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Workshop on Materials Science and Physics of Non-Conventional Energy Sources

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"Fuel Cells: Present Status and Future Perspectives"

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INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS

"Workshop on Materials Science and Physics of Non-Conventional Energy Sources"

Lecture on: "Fuel Cells: Present Status and Future Perspectives"

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SUMMARY

Fuel cells are electrochemical devices that convert fuel energy directly into electricity without thermodynamical losses. Invented only one year after the Volta pile, they developed very slowly for over a century and a half before they were given their first practical application consisting in powering the elctric equipment on board Gemini spacecraft.

A major industrial interest in their use as grid-connected or stand-alone ground power generators exploded in recent years, first in the United States and Japan, then also in Europe.

In this paper we review the reasons for this slow historical development and present acceleration and compare the features of fuel cells and conventional electric generators.

INTRODUCTION

Fuel cells are electrochemical devices that convert fuel energy directly into electric energy. They are essentially inverted electrolyzers. Instead of using up electric energy to break down a molecule into its gaseous components (e.g. $H_2O \rightarrow H_2 + \frac{1}{2} O_2$) they use the opposite combining, exothermic reaction. The conversion of the potential chemical energy of the reaction into electric energy rather than heat is obtained by dividing the reaction into two semireactions between each reactant and an electrolyte. If the two semireactions occur on two opposite surfaces of the electrolytic mass (into which the ions released in one semireaction and recombined in the other slowly migrate) an excess of electrons will be found on one surface and an electron deficiency on the other. These electron charges, picked up by two electrodes, may be recombined by connecting the electrodes to an external circuit, which means exploiting electric energy. The process is slow because the rate determining step which controls it is the ionic diffusion in the electrolyte <u>against</u> the electric field generated by the separation of the charges, and under the effect of the chemical potential gradient. It is really the slowness of the ionic diffusion process which allows the combination to take place in a "controlled" low-entropy manner thereby preventing the dissipation of the chemical energy in the thermal agitation of the molecules. (It should be recalled that if no electrolyte is interposed between the reactants the direct combination of hydrogen and oxygen in proportions suitable for water formation is explosive).

Fig. 1 shows this principle[1] which is common to all galvanic cells or electric batteries. It was Davy who noted only one year after the invention of the voltaic pile that its electrodes have two distinct functions, chemical reactants and charge collectors and carriers. For this reason the elctrodes which participate in the reaction, wear out thereby causing the pile to run down. If the two functions are separated by using a conductive but chemically inert and porous material to make the electrodes, so that the fluid reactants may reach the zone of contact with the electrolyte, an evergreen galvanic cell or fuel cell (FC) is obtained.

It must be pointed out that in ordinary batteries the metal electrode ions tend to move into the electrolytic solution already at ambient temperature and without catalysts. The oxidation and reduction of gaseous reactants made up of polar molecules, on the other hand, must be favoured by raising the temperature and using suitable catalysts. At this point we can already discriminate two factors which account for the increased complexity of the fuel cell compared with an ordinary galvanic cell. The first is the electrode porosity which must allow the reactants to reach the zone of contact between reactants, electrode and electrolyte (sometimes in the presence of a catalyst) but prevent the rise of the electrolyte in the pores by capillarity. The second is the need for high temperatures or expensive catalysts which however are effective only if an optimal surface-to-volume ratio can be attained (i.e. dispersion into very fine but strictly calibrated particles).

As a rule, all exothermic reactions between fluid reactants may be exploited in a suitable fuel cell. Hydrogen and carbon monoxide oxidation reactions are usually preferred because the reaction products (water vapour and carbon dioxide, respectively) are gaseous (which favours their removal) and chemically nonaggressive (which facilitates the choice of construction materials) and because one of the two reactants (oxygen) is available in practically unlimited amounts in the atmosphere. In theory, the complete conversion of the chemical energy produced by hydrogen oxidation into electric energy should give an open-circuit electromotive force of 1.229 V. In practice, polarization effects and resistive voltage drops will reduce the working voltage to V = 0.65 Volt/cell. For this reason, a great many fuel cells connected in series, the so-called fuel-cell stack, are required for practical applications.

It is a well-known fact that hydrogen is only found in nature in traces. It is consequently not a primary fuel. The stack is therefore provided with a reformer which converts the primary fuel (coal, oil, natural gas, biogas) into a hydrogen-rich gas.

