at 65°C and atmospheric pressure, with 9 N KOH electrolyte. When the air pressure was 15 psig, the cell could give 0.8 V at 200 mA/cm². The electrolyte was circulated through the cell. The Union Carbide alkaline fuel cell stack is shown in Fig. 2.12.

2.5.7 General Electric Electrodes with Waterproofing (1965)

At General Electric, Niedrach and Alford (1965) used waterproof Teflon[®] in the electrodes to achieve "controlled wetting," establishing the gas-electrolyte interface. This development was tested with low-temperature fuel cells using aqueous electrolytes to control the extent of the electrolyte permeating within the electrode, effective at ambient gas pressures and with a thin electrode (between 5 and 10 mils). The Teflon was mixed with catalyst (platinum black) and then pressed and sintered onto a screen (nickel, silver, platinum). To form the electrode, the screen was sandwiched by two films of Teflon mixed with catalyst, with the catalyst facing the screen. One of the catalyst films was prepared on a film of Teflon. The films were prepared by spraying a Teflon suspension diluted with water onto a foil in a circular area

2 e

electrode prep.

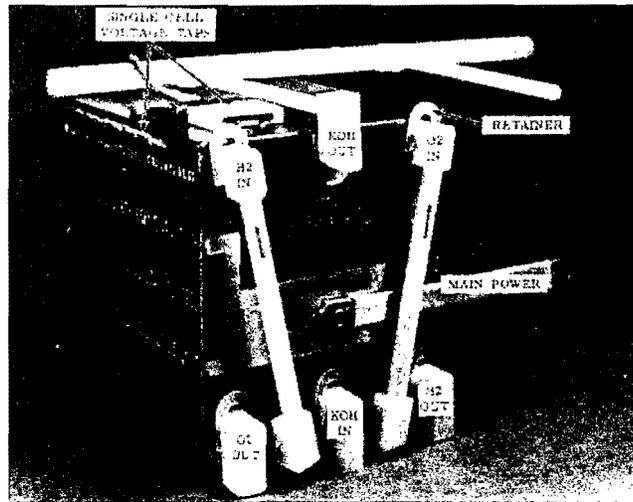


FIGURE 2.12 The Union Carbide alkaline fuel cell with the "thin electrode" technology. This was used in a fuel-cell-powered van in 1967. (Reprinted with permission from SAE paper 670176. Copyright 1967 Society of Automotive Engineers, Inc.)

5 by 5 in², heating the foil to evaporate the water, and then pressing at 350°C to a thickness of 1/8 in., allowing the Teflon to sinter and to reject the wetting agent. The film with the catalyst was prepared by mixing 0.3 g of platinum black with Teflon on a foil, spreading the mixture uniformly, and then drying at 250–350°C. The screen was placed over the spread, and the second spread placed on top of the screen with the catalyst mix facing the screen. The sandwich was pressed for 2 minutes at 1800–3000 psi at 350°C to sinter the Teflon. The aluminum foil was dissolved by warm 20% NaOH. The electrodes had a catalyst layer composed of 35 mg Pt mixed with 3.2 mg Teflon, which was spread over a Teflon film of 1.6 mg Teflon/cm². This type of electrode is shown in Fig. 2.13.

2.5.8 Orbiter

The alkaline fuel cell was selected for the Orbiter program (space shuttle) but was redesigned with more active catalysts so that the pressure and temperature could be lowered. With platinum-based catalysts, the operating pressure was dropped to 4 bar absolute and the temperature was reduced to 93°C. Platinum was used for the anode (with a loading of 10 mg platinum per cm²), and platinum was alloyed with gold

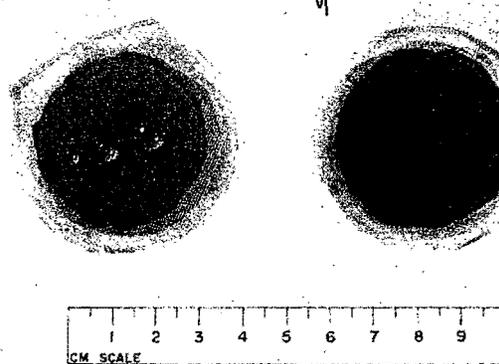


FIGURE 2.13 The electrode on the left has Teflon to control the degree of wetting by the liquid electrolyte (Niedrach and Alford, 1965). (Reproduced by permission of The Electrochemical Society, Inc.)

for the
were pl
held in

2.6

In the
methan
time, m
but, if a
be circu
Before
Marko (
"new pe
(ethano
which c
electroly

Direct
(Tarmy
in the
(Murray
but also
based on
(1965)
revived
Propulsi
(Suramp

2.6.1

At Shell
as the el
reaction,
different
with acic
was proc
it diffuse

Of the
(60–70°C
in tests p

Shell t
gen–air f
by a pal
electrolyt
also mini
plastics c
electrode
chloride
platinum
could be
circulate

for the cathode (20 mg platinum per cm^2). Both catalysts were bound by PTFE onto nickel screens that were plated with gold for protection against corrosion. The 32% potassium hydroxide electrolyte was held in an asbestos matrix (Warshay and Prokopius, 1990).

2.6 The Direct Methanol Fuel Cell

In the 1960s, the hope for a "direct" fuel cell emerged again, but instead of using coal, the fuel was methanol. Methanol, as opposed to coal, could be electrochemically oxidized at the electrodes. At the time, methanol was being used in fuel cells "indirectly," undergoing steam reforming to produce hydrogen, but, if a fuel cell could use methanol directly to produce electricity, then the fuel reforming step could be circumvented, allowing for a simpler system.

Before the major efforts of the 1960s, there was an instance of the use of methanol by Kordesch and Marko (1951). They described the development and performance of new carbon electrodes and identified "new possibilities for the building of fuel cells," such as the use of aldehyde (formaldehyde) and alcohols (ethanol and methanol) as fuel. The electrical current from alcohol was lower than that of formaldehyde, which could supply a small current of 0.3 mA/cm^2 at 0.8 or 0.9 V using carbon electrodes in an alkaline electrolyte of KOH.

Direct methanol fuel cells were developed by researchers at Shell (Williams et al., 1965) and ESSO (Tarmy and Ciprios, 1965) with aqueous acid electrolytes that would not react with the CO_2 produced in the electrochemical reaction. Alkaline electrolytes were tested by researchers at Allis-Chalmers (Murray and Grimes, 1963), who expected the degradation of the electrolyte by carbonate formation but also recognized the better compatibility of materials. For methanol oxidation on the anode, catalysts based on alloys between noble metals were more effective than pure metal catalysts, and Binder et al. (1965) studied different combinations in both acid and alkaline electrolytes. In 1992, research was revived following the technical improvements of the solid polymer fuel cell, as scientists at the Jet Propulsion Laboratory developed a direct methanol fuel cell using the same solid polymer electrolyte (Surampudi et al., 1994).

