

The internal resistance of non-polluting, high-temperature solid oxide fuel cells operated on natural or coal gas must be minimized for efficient and cost effective electricity generation.

Fuel Cells

Fuel cells are electric batteries capable of converting atmospheric hydrogen and oxygen (and in some cases natural gas and coal gas) into electricity, heat and water without combustion. They comprise an anode and a cathode separated by an electrolyte, and the main types are usually named after the electrolyte. Table 1 specifies the principle parameters while Fig. 1 shows the basic structure of a fuel cell and the electrochemical reactions taking place in the various types.

As an individual fuel cell only produces about 0.5–1.0 V it is necessary to stack cells. Several geometries are possible apart from the planar configuration illustrated in Fig. 2. For instance, tubular arrangements that are more easily produced, but for which the electricity losses in the cell stack are larger as the current path is longer. The electrodes must be good electronic conductors as well as being porous in order for the fuel gas to penetrate and react. The porous structure should be designed to provide the largest possible contact area between the ion-conducting electrolyte, the electron conducting electrode and the gas phase.

Processes in a fuel cell involve the direct conversion of chemical energy to electricity without using thermal energy in an intermediate step. Consequently, fuel cells are not subject to the thermodynamic limitations found in a Carnot engine (piston engine or turbine) and it is therefore in principle possible to achieve a high efficiency. Furthermore, the temperature in a fuel cell is low compared to that of a flame so nitrous oxide is not evolved, which is why fuel cells are less polluting. Other advantages include a low noise level (the only rotating components are found in pumps) and a modular structure, implying that both the price per kW installed and the efficiency are roughly independent of the size of the unit.

Early History

In 1839, the English physicist Sir William Grove made the remarkable discovery that when water was decomposed during the

Mogens Mogensen manages Danish and EC solid oxide fuel cell projects. He received a masters in chemical engineering from the Technical University of Denmark and a Ph.D. in corrosion science from the university in 1976. After holding various positions in the university, he joined the Hellesen Research Laboratory before moving in 1980 to the Materials Department, Riso National Laboratory, P.O. Box 49, DK-4000 Roskilde.

Niels Christiansen heads the Advanced Ceramics Group at Haldor Topsøe A/S, Ny-møllevej 55, DK-2800 Lyngby. He received a masters in chemistry from the Technical University of Denmark and has worked on advanced materials at the Danish Technological Institute.

FAMILIAR PRINCIPLES FOR ELECTRICITY GENERATION

M. Mogensen¹, N. Christiansen²

¹ Risø National Laboratory, Denmark

² Haldor Topsøe A/S, Denmark

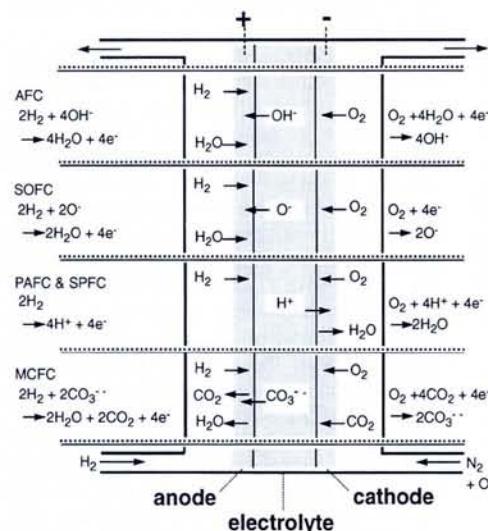


Fig. 1 — An illustration of the basic structure of a fuel cell: fuel gases are fed at the anode and cathode which are separated by an electrolyte. The electrochemical reactions arising in the five principal types of fuel cells are indicated.

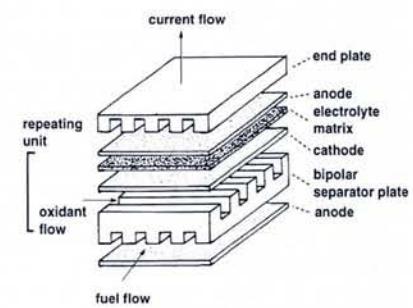


Fig. 2 — An expanded view of the basic fuel cell structure with the repeating unit of the fuel cell stack.

sufficient to keep 25 ordinary electric bulbs alight, but only for a short time as the precipitation of carbonate around the coal anodes blocked the cells.

A important era was introduced when F.T. Bacon started in 1933 the development of alkaline fuel cells based on an aqueous solution of potassium hydroxide at 200 °C, where hydrogen and oxygen at 45 atmospheres were brought in contact with electrodes of porous nickel. But it was not until 1959 that a demonstration unit was ready.