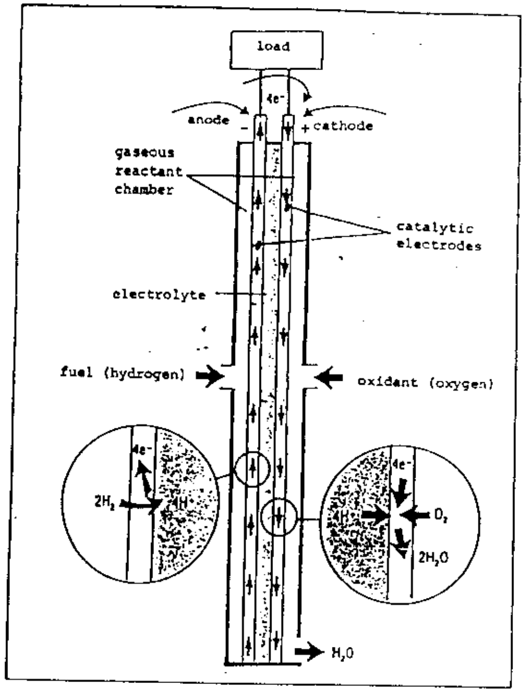


Fig. 1 - Diagram of a fuel cell: the example refers to a solid polymeric electrolyte fuel cell[1].

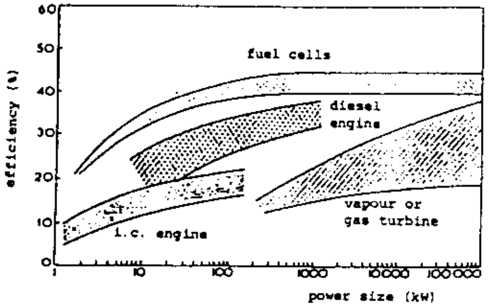


Fig. 2 - Comparison between electric conversion efficiency curves as a function of power size for different electric generator types[3].

Finally, fuel cells, like all electrochemical cells, produce direct-current electricity. A dc-to-ac inverter is consequently required for connecting the stack to the mains or supplying users in remote areas[2].

FEATURES OF FUEL CELL STACKS

The reason for the heavy R&D investments in FC projects lies in the fact that the direct chemical-to-electric energy conversion has some highly advantageous intrinsic characteristics. Since it must not go through the classical thermomechanical cycle, this kind of energy conversion is subject to neither the theoretical efficiency limitation of all thermodynamic cycles nor the burdensome scale factors which, in traditional thermal power plants, impose the use of a centralized power generation with the ensuing environmental impact concentration and the increasing difficulty in finding suitable power plant sites.

It is a well-know fact that a modern thermal power plant will reach its maximum efficiency of 41-43% only if its size exceeds 800 MW. (These percentages do not allow for possible combined gas-vapour cycles but, quite apart from the complexity of these systems, also FC stacks favour waste-heat retrieval in turbines. A comparison between the two systems must therefore only be made by considering the chemical, thermal, mechanical and electrical processes on one side and the electrochemical process on the other). On the contrary, as shown in Fig. 2[3], FC stack power generators reach efficiency values η comparable with those of thermal power plants already with sizes P of only a few hundred kW. From these rated powers onward the curve $\eta(P)$ levels down.