2.6.1 Acid Electrolyte: Shell (1965) and ESSO (1965)

At Shell Research Limited (Thornton Research Centre), Williams et al. (1965) chose acid over alkaline as the electrolyte because it was unaffected by the carbon dioxide produced in the methanol oxidation reaction. Also, with acid electrolytes, the water removal from the fuel cell was simpler. Because of the different directions of ion transport in the acid and alkali electrolytes, water was produced at the cathode with acid, and it was removed by the excess air flow. On the other hand, for an alkaline system, the water was produced at the anode, where there was no gas flow, so the only way to remove it would be to have it diffuse through the electrolyte to the cathode, where it could be removed by air.

Of the different acids, sulfuric was selected over phosphoric because, at the low operating temperatures (60–70°C) intended for the system, sulfuric acid had higher conductivity, and the oxygen electrodes used in tests performed slightly better in this acid.

Shell turned to the direct methanol-air fuel cell after deciding that their 5-kW demonstration hydrogen-air fuel cell system was too complex, operating on hydrogen produced from methanol and purified by a palladium-silver diffusion membrane. To minimize the corrosion of materials with an acidic electrolyte, the researchers chose to operate the cell at a low temperature, around 60°C, which would also minimize the methanol evaporation in the ambient pressure cell. At low temperatures, inexpensive plastics could be used as cell materials. For both anode and cathode, the catalyst could be applied to the electrode surface, which had a thin layer of gold as a conductor coated over a microporous polyvinyl chloride substrate (Williams et al., 1965). (The value of the gold-PVC substrate was $\$1.50/\text{ft}^2$.) Shell used platinum-ruthenium for the anode and platinum for the cathode (Andrew and Glazebrook, 1966). (This could be done on two sheets of plastic or on both sides of one sheet of plastic. The electrolyte would circulate on one or both sides of the fuel electrode.)

An eight-cell prototype was built in 1963 and produced 3.15 W at 1 A; after two years, it could still produce 2.85 W at 1 A, an indication of the durability of the materials. It used sulfuric acid electrolyte (6 N) with 1 M methanol mixed and circulated with electrolyte. A fuel cell stack with 40 cells was constructed and produced 300 W at 12 V and 60°C. In both fuel cell stacks, the circulating electrolyte-methanol mixture emitted an ester-like odor, which upon analysis was found to contain formaldehyde and formic acid, intermediates that were expected, and also traces of acetic, propionic, butyric, and isobutyric acids, which had a source that had yet to be identified. These compounds had a poisoning effect on the anode catalyst, so a better catalyst was needed that could suppress the formation of these side reactions while also being effective for methanol oxidation.

The ESSO Research and Engineering Company developed direct methanol-air fuel cells with the goal of delivering a portable battery for military communications systems to the U.S. Army Electronics Laboratories (Tarmy and Ciprios, 1965). The work began in 1962, and by 1966 they had demonstrated a 60-W, 6-V unit that was self-sustaining. The cells used 3.7 M sulfuric acid electrolyte, and a control system added water to maintain the acid concentration. Methanol concentration was 0.75 M, which was found to be optimum, and it was controlled by a diffusion membrane that limited the diffusion to an electrode. The current was proportional to the concentration. The temperature range was 60 to 80°C, which could be regulated by the air flow rate that controlled the water removal. Ambient temperature air was supplied by a small blower and then humidified in a water economy unit that had a moisture-permeable membrane separating the countercurrent flows of fresh, ambient air and warm, wet exhaust air. The electrodes were supported by 52 mesh tantalum screens, 4 mil thick, on which 25 mg/cm² of anode catalyst was pressed, and for the cathode, 9 mg/cm² of platinum mixed with Teflon.

A demonstration unit produced 82 W at 6.0 V and 13.6 A, with the stack producing 99 W (7.0 V, 14.1 A), and the control systems consuming 15 W of the 17-W parasitic power loss. In continuous operation, the performance dropped to 60 W at 6.0 V.

At 60°C (140°F) for a single cell, terminal cell voltages of 0.50 V at 54 mA/cm² (50 A/ft²) and 0.40 V at 108 mA/cm² (100 A/ft²) were attained. In the 16-cell battery with larger electrodes, the performance was 50 mV less than the 0.46 and 0.31 V in the same size electrodes. In separate studies of a 16-cell module, Tarmy and Ciprios found that low methanol concentrations and high methanol conversion levels caused the electrodes to "starve," increasing polarization from 0.30 V at 4 vol% inlet methanol concentration to 0.44 V at 1 vol%. However, a lower methanol concentration could improve cathode performance because less methanol would migrate to the platinum cathode where it would be oxidized by the air, causing a mixed potential at the electrode and reducing the efficiency of the cell. Air flow was between two and ten times stoichiometric, variable in that range depending on the temperature control (water removal) needed.

2.6.2 Alkaline Electrolyte: Allis-Chalmers Manufacturing Company (1963)

Murray and Grimes (1963) at Allis-Chalmers Manufacturing Company (Research Division) developed a methanol fuel cell with an alkaline electrolyte, potassium hydroxide. The methanol was mixed into the potassium hydroxide to give an electrolyte concentration of 6 M CH₃OH and 6 M KOH. For the anode, because the oxidation of methanol would produce the intermediate formate ion on platinum catalyst, palladium was added. Palladium by itself was a poor catalyst for methanol oxidation, but the platinum and palladium mixture performed well as the anode catalyst, oxidizing the methanol to carbonate. Nickel plaques supported the anode and cathode catalysts. Two cathode catalysts were tested, with the silver metal and the cobalt oxide spinel (Co₃O₄) showing adequate current capacity for operating in a fuel cell. The cobalt oxide spinel did have a limitation because its performance was deactivated after flooding conditions and the subsequent adsorption of methanol, which would happen if the oxidant supply were stopped or during shutdown.

Small single cells, approximately 40 cm², were used for life testing to investigate the long-term performance at different temperatures with the cell voltage held at 0.3 V. The performance gradually decreased over a period of 70 hours at 60°C and 94 hours at 30°C because the hydroxide was converted to carbonate;

when th
to a lev
anode v
slightly
improv:

A mx
a sheet
and 5 p
ft² usin
at 40°C
effect o
of hydr
Altho
recogni
regener
with cal
The fue
in pract

2.6.3

Binder
alkaline
catalyst
differer
being C
electro
from 80
rutheni
cm² an
constar
loading
hypothe
the opt
on the

The
adsorp
into ca
the cat
catalyst
oxidati

2.6.4

Develo
fuel cel
1992 w
1998).
feed) r
was co
liquid

A; after two years, it could still be used. It used sulfuric acid electrolyte. A fuel cell stack with 40 cells was tested. In the stacks, the circulating electrolyte was found to contain formaldehyde, acetic, propionic, butyric, and other compounds that had a poisoning effect. These compounds had a poisoning effect and suppressed the formation of these

methanol-air fuel cells with the goal was to the U.S. Army Electronics Research Laboratory. By 1966 they had demonstrated a fuel cell with sulfuric acid electrolyte, and a control system. The concentration was 0.75 M, which was a concentration that limited the diffusion of oxygen. The operating temperature range was 60 to 80°C, and the oxygen removal. Ambient temperature operation. A unit that had a moisture separator, ambient air and warm, wet exhaust. The separator was 1/8" thick, on which 25 mg/cm² of platinum was mixed with Teflon.