Low-Temperature Fuel Cells

The main reason why the alkaline fuel cell has not yet experienced commercial success is because it does not tolerate carbon dioxide which reacts with the hydroxide to form a carbonate, thus destroying the electrolyte. The CO₂ in both the hydrogen and the oxygen fuel gases must be reduced to a few ppm — a fairly expensive process. Recognition of this led in the 1960's and 1970's to the development of CO₂-tolerant cells. One of these (the solid proton conductor fuel cell — SPFC) employs an expensive polymeric proton conductor ion-exchange membrane as the electrolyte. The anode is poisoned by CO at the relatively low operat-

ing temperature so hydrogen made by reforming hydrocarbons cannot be employed without a purification stage, which increases costs. Consequently, SPFC's have not yet been put to use except in the area of space travel.

The other type of CO₂-tolerant fuel cell is the phosphoric acid fuel cell (PAFC). In about 1970, a group at United Technology Corporation, Connecticut, USA, called attention to the fact that phosphoric acid can be exploited as a CO₂-rejecting electrolyte at 150–200 °C. A large-scale development programme resulted in a demonstration unit of 4.5 MW and a 11 MW unit is presently being tested in Japan. Although the PAFC's generate electricity at prices similar to those for conventional plant, it is anticipated that their market share will be limited.

The low-temperature fuel cells have a generic problem in that they cannot convert hydrocarbons or carbon monoxides directly; it is necessary to fuel them with hydrogen which usually has to be produced from fossil fuel. Furthermore, the hydrogen must not contain CO, except in the case of PAFC's which tolerate CO concentrations approaching 100 ppm. Reforming fossil fuel into hydrogen involves a considerable energy loss. People working with power stations often calculate the efficiency by taking the Higher Heating Values (HHV) of the primary fuel as the starting point. The HHV is numerically equal to the change in the standard enthalpy ΔH°₂₉₈ at 298 K and one atmosphere, but with an opposite sign. The overall efficiency of low-temperature cells is only about 40% of the HHV for methane. As the main argument in favour of fuel cells should be a higher efficiency, this argument is lost as gas turbines used for electricity generation have today efficiencies of about 40%.

High-Temperature Fuel Cells

High-temperature fuel cells based on molten carbonate (MCFC) and solid oxide (SOFC) electrolytes can convert natural gas as well as CO either by internal reforming or by direct electrochemical reaction. They are therefore much more efficient than low-temperature cells. Both types were invented by E. Bauer, the Swiss chemist, in the 1920's and 1930's, but it was not until the 1980's

Table 1 — Characteristics of the most important types of fuel cells.

	Alkaline AFC	Solid proton conductor SPFC	Phosphoric acid PAFC	Molten carbonate MCFC	Solid oxide SOFC
Electrolyte	aq. HOH	polymer H ⁺ cond.	H ₃ PO ₄	KLiCO ₃	ZrO ₂ + Y ₂ O ₃
Anode	porous Ni	graphite + Pt	graphite + Pt	porous Ni	Ni + Zr(Y)O ₂
Cathode	"	"	"	NiO ₂ + Li ₂ O	LaMnO ₃ + Sr
Fuel	pure H ₂	pure H ₂	H ₂ (CO-free)	H ₂ + CO + nat. gas	H ₂ + CO + nat. gas
Opern. temp. °C	100	100	200	650	1000
Efficiency, %	≈ 40	≈ 40	≈ 40	≈ 60	≈ 60
Price, \$US/kW	≈ 20	≈ 700	≈ 200	≈ 80	≈ 150

that their development was accelerated. Demonstration units of 25 kW of both types have been built.

Carbon dioxide must be added to the cathode together with air in MCFC's since it is the CO₃²⁻ ions which carry charge. Carbon dioxide is generated at the anode if methane is converted in the cell so it is necessary to extract the CO₂ from the anode exhaust and recycle it to the cathode. The most important problem facing MCFC's today is the extremely corrosive nature of the O₂²⁻ and CO₂-saturated molten salt, which limits the lifetime of the cell.

SOFC's made entirely from solid oxides seem to have the greatest potential and both high efficiency (> 50%) and a long lifetime (> 50 000 hours) have been demonstrated. The main challenge is to develop a sufficiently inexpensive and reproducible fabrication technology for the thin ceramic layers which constitute the electrodes and the electrolyte. While this will take at least 10 years, the prospects are so good that considerable effort is being made worldwide to realize the potential of SOFC's.

Efficiency

The maximum amount of work that can be obtained from a chemical reaction is equal to the Gibb's free-energy change ΔG given by the well-known formula $\Delta G = \Delta H - T\Delta S$ for an enthalpy ΔH and an entropy ΔS . The theoretical efficiency η_t which can be achieved by a fuel cell working at a temperature T is therefore

$$\eta_t = \frac{\Delta G}{\Delta H^o_{298}} = \frac{\Delta H - T\Delta S}{\Delta H^o_{298}} \quad (1)$$

where ΔG , ΔH and ΔS refer to the operating conditions. For Carnot engines,

$$\eta_t = \frac{T - T_0}{T} \quad (2)$$

where T_0 is the temperature of the exit gas.