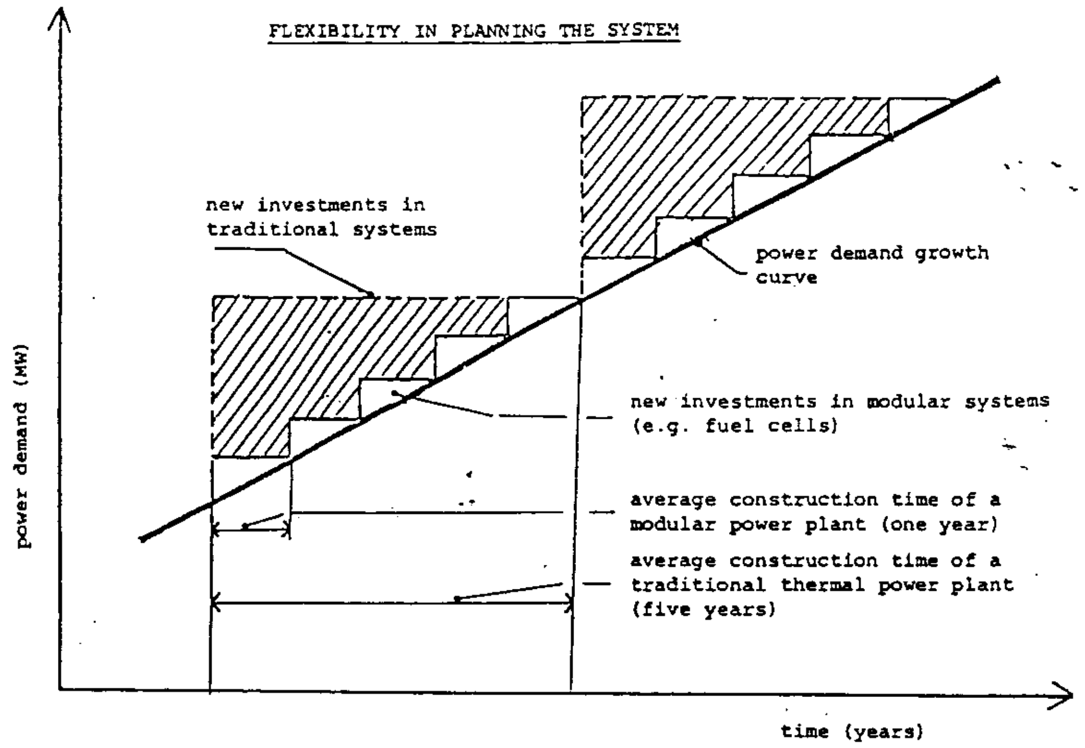
FC generation therefore implies no power concentration and this offers following advantages.

1) It favours dispersed or on-site generation with energy being distributed in the territory by a fluid vector (oil, natural gas, etc.). This feature simplifies to a considerable extent the problem of finding suitable power plant sites.
2) Also in large-sized generating stations with several tens or hundreds of MW the stack may be of the modular type, mass-produced in standard sizes of a few hundred kW, assembled on the spot and undergoing scheduled shop maintenance on a turnover basis.
3) Stack modularity simplifies system engineering, cuts down design and construction time, and keeps investments in line with the demand rate. A modular layout permits investments to approximate the power demand curve in a stepwise manner whereas in traditionally configured plants where scale factors favour large standard units investments must be planned well in advance and over the whole erection period, as shown in Fig. 3 where the hatched areas represent unused investments[4].

But the most important advantage is the fact that there is absolutely no NO_x production. NO_x is the deadly nitric oxide mixture which is generated in the flame of traditional thermal power plant burners in proportions that are no longer accepted by the rules of developed countries. Fuel cells generate no NO_x because their electrochemical reaction takes place at temperatures well below 1000°C.

In traditional thermal power plants the pollution problem has five specific faces:

- particulates production,
- CO_2 production,
- NO_x production,
- SO_2 production,
- thermal pollution.



//// = excess of power, i.e. unused investments

Fig. 3 - The figure shows the new investments in traditional (large hatched steps) and modular (thin continuous line small steps) systems required for following up a given power demand growth curve (thick continuous line)[4].