The stack producing 99 W (7.0 V, 14.1 A) with a power loss. In continuous operation,

at 54 mA/cm² (50 A/ft²) and 0.40 V on larger electrodes, the performance was good. In separate studies of a 16-cell stack and high methanol conversion, at 0.30 V at 4 vol% inlet methanol concentration could improve cathode performance where it would be oxidized. The efficiency of the cell. Air flow was controlled depending on the temperature control

Manufacturing Company (1963)

General Electric (Research Division) developed a fuel cell. The methanol was mixed into the electrolyte. The electrolyte was 6 M KOH. For the anode, the formate ion on platinum catalyst, the ethanol oxidation, but the platinum was poisoning the methanol to carbonate. Nickel catalysts were tested, with the silver catalyst capacity for operating in a fuel cell. The performance was deactivated after flooding. It could happen if the oxidant supply were

cut off. To investigate the long-term performance. The performance gradually decreased. The hydroxide was converted to carbonate;

when the concentration of KOH reached 2 M, the electrolyte was replaced, but the performance recovered to a level below the initial current density. The performance was separated into two half-cells, and the anode was identified as the main cause of the decreasing current density while the silver cathode improved slightly because of better wetting characteristics. The performance of the anode could be "regenerated," improving the current density.

A module of 40 cells was constructed in a bipolar configuration with anode and cathode attached to a sheet of nickel, and the electrode size approximately 480 cm². It operated at 49°C (120°F) between 0 and 5 psig, producing 440 W at 0.4 V and 53.1 A/ft² and a maximum of 730 W at 0.25 V and 140.4 A/ft² using oxygen as oxidant. A module of 80 cells of smaller electrode area was also constructed, operating at 40°C, which produced 500 W constantly over a period of 5 hours; the constant performance was an effect of the internal heating of the module from 40 to 57°C, which compensated for the consumption of hydroxide ion in the electrolyte.

Although using an alkaline electrolyte would facilitate construction of the methanol fuel cell, it was recognized that the disadvantage would be carbonate formation. Murray and Grimes suggested that a regeneration process of returning carbonate ion to hydroxide ion would be the precipitation reaction with calcium ion. Despite the economic feasibility of using lime, the disposal of CaCO₃ would be difficult. The fuel cell could be a means to consume surplus hydroxide solution from Cl₂ production plants, but in practical terms, reliable and economical regeneration technology would first have to be developed.

2.6.3 Catalysts and Electrodes

Binder et al. (1965) tested noble metals (Ru, Rh, Pd, Os, Ir, Pt) and their alloys as half-cell electrodes in alkaline and acidic electrolytes. In potassium hydroxide (KOH, 5 M = 5 N), the most active Raney-type catalyst at 50 mA/cm² and 80°C was Pt, followed by Pd, Ru and Rh, Ir, and Os. The performance was different when using sulfuric acid (H₂SO₄, 2.25 M = 4.5 N), with the most active Raney-type catalyst being Os, followed by Ru and Ir, Pt, Rh, and Pd (50 mA/cm² and 80°C). The polarization of the Pd electrode in acid could be reduced by alloys, and the addition of Ru (50 wt%) caused a drop in polarization from 800 (Pd) to 459 mV (PdRu alloy) at 25°C and from 570 to 290 mV at 80°C. Platinum alloyed with ruthenium gave the best performance of all alloys in H₂SO₄, having a polarization of 230 mV at 50 mA/cm² and 80°C. In a test of durability for 600 hours, the PtRu in acid supplied 2000 mA/cm² with a constant polarization of about 420 mV. (In a 1968 paper, Liebhafsky and Cairns noted that the metal loading was nearly 200 mg/cm², a detail covered in an earlier paper by the research group.) Binder et al. hypothesized that the high activity of the alloy was attributable to the magnetic susceptibility that allowed the optimum sorption of all reactants, noting, though, that magnetic susceptibility data were unavailable on the catalysts. However, they acknowledged that the methanol oxidation mechanism was still unclear.

The methanol oxidation mechanism on platinum in acid was reviewed by McNicol (1981). It involves adsorption of the methanol on the platinum catalyst, dehydrogenation, and oxidation of the molecule into carbon dioxide. The intermediate step of dehydrogenation produces a molecule that is a poison to the catalyst, slowing down the next step of oxidation. Therefore, to improve the performance of the catalyst, it should have improved resistance to poisoning by the dehydrogenated molecule or have improved oxidation ability of the molecule.

2.6.4 Nafion® Electrolyte: Jet Propulsion Laboratory (1992)

Development of the direct methanol fuel cell (DMFC) was revived after the success of the solid polymer fuel cell (SPFC). Jet Propulsion Laboratory began developing a DMFC with a Nafion membrane around 1992 with Giner Inc. and the University of Southern California (Surampudi et al., 1994; Narayanan et al., 1998). Because of the solid polymer electrolyte, the methanol fuel was delivered to the anode (liquid-fed) rather than through the electrolyte as had been done with the sulfuric acid electrolytes. The cell was constructed in a manner similar to that of the SPFC, but the catalyst was PtRu. As with cells with liquid electrolyte, methanol crossover was still a problem.

Verbrugge (1989) of the General Motors Research Laboratories modeled the transport of methanol across a Nafion 117 membrane to determine the extent of the "chemical short" that would occur in a methanol fuel cell using a solid polymer electrolyte membrane. The transport coefficients used in the model were based on model fits to experiment data taken from a diffusion cell (no migration or convection). The membrane was treated with 1.0 N sulfuric acid and the cell temperature was 25°C. With the model results, Verbrugge concluded that a new membrane system should be investigated.

2.7 The Phosphoric Acid Fuel Cell

The phosphoric acid fuel cell was developed to use natural gas, but with the fuel first chemically reformed to produce hydrogen. Because a byproduct of the reforming reaction was carbon monoxide, which would lower the efficiency of the anode, the fuel cell temperature was raised to increase the rate of carbon monoxide removal. (Phosphoric acid could be used with platinum electrodes at temperatures above 100°C, but sulfuric acid could not because it would be chemically reduced in the presence of platinum.) Besides the improvement in the performance of the fuel cell, another advantage of using higher temperatures was an improvement in the heat management of the fuel reformer; the chemical reaction that produces hydrogen from natural gas is endothermic, so the heat from the fuel cell supplies the energy required to sustain the reforming reaction.