Entropy effects

Proponents of fuel cells often claim that the comparison of Eqs. 1 and 2 demonstrates that fuel cells can achieve higher efficiencies than Carnot engines. However, this is a very simple argument. Fig. 3 comparing the theoretical efficiency of fuel cells for three different fuel gases (H₂, CO and CH₄) with the Carnot curve shows that only CH₄ gives a higher efficiency over the entire

temperature range between 25 and 1000 °C. Differences between the temperature dependences for the three fuel gases stem from changes in the numbers of molecules during reaction. The number for the reactions $2H_2 + O_2 \rightarrow 2H_2O$ and $2CO + O_2 \rightarrow 2CO_2$ is changed from 3 to 2, resulting in a loss of entropy, whereas there is no change for the reaction $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$.

For a fuel cell running on hydrogen, it is seen from Fig. 3 that low-temperature operation is the most advantageous. However, this is only true in practice in special situations where a direct source of hydrogen is available. Hydrogen is normally made from reacting coal, oil or gas with water. A large amount of heat has to be added at a relatively high temperature (600–700 °C) during the reforming process — heat which is recovered in the fuel cell, but at too low a temperature. So low-temperature fuel cells, which can only operate with hydrogen, have efficiencies slightly above 40% of the HHV for fossil fuels. However, it is possible in practice to increase the efficiency in the case of high-temperature cells by using methane (natural gas), noting of course that the theoretical efficiency will not be reached as there are always losses.

Losses

Losses developed in the form of heat owing to the internal resistance of the fuel cell stack are determined by the conductivities of the materials used to construct a cell, and by polarization of electrodes caused by a higher than average concentration of reaction products at the electrodes than in the bulk of the electrolyte. The resistance can be reduced by choosing a design having a short conducting path in the thin electrodes. This is achieved in the planar design (Fig. 2) where the current need only flow across one-half of the width of the gas channel in the electrodes (typically about 1 mm) in order to reach the thicker material connecting cells.

The internal resistance means that the efficiency and power of a fuel cell depend upon the load. The internal resistance R_i (including electrode polarization) is to a first approximation independent of the current density I , so Ohm's law is applicable and the following correlation is found empirically

$$P = EI - R_i I^2$$

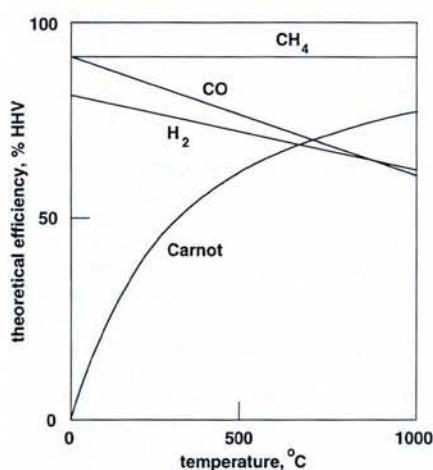


Fig. 3 — Comparison between the theoretical efficiency of fuel cells for CH₄, CO and H₂ fuel gases and the Carnot efficiency.

for a power density P (in W/m^2) and an open circuit voltage E (also called the electromotive force) of about 1 V for fuel cells. This equation looks simple, so it should be remembered that E is a function of position as the composition of the fuel gas varies along the cell because of the increasing degree of conversion of the reactant gases. Second, the internal resistance is not exactly constant because the polarization resistance is weakly dependent on the current density.

The cell voltage U is given by:

$$U = E - R_i I$$

and the voltage efficiency η_V is defined as $\eta_V = U/E$.

The electromotive force $E = \Delta G/nF$ where n is the number of electrons per mole and F is Faraday's number. The real efficiency η as a fraction of the HHV of the fuel is:

$$\eta = \eta_t \eta_V \alpha$$

where α is the fuel utilisation factor (the ratio of the amount of fuel converted to the amount supplied). Elimination leads to:

$$\eta = \alpha n F U / \Delta H^\circ_{298}$$

where the loss for reforming coal into hydrogen is not included.

Figs. 4a and b illustrate what happens to the power density P and cell voltage U for realistic values of R_i for SOFC's. The largest R_i value of $1.8 \Omega \text{cm}^2$ is for a stack, the medium value of $0.45 \Omega \text{cm}^2$ for a single cell, and the lowest value of $0.09 \Omega \text{cm}^2$ is the value calculated from the measured conductivity of the electrolyte and electrode materials assuming in effect that the electrodes are unpolarized (*i.e.*, they have an unlimited electrocatalytic effect). The curves illustrate the importance of the internal resistance for SOFC's as it determines the power density and the cell efficiency.