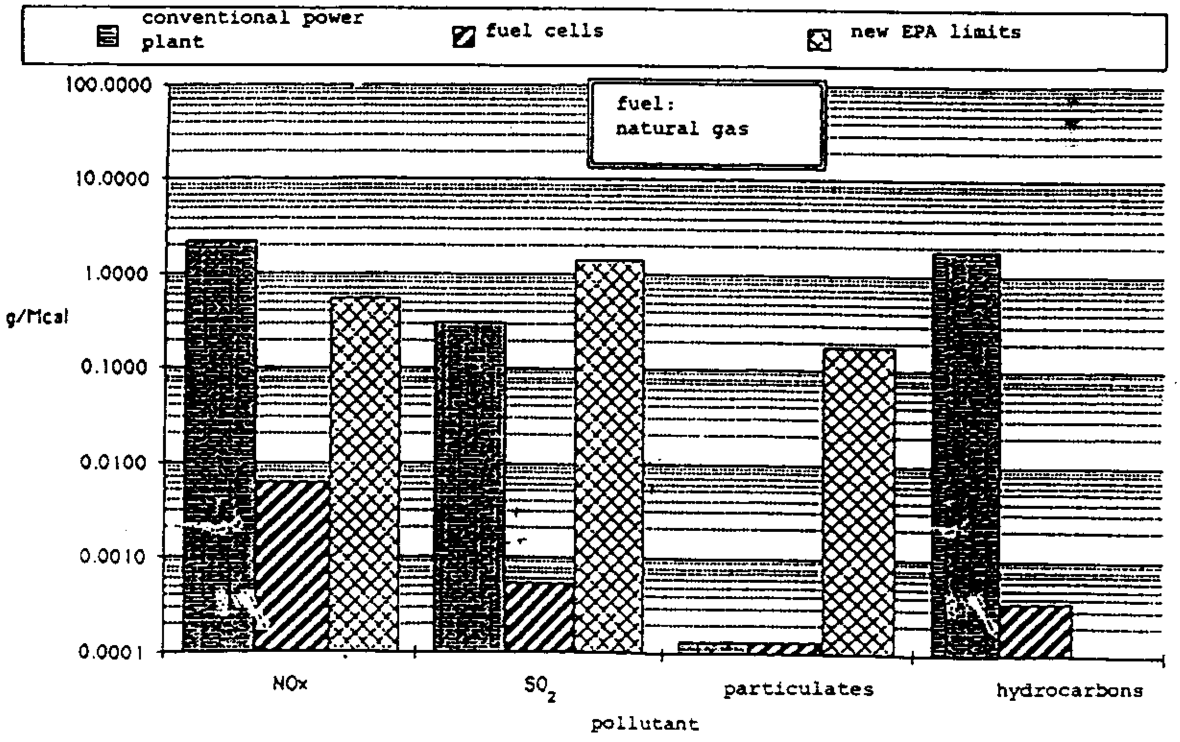


Fig. 4 - Comparison between pollutant emissions from natural gas-fuelled power plants. When assessing the exiguity of the fuel cell NO_x emission it should be borne in mind that the ordinate scale is logarithmic.

Of these, the first and fourth are definitely absent from the fuel cell exhaust since fuel cells cannot burn reformed gas containing sulfur or solid particles. At first sight it may appear that the use of fuel cells involves an additional primary fuel purification outlay as compared with thermal power plants. Actually, the opposite is true since the new trend calls for the removal of these two pollutants before the combustion (or even before the fuel conveyance) and FC stacks are consequently on an equal competitive footing with thermal power plants complying with antipollution regulations.

The CO_2 production is obviously the same irrespective of the oxidation method used (electrochemical or combustion) provided the primary fuel is the same.

The highly dangerous NO_x however is only generated in the burner flame but not in fuel cells. A "complete" NO_x catalytic reduction is expensive and would put boiler burners at an economic disadvantage with respect to fuel cells. Waste heat percentages being equal, thermal pollution impairs with increasing chimney plume temperatures.

The continuous discovery of new natural gas reservoirs in the last fifteen years has seriously limited the importance of the world oil and coal resources as a bottleneck for generable energy. In addition, increasing power demand has established the amount of NO_x vented to the atmosphere as a new bottleneck.

In view of the above, competitiveness between thermal power plants and fuel cells can no longer be assessed in terms of investments and operating costs only and the absence of NO_x will amply balance out slightly higher costs.

Figures 4 and 5 show a comparison between pollutants produced by oil and natural gas-fuelled conventional power plants and fuel cells. The superiority of the fuel cells is overwhelming.

The Italian National Energy Plan approved by the Council of Ministers in August 1988 takes into account the fuel cell technology advantages in terms of both energy saving and environmental impact.

MAIN CONCEPTS AND THEIR STATE OF THE ART

A fuel cell can use different electrolytes. The type of electrolyte determines the operating temperature, the larger or lesser need for catalysts, the acceptability of different fuels and oxidants and their impurity content and the choice of electrode and construction materials. For this reason the chemical nature of the electrolyte (acid, alkaline, molten carbonates, (high temperature) solid oxides) is used for classing fuel cells. Grove, in 1839, made the first laboratory prototype of an acid fuel cell. Next came the MCFCs (molten carbonate fuel cells, A. Becquerel, 1855) and the SOFCs (solid oxide fuel cells, Nernst, 1912). AFCs (alkaline fuel cells, Bacon) were made in England from 1932 to 1939. In 1955 Grubb, an American researcher working with General Electric, devised an acid fuel cell with completely new characteristics, the solid polymeric electrolyte fuel cell (SPEFC) which, although a late arrival, was the first to find a practical application as a source of electric power on board the Gemini spacecraft. At about the same time alkaline fuel cells were used as an Apollo spacecraft electric power source.