The development of the phosphoric acid fuel cell occurred during the TARGET program, which met its goal in 1975 of demonstrating the technology as electrical power systems for homes supplied with natural gas. The fuel cell systems produced 12.5 kW of electricity, and after the program fuel cell power plants of megawatt (MW) size were tested. The use of carbon in the fuel cell as catalyst support decreased the amount of platinum necessary for the electrodes, decreasing the cost of the fuel cell to acceptable levels.

2.7.1 Pratt & Whitney Aircraft Division and the TARGET Program (1967–1975)

The culmination of the TARGET program (Team to Advance Research for Gas Energy Transformation) in 1975 was the demonstration in homes of phosphoric acid fuel cells operating on natural gas (Appleby and Foulkes, 1989). The program was initiated in 1967 by Pratt & Whitney Aircraft Division of the United Technologies Corporation, responsible for developing the fuel cell, with sponsorship from 32 U.S. gas companies that wanted a share of the electricity market at a time when heating for homes was being shifted toward electricity and away from natural gas. (A utility in Canada also sponsored the research; in 1972, two gas utilities in Japan joined.) The fuel cell would allow their natural gas to be converted to electricity for on-site power for commercial, industrial, and residential applications. The electric power of the fuel cell was rated at 12.5 kW, the maximum power required by a residence, and the goal of the gas utilities was to lease the unit to homeowners. The units were to provide, in addition to electricity, heat, humidification and purification of air, and waste processing.

The prototype 12.5-kW fuel cell developed in the program, and shown in Fig. 2.14, was called the "PC-11" (Power Cell-11). It operated on hydrogen produced from natural gas, propane, and light distillate liquid fuels by the steam reforming reaction. Heat was supplied for the endothermic steam reforming reaction by burning the excess fuel from the anode of the fuel cell. The reactor was located in the same unit as the fuel cell, but the DC-to-AC inverter was in a separate unit.

Sixty PC-11 units were tested in the U.S., Canada, and Japan by the end of the program, with each site operating for about three months to identify the environmental effects on the fuel cell, system reliability, and response to peak demands, as well as economic and business factors. The PC-11 was a prototype, and it exceeded the targeted cost of \$150/kW (1967) because of its high platinum content. Its service life was also shorter than the goal of 40,000 hours.

The PC-19, a 1-MW phosphoric acid fuel cell system, was tested in 1977 (see Fig. 2.15). This model incorporated lower platinum loadings in the electrode because of carbon supports. The PC-19 produced 698,000 kWh in 1069 hours of operation, giving experience for the future 4.5-MW units.

FIG
left
(Co:

FIGU
was us

Tw
kW (I
of cor
electr
a fuel
compl
The
the or
period
based
AC in
and 15

the transport of methanol (or other fuels) that would occur in a fuel cell (no migration or temperature was 25°C. With this design, it would be investigated.

The first chemically reformed fuel was carbon monoxide, which would increase the rate of carbon monoxide oxidation at temperatures above 1000°C in the presence of platinum. (The advantage of using higher temperatures is that the chemical reaction that the fuel cell supplies the energy for is exothermic.)

The TARGET program, which met the needs for homes supplied with natural gas, the program fuel cell power was reduced as catalyst support decreased the fuel cell to acceptable levels.

TARGET

(for Gas Energy Transformation) operating on natural gas (Appleby Aircraft Division of the United States) with sponsorship from 32 U.S. gas utilities. The heating for homes was being investigated and also sponsored the research; the goal was to convert natural gas to be converted to electricity for residential applications. The electric power was to be used for a residence, and the goal of the program was to provide, in addition to electricity,

as shown in Fig. 2.14, was called the PC-11. It used natural gas, propane, and light oil as fuel for the endothermic steam reformer. The reactor was located in a separate unit.

At the end of the program, with each unit, the effects on the fuel cell, system efficiency, and business factors. The PC-11 was a demonstration unit of its high platinum content. Its design was based on the PC-19.

In 1977 (see Fig. 2.15). This model was a demonstration of the carbon supports. The PC-19 produced a 4.5-MW unit.



FIGURE 2.14 The PC-11 12.5-kW residential fuel cell developed during the TARGET program. The unit on the left contains the fuel cell and the natural gas fuel processor, and the unit on the right is the electrical inverter. (Courtesy of UTC Fuel Cells.)



FIGURE 2.15 The PC-19 1-MW plant, with the phosphoric acid fuel cells contained in the upright vessels. Carbon was used as support for the fuel cell catalysts, reducing the platinum loading. (Courtesy of UTC Fuel Cells.)

Two demonstration units of 4.5-MW AC were constructed in New York and in Goi, Japan, with 240-kW (DC) stacks as building blocks. The plant in New York (Manhattan) never did produce power because of construction and licensing delays and technical problems with the stack (reactant crossing between electrodes because of voids in the electrolyte). However, it did receive a license to operate, showing that a fuel cell plant could comply with standards and codes. It was to have operated in late 1978 and to have completed testing in 1979, but after numerous delays and extension, the project was terminated in 1985.

The Goi plant was installed for the Tokyo Electric Power Company (TEPCO) within 38 months of the order, and the construction cost was \$25 million (1980 dollars). It produced 5430 MWh over a period of 2423 load hours between 1983 and 1985 (Shibata, 1992). The electrical efficiency was 36.7% based on the higher heating value (HHV) of hydrogen and on the electrical output after the DC-to-AC inverters (Anahara, 1993). Twenty stacks (with 439 cells each) operated at 2.5 bar (2.5 kg/cm²) and 191°C (Shibata, 1992).

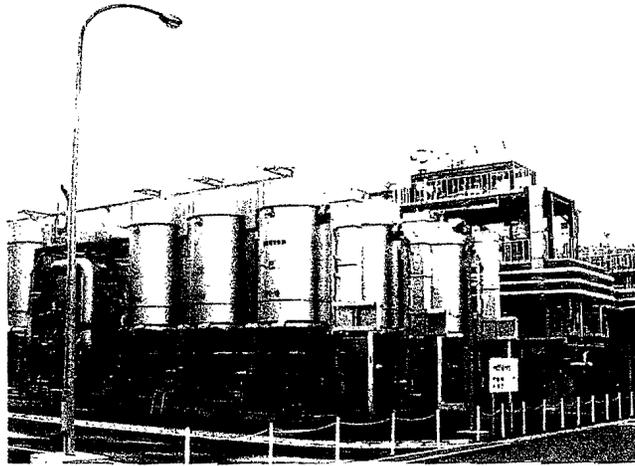


FIGURE 2.16 The 11-MW plant in Goi, Japan based on PC-23. The fuel cells are contained in the upright cylindrical vessels. (Courtesy of UTC Fuel Cells.)