Applications

Spacecraft

Alkaline cells were developed in the 1960's for the Apollo spacecraft used to explore the moon as they offered useful energy and power densities without the production of waste. The only reaction product is pure water which formed part of the astronauts' water supply. It is interesting to note that the first fuel cell which was employed had a polymeric proton electrolyte developed by General Electric for the Gemini programme but that had not been taken up. This particular type of lightweight design was adopted as space travel requires reduced weight. The "old" alkaline fuel cell of an unique design was chosen for the latter stages of the Apollo programme as its power per unit of weight was higher than for the proton conductor cell. A special space version of the alkaline cell, typically generating 18 kW for a 120 kg device, is used today for spacecraft.

Precious metals are the optimum electrode materials for low-temperature fuel cells, and in the case of the spacecraft version, one electrode is made from a mixture of gold and platinum on gold-coated nickel and the other (oxide) electrode from a Pt-Pd alloy coated material. Although NASA has not published the prices of fuel cells for space travel, figures on the order of 1-2

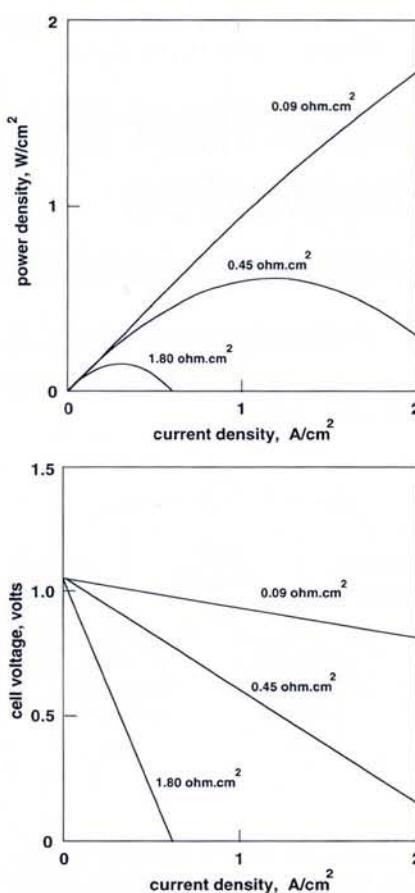


Fig. 4 — The power density (upper) and cell voltage (lower) of a solid oxide fuel cell calculated as a function of the current density for three different values of the internal resistance R_i of the cell (including polarization resistance). The electrodes are unpolarized along the uppermost curve in each diagram, corresponding to the resistance calculated from the conductivities of the electrolyte and electrode materials.

perately below \$US 200 per kW of power illustrates that the construction cost is not decisive. The reason is that the lifetime of a car engine is normally less than four months of continuous operation. Such a short lifetime is unacceptable for a power station, where the requirement is many years.

Everyday applications

Opportunities offered by fuel cells having the capability to influence everyday life to a considerable extent will eventually be realized. For example, most types of fuel cells are reversible in that they can be operated as electrolyzers where current is passed into the cell. So fuel cells could be connected to windmills and used to produce oxygen and hydrogen from water when conditions permit: in calm weather, the hydrogen would be fed back into the fuel cell to generate electricity. According to some experts, SOFC's are especially suited for water electrolysis.

Fuel cells do not take up much space and since the oxide fuel cell, for instance, operates with natural gas, it seems reasonable to consider placing fuel cell systems in every house with natural gas at its disposal. A 25 kW plant sufficient to meet heating and electricity requirements will probably take up no more room than a central heating system does today.

Special applications

Apart from applications in transport, large-scale power generation, and everyday uses there remain a number of unique possibilities. Combined electricity and chemical production is possible (*e.g.*, the selective oxidation of methanol to formaldehyde and the oxidation of ammonia for fertilisers). Research is underway in the area of miniature implanted devices for powering cardiac pacemakers and pumps using blood sugar as the fuel. Finally, there is work in Germany to couple biological systems (*e.g.*, algae production) with fuel cells. In these bio-fuel cells, microorganisms produce convertible substances from CO_2 and the sun's energy in a chamber that is connected directly to the anode of a fuel cell.

Conclusion

Some 1000 M\$US is presently being spent annually on the world-wide research and development of fuel cells. Given this enormous effort, it is certain that electric power generation plants based on high-temperature fuel cells will emerge. Probably operated on natural gas and coal gas, they will be economically competitive with conventional approaches. Nitrous oxide is not produced, sulphur emission should be negligible, and CO_2 production per kWh will be reduced by about 50 percent.