Ground applications had a different history. After many years of experimental trials the most reliable and long-lived fuel cell turned out to be the phosphoric acid fuel cell (PAFC) which was successfully tried out over a period of several years in stationary power plants of a few MW. MCFCs look very promising because they are cheap and versatile (they can use coal) but so far only Japanese prototypes of about 10 kW have been tested for a few hundred hours and an American 2.3 kW prototype has been kept running for 5000 hours.

SOFCs look even more promising but an optimal design has not yet been achieved. Research has already provided fairly exhaustive information on materials but the cell geometry has been substantially revolutionized and it is still debatable whether the last proposals may be regarded as final.

AFCs, the most advanced fuel cells in terms of the state of the art, operate at low temperatures (about 90°C, although prototypes working at about 300°C have been built). Unfortunately they cannot be fed with primary fuels and used in ground power plants because traces of even less than 1% of CO (carbon monoxide) and/or CO_2 (carbon dioxide) in the fuel or oxidant will produce viscous or insoluble (bi)carbonates in the alkaline electrolyte which will kill the AFC after a few hours of operation. The acceptability limit of carbon oxidation products is in the order of 0.1% or even less and the purification of fuel and especially air to these extreme limits (by removing CO and CO_2 from the former and CO_2 from the latter) is so cumbersome and expensive that AFCs are practically ruled out from this kind of ground application.

In practice, AFCs can only be fed with pure hydrogen and oxygen. Both are found in space vehicles (where, for reasons of weight, they are anyway stored as pure elements) and on earth, in the chlor-alkali industry of which they are a by-product available in large quantities. It has been estimated that an (alkaline or acid) fuel cell stack fed with waste H_2 which in a chlor-alkali plant would normally be burned in the flare, could cover 15 to 25% of the plant's electric energy requirements, with an appreciable saving of operating costs[5].

Hydrogen economy supporters envisage the possibility of using AFCs (or PAFCs) for converting into electric energy, in Europe, the H_2 and O_2 produced by electrolysis in Canada (or Central Africa) where there are still considerable unused hydroelectric power sources[6]. The speaker