The 4.5-MW power plants led to a larger demonstration of an 11-MW power plant (scaled down from the original plan of 27 MW) in Goi, Japan. The goal was to examine the suitability of fuel cells using natural gas as a “distributed” or “dispersed” power source and also to lead the technology to commercialization (Shibata, 1992). The 11-MW plant, shown in Fig. 2.16, was constructed for TEPCO by Toshiba using 18 stacks (model PC-23 producing 670 kW each) from International Fuel Cells (now UTC Fuel Cells). Construction began in January 1989, and the designed power level of 11 MW was attained in April 1991. The fuel cells operated at 7.3 bar gauge pressure (7.4 kg/cm² gauge) and 207°C, and the net electrical efficiency was 41.1% (HHV of hydrogen, after inverters) (Anahara, 1993).

2.7.2 Japanese Companies and the Moonlight Project (1981–1992)

At the same time that phosphoric acid fuel cells were being demonstrated in Japan, Japanese companies were developing their own fuel cell technology with support from the government (as reviewed by Appleby and Foulkes, 1989). The goal of the Moonlight Project in Japan was to develop energy conversion systems with efficiencies higher than those attainable in 1974. In 1981, fuel cell technology was transferred from the Sunshine Project to the Moonlight Project as part of a ten-year plan to develop fuel cell power plants of the 1-MW scale. Phosphoric acid fuel cell technology received the majority of the funding between 1981 and 1986 (\$30 million out of \$44 million; 1985 dollars, 250 yen = \$1.00). The goal for phosphoric acid fuel cells was to demonstrate two 1-MW power plants operating on reformed fuels in 1986. In 1987, the project was extended to 1995 because of advances in molten carbonate fuel cell technology.

The 1-MW power plants could be generated by either “dispersed” or “central” construction. Mitsubishi Electric Company and Fuji Electric Company were to build together the lower-pressure (4.87 atm) dispersed fuel cells, and Hitachi Limited and Toshiba Corporation were to build together the higher-pressure (6.8–7.7 atm) central type. While working together to construct the power plant, the companies also pursued their own technology independently; by doing it this way, they expected to have a greater number of combinations of technologies from which to choose when settling on the final design.

2.7.3 Use of Carbon

The phosphoric acid fuel cell was made economically feasible when carbon was found to be stable in the fuel cell environment, according to a review by Appleby (1984). Although the carbon oxidation reaction was favorable thermodynamically, it was unfavorable kinetically. Even in the conditions of the phosphoric acid fuel cell (an acid electrolyte, an oxidizing reactant, and temperatures above 150°C), carbon was

found to be stable, high surface area phosphoric acid then in current catalyst support

The first application form of machine The current conditions dimensional stability a thickness that was a concern with the difference it, and the presence a hydrophilic electrolyte held electrode back substrate for the

Before carbon with the hopes the current collection the two substrates down to 1 mg Therefore, this

The surface by depositing Technologies (conductive of at the cathode. combined with cell cathodes a

The most success at the Prototec chloroplatinic drying. The Pr

The problem Whitney Aircraft found that in compound initial was worse at electrode surface decreased the

2.8 The

In light of the electrolyte for water in the simultaneous solid polymer alkaline electrolyte (1960) and pro

found to be chemically stable. The other characteristics such as corrosion resistance, electrical conductance, high surface area, low density, and low cost made it a breakthrough in the development of the phosphoric acid fuel cell. Carbon, in its differently fabricated forms, was first used in endplates (graphite), then in current collectors (carbon felt), then in electrode substrates (an electrode), and ultimately in catalyst supports.

The first application of carbon, around 1968–1969, was as endplates (also separator plates) in the form of machined graphite. By around 1970, carbon felt or carbon paper was used as a current collector. The current collector had been a gold-covered tantalum screen, which could be considered a two-dimensional sheet. It was envisaged that the current collector could be a three-dimensional sheet, with a thickness that could be used to control the interface between the electrode and the electrolyte. This was a concern because of the boundary of the electrolyte as well as the change in electrolyte volume with the different operating conditions; the consumption of electrolyte required a reservoir to replenish it, and the production of water required a reservoir for the excess to be stored. Trocciola (1975) used a hydrophilic material (carbon paper) as a pathway to allow the reservoir electrolyte to reach the electrolyte held in the matrix (pressed asbestos 20 mils thick). (Today, the current collector is also the electrode backing substrate.) Between 1972 and 1973, carbon was used as the electrode, acting as a substrate for the catalyst layer.

Before carbon was used as a support for the platinum catalyst, it was first used to “dilute” the catalyst with the hopes of increasing the catalyst surface area. Without carbon, the catalyst had been bound to the current collector by PTFE with the lowest loadings around 2 to 3 mg/cm² because of mixing between the two substances. Dilution with carbon did allow the platinum black to be applied in continuous layers down to 1 mg/cm². With more carbon, though, the platinum was buried, leading to poor utilization. Therefore, this method was unsuccessful in increasing the catalyst surface area.

The surface area was increased by altering the way in which the catalyst was prepared. It could be done by depositing the platinum onto the carbon, using the carbon as support. About 1973–1974, at United Technologies Corporation, furnace black (Vulcan XC-72 produced by Cabot Corporation, the most conductive of commercially available furnace blacks) was used as carbon support for the platinum catalyst at the cathode. This furnace black had a surface area of about 250 m²/g, and its surface properties when combined with Teflon dispersions (e.g., DuPont Teflon 30) were excellent for use in phosphoric acid fuel cell cathodes and anodes at 150°C.

The most successful impregnation method was developed in 1973–1974 by Petrow and Allen (1976) at the Prototech Company. Earlier methods had involved impregnating the support with, for instance, chloroplatinic acid, and then reducing it by either a solution-phase method or in the gas phase after drying. The Prototech method could produce colloidal platinum particles 15 to 25 angstroms in size.

The problem of carbon corrosion was addressed by Kinoshita and Bett (1973, 1974) at the Pratt & Whitney Aircraft Division. These researchers tested Spectra from Columbian Carbon Company and found that in phosphoric acid at 135°C, the corrosion current was produced from the oxidized carbon compound initially present on the surface and then by carbon oxidation to carbon dioxide. The oxidation was worse at higher temperatures. Using cyclic voltammetry to measure the electrical charge on the electrode surface, they found that treating Vulcan XC-72 at temperatures between 2000 and 2700°C decreased the amount of oxidized species that were present in the “as received” form.

2.8 The Solid Polymer Fuel Cell

In light of the difficulties of sealing and circulating a liquid alkaline electrolyte, the solid polymer electrolyte for a fuel cell was perceived as simpler. However, it was still necessary to manage the liquid water in the system, removing product water from the cathode in order to prevent flooding while simultaneously maintaining the amount of water needed by the membrane for conducting protons. The solid polymer was an acid, which would allow use with CO₂ without reacting with the gas as would an alkaline electrolyte. The solid polymer fuel cell was developed at General Electric (Grubb and Niedrach, 1960) and provided on-board electrical power for the Gemini Earth-orbiting program. A new polymer



ed in the upright cylindrical

plant (scaled down from
ability of fuel cells using
technology to commer-
d for TEPCO by Toshiba
el Cells (now UTC Fuel
11 MW was attained in
and 207°C, and the net
1993).

1-1992)
pan, Japanese companies
i (as reviewed by Appleby
ergy conversion systems
ogy was transferred from
op fuel cell power plants
of the funding between
The goal for phosphoric
d fuels in 1986. In 1987,
cell technology.
construction. Mitsubishi
wer-pressure (4.87 atm)
ild together the higher-
wer plant, the companies
pected to have a greater
in the final design.

found to be stable in the
arbon oxidation reaction
ditions of the phosphoric
ove 150°C), carbon was

formulation (Grot, 1972) improved the performance and durability of the electrolyte, and with improvements in electrode fabrication (Raistrick, 1986), the fuel cell was seen as the type that could be made practical, especially for road vehicles (Prater, 1990). The challenge was to overcome the detrimental effect that CO, a byproduct of the hydrogen extraction reactions, would have on the platinum-based catalyst. A technique called "air bleed" (Gottesfeld and Pafford, 1988) was developed that would make it possible for this type of fuel cell to operate on hydrogen derived from alcohol or hydrocarbon fuels.

2.8.1 Grubb and Niedrach at General Electric (1960)

Grubb and Niedrach (1960) developed a fuel cell with a solid ion-exchange membrane electrolyte in 1960. The ion-exchange membrane was a polymer sheet, 0.06 cm thick, made of cross-linked polystyrene with sulfonic acid (HSO_3) groups at the ends of the side chains and bound with an inert binder. According to Grubb (1959, in Grubb and Niedrach, 1960), the membranes, in the hydrogen form, had a conductivity equivalent to that of a solution of 0.1 *N* (Normal, 0.5 *M*) sulfuric acid, H_2SO_4 . But to maintain high conductivity, the membrane required water (100% humidification at 25°C), so the inlet gases were bubbling through water and humidified. Although the membrane was soaked with water, the acidity was not diluted because the membrane rejected water when it was saturated.

Two types of cells were constructed, a smaller one ("Type 1") with an active area of 25 cm² and a larger one ("Type 2") with 50 cm² active area. The Type 1 cell, because of its smaller area, was used to compare the performances of screen and foil electrodes pressed against the membrane with only the pressure exerted by the flanges at the periphery of the housing. With platinized nickel screen electrodes, the Type 1 cell reached higher current densities than it did with platinized platinum and palladium electrodes. When the screen (0.0076-cm or 0.003-in.-diameter nickel wire) was rolled to give a thickness of 2 mil (originally 6 mil or 0.015 cm), increasing its contact area with the electrolyte, the cell gave the best performance of 0.75 V at 2.5 mA/cm² on hydrogen and oxygen (after 10 seconds; at steady state it produced 1.6 mA/cm² at the same load resistance). The open circuit voltage of the cell with H_2 and O_2 was 0.90–0.96 V instead of 1.23 V, and the loss was identified as occurring at the cathode, referencing the non-reversible potential of an O_2 half-cell in sulfuric acid solutions at room temperature.

The Type 2 cell with a radial-flow backing plate (flow field plate) and nickel screen electrodes, shown in Fig. 2.17, was used for tests of longer duration. A 15-hour test was run to determine the effect of carbon dioxide on cell performance, and with a fuel mixture of 33 mol% H_2 and 67 mol% CO_2 , the performance of the cell remained at the same levels as shown on a polarization curve. All of the tests on both types of cells were conducted at 25° ± 3°C.

Grubb and Niedrach noted that because the membrane had low permeability to gases, was solid, and was thin, it had advantages over the electrolytes used at the time. Because it had a low gas permeability, the membrane electrolyte acted as a gas separator. The electrolyte, as a non-leachable solid, would not

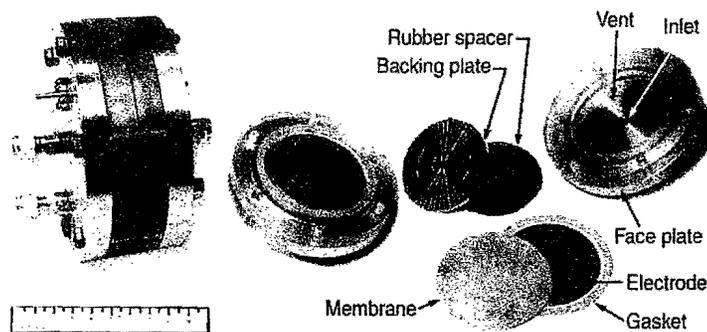


FIGURE 2.17 These photographs show the Type 2 fuel cell design, assembled (left) and disassembled (right), with an ion-exchange membrane as electrolyte that was developed at General Electric Company (Grubb and Niedrach, 1960). (Reproduced by permission of The Electrochemical Society, Inc.)

require
the "spa
relative,
the cont
oxygen r
Gener
when th
nologies
Fuel Cell
cell is ger

2.8.2

The mai
cell built
hydrogen
water for
21–29, 1'

The p
assembl
Kel-F® (
The mer
platinum
sheet bo
was left
the cool
cell. (The
water wa
stacked s
cell. Thre
noise da

The sy
pressuriz
oxygen w
to reach
depende
accumula
Therefore
to the tit
difficult
technolog

The fu
a rate of
mance of
A on Day
current u

2.8.3

Grot (197
able to w

yte, and with improve-
e that could be made
e the detrimental effect
atinum-based catalyst.
would make it possible
rbon fuels.

embrane electrolyte in
ross-linked polystyrene
inert binder. According
orm, had a conductivity
. But to maintain high
o the inlet gases were
h water, the acidity was

e area of 25 cm² and a
taller area, was used to
embrane with only the
ickel screen electrodes,
atinum and palladium
olled to give a thickness
olyte, the cell gave the
conds; at steady state it
the cell with H₂ and O₂
he cathode, referencing
temperature.
reen electrodes, shown
determine the effect of
and 67 mol% CO₂, the
urve. All of the tests on

to gases, was solid, and
a low gas permeability,
chable solid, would not

require pumps and controls for circulation. The total multilayer thickness of less than 1 mm increased the "space factor" or power density, which "compensate[ed] for the lower current density of this cell relative, for example, to that of Bacon." In their future work, Grubb and Niedrach wanted to improve the contact between the electrodes and the membrane and also to achieve a higher potential for the oxygen reduction reaction.