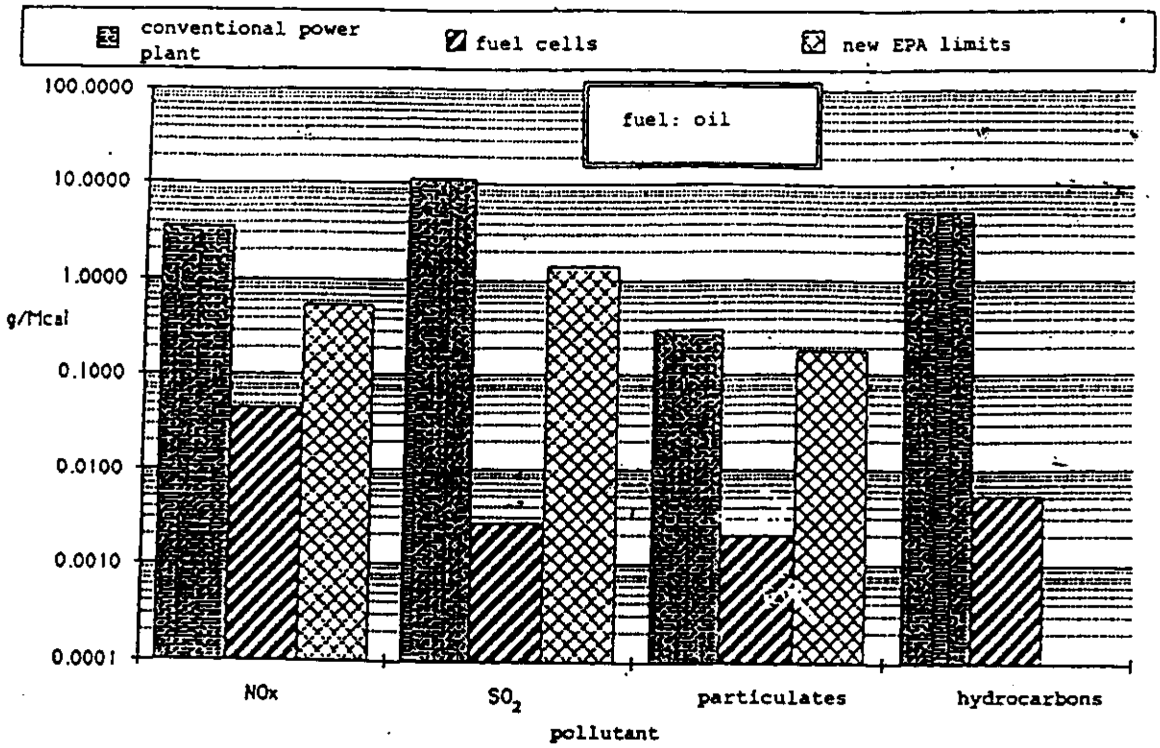


Fig. 5 - Comparison between pollutant emissions from oil-fuelled power plants. When assessing the exiguity of the fuel cell NO_x emission it should be borne in mind that the ordinate scale is logarithmic.