General Electric Company registered the Solid Polymer Electrolyte® (SPE®) as a trademark name, and when the technology was sold in 1984, transferred it to the Hamilton-Standard Division of United Technologies Corporation. (From the Hamilton-Standard Division, the technology was moved to International Fuel Cells — now UTC Fuel Cells — a unit of United Technologies Corporation.) Today, this type of fuel cell is generically called the solid polymer fuel cell (SPFC) or the proton exchange membrane (PEM) fuel cell.

2.8.2 Gemini Space Missions (1962)

The main electrical power source for the two-man Gemini vehicle was an ion-exchange membrane fuel cell built by General Electric under contract by McDonnell Aircraft Corporation (Oster, 1962). The hydrogen and oxygen reactants were stored cryogenically, and the water product was used as drinking water for the crew on long missions. The first mission with the fuel cell was Gemini 5, which flew August 21-29, 1965.

The power system consisted of three stacks of fuel cells, each with 32 membrane and electrode assemblies (Cohen, 1966). The membrane was a polystyrene sulfonic acid electrolyte mixed with a Kel-F® (a registered trademark of 3M Company until 1995; polychlorotrifluoroethylene) backbone. The membrane was covered on both sides by titanium screen electrodes, which were coated with platinum catalyst. The anode side of the membrane and electrode assembly was enclosed by a titanium sheet bonded at the edge of the membrane, forming a manifold for hydrogen gas. The cathode side was left open for the oxygen gas. On the outer face of the titanium sheet were two loops of tubing for the coolant, and in between each pass of the tubing were wicks to remove the product water from the cell. (The water moved by capillary action within the wicks to a collecting point made of felt, and the water was separated from the oxygen by a porous ceramic plate and stored in a tank.) The cells were stacked so that the tubing and wicks of one cell made contact with the oxygen electrode of the adjacent cell. Three stack modules were encapsulated by a vessel that was insulated with foam for vibration and noise damping and for temperature control.

The system operated at low temperatures of 21°C (70°F) and low pressures. The hydrogen gas was pressurized at 0.12 bar (1.7 psi) above the water vapor pressure (water used for humidification), and oxygen was at 0.035 bar (0.5 psi) above the hydrogen pressure. The reactant gases were humidified prior to reaching the membrane because the conductivity of the polystyrene sulfonic acid membrane was dependent on water content. Besides being added to the system, water was also produced in the reaction, accumulating within the pores of the electrode, flooding them, and decreasing the fuel cell performance. Therefore, the electrodes were made wetproof by PTFE, which was also used to bind the platinum catalyst to the titanium screens, and wicks were inserted into the electrodes to pull water away from the cell. The difficult management of water in the system was a reason for the selection of an alternative fuel cell technology over the solid polymer fuel cell for the later space programs (Warshay and Prokopius, 1990).

The fuel cell stacks produced 1 kW (620 W average). In tests for durability, the cell voltage decayed at a rate of 1 to 5 mV per hour mostly because of degradation within the membrane. The average performance of one of the stack modules during the mission was 26.5 V at 16 A on Day 1, rising to 27 V at 16 A on Day 8. The lower voltage on the first day was attributed to the water imbalance caused by the low current used when the fuel cell was in standby mode before the launch.

2.8.3 Nafion Polymer as Electrolyte (1972)

Grot (1972) at E.I. du Pont de Nemours & Company introduced a polymer named "XR" that was stable, able to withstand the chemical degradation mechanism with H₂O₂, which would destroy membranes

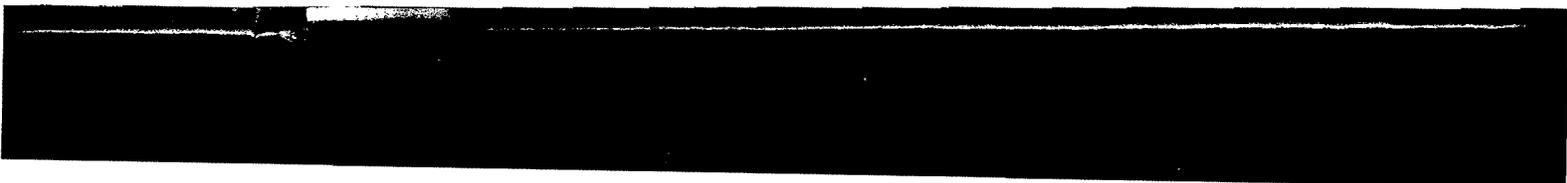
Inlet

se plate

electrode

asket

disassembled (right), with
any (Grubb and Niedrach,



based on polystyrene (as was used by General Electric for the Gemini stacks) within a short time. With the XR membrane and its stability, fuel cells could be used in long-term service in space (Biosatellite Program 1966–1969). This membrane's chemical and temperature stability derived from the PTFE backbone. It could be produced with an equivalent weight of 1150 to 1200, which would give a good compromise between the electrical (resistance) and mechanical (tensile strength) characteristics of the membrane because of water absorption. Grot also proposed using a supporting fabric to increase the mechanical firmness of the membrane. The limited stability of diaphragms led to the use of nonselective porous diaphragms such as asbestos. But the XR diaphragm could withstand chemicals (sulfuric acid and halogens, with the exception of fluorine) up to 120°C and temperatures up to 200°C. The XR diaphragm was a strong acid, and could be workable. This polymer became known as Nafion®, a registered trademark name of E.I. du Pont de Nemours & Company (Grot, 1975).

2.8.4 Los Alamos National Laboratory: Nafion in Catalyst Layer (1986)

Raistrick (1986) of the Los Alamos National Laboratory devised a method to make electrodes that reduced the amount of catalyst required to attain a current. A proton conductor was incorporated in the electrode structure, and thus the protons within the catalyst layer could be conducted to the membrane. This idea came from the differences in surface area measurements using cyclic voltammetry in which an electrode with 0.35 mg Pt/cm² electrode showed only 0.1 cm² Pt per cm² electrode when bonded to a solid polymer electrolyte (Nafion 1117) but ~200 cm² Pt per cm² electrode when in contact with 2.5M H₂SO₄. The catalyst side of a conventional electrode was painted with a solution of 5% Nafion made soluble by alcohols and water, and after the solvents were evaporated the electrode was pressed against the membrane. Another process was spraying the electrode with a 1% solution of Nafion and determining the number of layers that were required to improve conductivity; the performance level with 32 coats remained the same as that with 16 layers. The polarization of the electrode was comparable to an electrode with 4 mg Pt/cm² pressed onto the membrane.

2.8.5 Ballard Power Systems (1990)

Ballard Power Systems (Prater, 1990) began development of solid polymer fuel cell technology in 1984 under contract to the Canadian Department of National Defense, which had determined in 1983, with the Canadian National Research Council, that the technology could be applicable in the military as well as commercial products. The first goal was to develop stack hardware to operate on hydrogen and air (as well as pure oxygen), and the second goal was to demonstrate operation on products of reformed hydrocarbon fuels. In developing the hardware for the cell ("MK 4," with an active area of 50 cm²), improvements were made in distributing air to the back of the porous cathode, in removing water produced in the reaction, and in designing the manifold for cells in a multi-cell stack. An example of the performance on H₂ and air is 0.7 V at 500 A/ft², using hydrogen at 1.15 stoichiometry, air at 2.0 stoichiometry, 50 psig, and Nafion 117 as the membrane electrolyte. To test the feasibility of using reformed hydrocarbon fuels, gases were mixed to simulate the composition, with H₂, 25% CO₂/0.3% CO. A selective oxidation reactor was used to lower the fraction of CO in the gas stream, and a CO-tolerant catalyst was incorporated with the platinum on the anode. At 400 A/ft², the cell voltage was 0.67 V (single cell, 30 psig, 185°F, Nafion 117), which was 95% of the performance achieved on H₂ and air.

The strategy to lower the cost of the fuel cell was to use less expensive materials and to use materials and fabrication techniques that could achieve higher performance. Graphite replaced niobium, which had been used in the Gemini fuel cells, as the material for the flow field plates. In 1987, Ballard tested a new membrane produced by Dow Chemical Company that allowed the cell to produce four times the current compared to that allowed by Nafion at the same cell voltage. With improvements in the fabrication of membrane electrode assemblies with Nafion 117, the limiting current density at 0.5 V was raised from 1000 to 1400 A/ft².

The power density was increased by a factor of 4.63 with the next generation of fuel cell hardware (MK 5), which had an electrode area of 232 cm² (0.25 ft²). This improvement was a result of a more

2.8.6

The p
to 100
the fu
the pc
stream
and 50
perfor.

2.9

Beginn
determ
contro.
becaus
efficien
cell sys
consider
constra
the mo
as havi
Power
demon:

2.9.1

General
vehicles
incorpo
and 160
the veh
hydroxi
cell syst
a temp
exchang

The r
or press
reactant
pressure
lating co
operatio

The d
13,700 r
silicon-c
motor. I
circuits, s

the coal and the electrolyte rather than between the coal and the oxidant, making it an "indirect" fuel cell. Another problem with this cell was that the alkaline electrolyte would degrade because of the carbon dioxide in the product of the oxidation reaction. Baur and Ehrenberg used hydroxide, carbonate, silicate, and borate as electrolytes; with carbonate electrolytes, the feeding of carbon dioxide to the cathode helped to reduce the concentration polarization, which Baur and Brunner discovered in 1935. Containing the molten carbonate electrolyte was difficult to manage, however, so Baur and Preis developed a fuel cell with a solid electrolyte using "Nernst-Mass," which was a mixture of zirconia and yttria compounds.

By this time, the four types of chemicals that are used today as electrolytes had been used in fuel cells: acid, alkaline, carbonate, and oxide. Although the first acid fuel cells used sulfuric acid, phosphoric acid was more stable at high temperatures and was used in the fuel cells developed during the TARGET program. In the 1960s, the General Electric Company developed a fuel cell that used a polymer with sulfonic acid functional groups as electrolyte. Alkaline fuel cells were developed by Bacon, and the technology was modified by Pratt & Whitney Aircraft for use in the Apollo space missions to produce electricity for on-board use. Different methods were devised to prevent the liquid potassium hydroxide electrolyte from flooding the electrodes, such as double-porosity electrodes, wetproofed electrodes, and an electrolyte matrix.

The modern development of the molten carbonate fuel cell electrolyte was influenced by Davtyan, who used mixtures that he presumed were solid but were shown by Broers and Ketelaar to have been a combination of molten and solid phases, including compounds of carbonate, phosphate, tungstates, and silicates, and a solid phase of rare earth oxides. Broers and Ketelaar chose carbonates over other compounds because they were compatible with the products of the reaction with hydrocarbon fuel. The Institute of Gas Technology and the General Electric Company continued research into molten carbonate fuel cells. The truly solid electrolytes of Baur and Preis were tested to determine mixtures that would be the most conductive, and Weissbart and Ruka at Westinghouse Electric Corporation chose zirconia and calcia.

The direct methanol fuel cell was a return to the hope of oxidizing fuel directly. Sulfuric acid was used as electrolyte, and, because the electrolyte was circulated through the fuel cell, the fuel could be delivered with the electrolyte. With this method of fuel delivery, methanol could also reach the cathode and react on it, decreasing the performance of the electrode and the cell. For the catalyst, platinum alloyed with ruthenium showed the best performance. After the development of the solid polymer fuel cell, researchers used the solid polymer membrane as electrolyte and revived the prospects of developing a practical direct methanol fuel cell.

The first solid polymer fuel cell of General Electric was difficult to operate because of the membrane. To maintain conductivity, the membrane had to contain water. Also, the service life of the membrane was short because the membrane degraded in the oxidative environment at the cathode electrode. With the Nafion membrane of the DuPont Company, the service life was extended because of the stable fluorine chemistry of the polymer. An improvement to the performance of the fuel cell was made by incorporating Nafion in the catalyst layer to give the electrolyte continuity between the catalyst and electrolyte, which increased the catalyst surface area of the electrode. Also, carbon supports for the catalyst, a technique developed for phosphoric acid fuel cells, improved the surface area for a given amount of catalyst. The flooding of the electrodes could be managed by wetproofing the electrodes with PTFE, as was done with alkaline cells.

The solid polymer fuel cell was deemed the most appropriate type for use in road vehicles because of its compatibility with the reaction products of hydrocarbon fuels, its low operating temperatures, and its high power densities. Prior to the development of the solid polymer fuel cell, the phosphoric acid fuel cell had been considered the technology best available for use in a bus. An alkaline fuel cell system was used by General Motors in a van to determine the feasibility of a fuel-cell-powered vehicle. The reactants were hydrogen and oxygen, stored on board, and the fuel cells were stored under the floor of the van — a design used today.

Reference

- Alder Wright, R. H., *History of Fuel Cell Technology*, 46, 37
- Anahara, R., *System*
- Andrew, M.F. K.R., E
- Appleby, A.J., *Carbon*, NJ, 198
- Appleby, A.J.
- Bacon, F.T., R
- Bacon, F.T., F
- Bacon, F.T., *J* 7C-170
- Baker, B.S. et *Techno*
- Baur, E. and F *für Elel*
- Baur, E. and *chemie*
- Baur, E. and 1912.
- Baur, E. and I 1937.
- Binder, H., K *of plati* York, 11
- Broers, G.H.J. Publish
- Broers, G.H.J. 303-304
- Cohen, J.M., 1
- Cohen, R., Ge Jersey, 2
- Dittmann, H. *Fuel Cel*
- Douglas, D.L. *Technol.*
- Ferguson, R.B. ence, N
- Gottesfeld, S. cells op
- Grot, W., Perf *Chemie*
- Grot, W.G., Pe
- Grove, W.R., (*Journal*