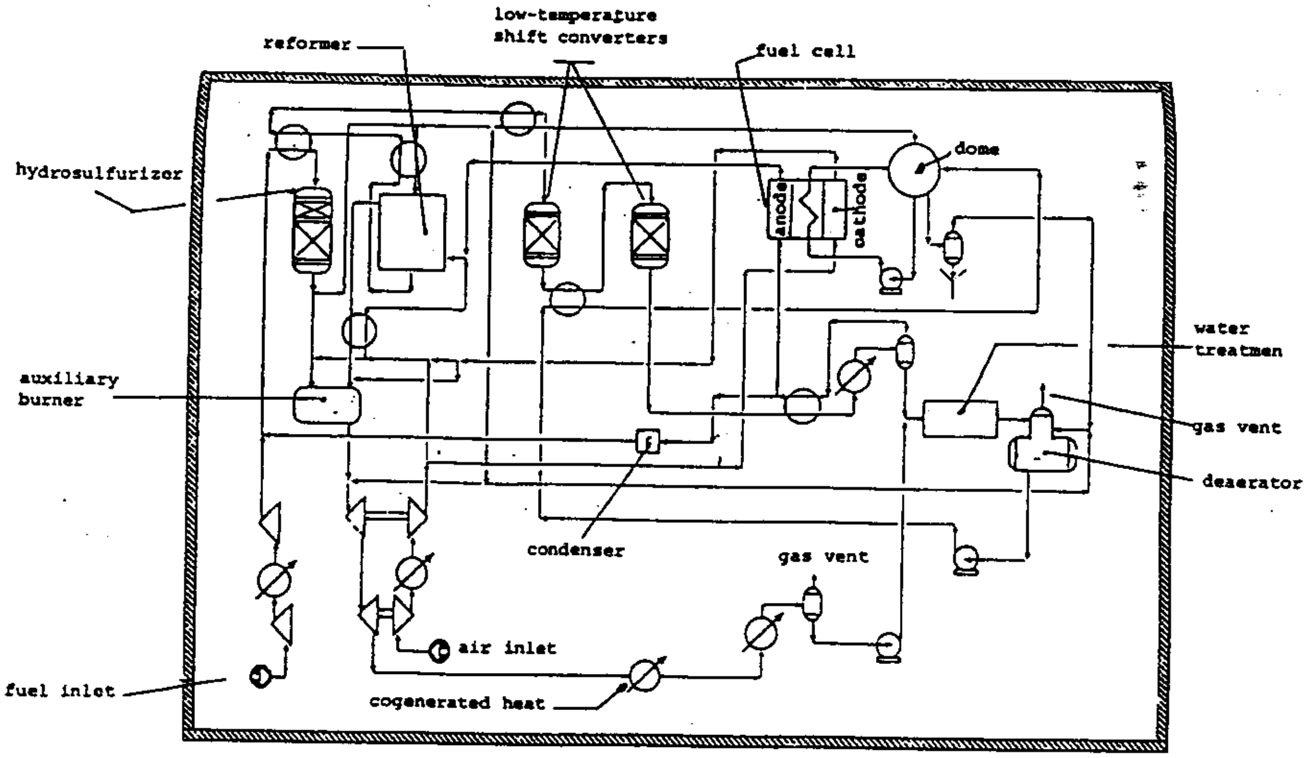


Fig. 6 - Diagram of the 1.35 MW PAFC unit designed by Ansaldo for AEM, Milan, within the framework of the national fuel cell research, development and demonstration program sponsored by ENEA and ECC[8].

however, is of the opinion that the electric power shortage will have to become much more acute before it justifies the very high insurance premium involved in carrying hydrogen across the Atlantic Ocean.

For these reasons the AFC, which is technically the most advanced fuel cell, seems to have only two important applcations, space flight and the chloralkali industry.

SPEFCs, already very sophisticated from a technical viewpoint, have so far only been used in small portable units, chiefly on board space ships for a different set of reasons (although a 300 W prototype powered at the Milan Trade Fair on June 29, 1982 a colour television set showing the Italy-Poland football match). SPEFCs operate at a temperature that is only slightly higher than room temperature (about 60-70°C) and consequently require large quantities of a very expensive platinum catalyst. The acid electrolyte is microincapsulated or laminated into a polymer membrane by means of a rather expensive manufacturing process. Therefore, with the current densities so far obtained (0.2-0.3 A/cm^2) SPEFCs cannot compete with the other electric generators except in such applications as space flight where reliability and the power-to-weight ratio are more important than costs.

Recently the Dow Chemical Company (Texas) has obtained current densities that are more than ten times higher (4 A/cm^2)[7] which, whilst creating new system engineering problems, may also make SPEFCs more competitive from an economical viewpoint.

Among the fuel cells that may be fed with primary-fuel reforming-gas (or directly with primary fuels) PAFCs (operating at about 180°C) are those that have been mostly tried and tested. Their state of the art is as follows. Two 5 MW units have been set up, an oil-fuelled one in New York City and a natural gas-fuelled one in Tokyo. The Tokyo unit worked for about three years and has now been dismantled to make room for a similar 11 MW modular prototype. These are the typical sizes of the dispersed-generation urban power stations and the purpose of the three above-mentioned prototypes is to show that they can be safely operated downtown.

In addition, about fifty 40 kW(e) PAFC generators have been successfully operating for years on civil and industrial users' premises in the United States, Japan and Canada (restaurants, laundries, heated swimming pools, telephone exchanges, etc.) both as grid-connected and stand-by generator sets fed with natural gas, peak-shaving gas, propane, etc. 40 kW is the typical size of on-site generators suitable both for stand-alone applications and cogeneration in a condominium or at single users'. The water-cooled PAFC prototypes of several MW or a few tens of kW mentioned so far are particularly suited for cogeneration and consequently for stationary installations. There are also air-cooled, mostly methyl alcohol-fuelled PAFCs best suited for portable units in field applications. The PAFC technology is highly developed in the United States and Japan with costs averaging 3000 $/kW, which is slightly higher but of the same order of magnitude as the cost per kW of conventional thermal power plants.

More promising from an economical viewpoint are MCFCs because they can burn low-grade fuels (coal gas, biogas, etc.) and because they operate at 650°C thereby producing a valuable waste heat which can be reused for generating further electricity. Very high total conversion efficiencies in excess of 60% may thus be reached. Considerable R&D resources have been invested in these fuel cells in the United States and, recently, in Japan but results so far obtained are limited to those mentioned above.

SOFCs have even higher operating temperatures (about 950°C) which increases their capability of burning low-grade fuels but results so far attained are even more limited than those of the MCFCs and consist of three 3 kW prototypes with a tubular geometry but presently still fed with pure hydrogen in bottles (Westinghouse) and a patent for a honeycomb construction which has been the object of widespread interest but has not yet been tried out (Argonne National Laboratory and Combustion Engineering). In Europe a German industry is developing a third SOFC concept, of planar geometry.

CONCLUSION

This much for the introductory lecture on fuel cells. This afternoon, in the seminar, we shall see more about their applications and world development programs.

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