Alkaline falling-film fuel cell
A breakthrough in technology and cost

K.H. Tetzlaff[a], R. Walz[a] and C.A. Gossen[b]

[a]*Hoechst AG, Verfahrenstechnik, 65926 Frankfurt am Main (Germany)*
[b]*Hoechst Celanese, Technical Center, Corpus Christi, TX 78469 (USA)*

Abstract

The work described in this paper was oriented towards fuel cells for practical applications, but mainly presents data obtained using half-cells. The economic significance of these data is discussed, together with the technical concept of fuel cell power stations and for transportation applications. The proposed fuel cell will generate power at much lower costs than conventional power plants, and a zero-emission vehicle with fuel cells will operate at lower fuel cost than a car with an internal combustion engine. The simple falling-film process leads to high power densities (6 kW/l) and low cost. The details given are valid for the use of hydrogen produced from fossil energy sources. Concentrated CO_2, a byproduct of this technology can be stored in discussed oil and gas fields at a very low cost to avoid global warming. Thus, this 'down-to-earth' hydrogen technology is as free from CO_2 emissions as solar–hydrogen technology.

Introduction

The fuel cell, discussed in this paper, is the result of a technology transfer from the research and development programme for alkaline electrolysis at Hoechst AG. For this reason, the development has been influenced by technical and economical considerations from the beginning. In contrast, previous developments of the alkaline fuel cell have been aimed at small units for the use in space, essentially, neglecting cost.

Because of the increasing cost of electricity, Hoechst AG in Frankfurt am Main, Germany, has developed chlor-alkali electrolysis cells with a very low energy demand. The results of this development are membrane cells with an area from 1 to 3 m^2, marketed by the subsidiary UHDE GmbH. Oxygen-consuming cathodes have been developed which allow the reduction of cell voltage by over 1 V, and which are robust enough for industrial use [1]. The falling-film process [2] has been developed for the operation of this gas-diffusion electrode. In this process, the electrolyte flows from the top through the cell. In this case the hydrostatic head is compensated by an equal but counteracted hydrodynamic pressure drop. For this reason, the pressure difference between the electrolyte on the front side of the electrode and the gas on the rear remains constant over the whole area of the vertical electrode. This is an important aid in operating a gas-diffusion electrode without a diaphragm. The application of the falling-film process in the fuel cell allows a very small distance between the electrodes, equal to ~0.5 mm, and a fast flowing electrolyte. The cell can therefore operate at

very high current densities. This characteristic property gives rise to the name 'falling-film fuel cell' (FFFC).

Results

Starting with a theoretical approach, the suitability of gas-diffusion electrodes under conditions of operation, which lead to a higher efficiency and higher current densities, were examined. These assumptions have been confirmed with half-cell measurements and complete laboratory-scale fuel cells. Partners willing to participate in the technical development of fuel cell modules are being sought.

Figure 1 shows the results of half-cell potential measurements. The position of the gas-diffusion electrode in relation to the Haber–Luggin capillary is shown on the left side. The cathode of a water electrolysis cell (i.e., a dynamic hydrogen electrode) serves as reference electrode, which consists of the same material as the anode tested. The reference cathode has a current density of 1 mA/cm^2 and is kept under the same temperature and pressure conditions as the remaining equipment. Operating conditions of 2.1 MPa (21 bar) and 100 °C were chosen for the following reasons:

(i) hydrogen is produced under industrial conditions at this pressure, and the energy of compression may be converted into electrical energy under reversible conditions according to the Nernst equation;

(ii) previous work has indicated that the polarization at the electrodes can be reduced by operating at higher pressure, and

(iii) the expected power density should offset the additional cost of high pressure containment.

The active surface of the electrodes in the half-cell was 2.25 cm^2. The electrodes were supplied with technical grade hydrogen. To simulate the flow characteristics of the falling film as precisely as possible, the electrolyte was forced through the gap between the gas-diffusion electrode tested and a ceramic diaphragm from top to bottom by means of a pump. The curves shown in Fig. 1 have been obtained with a current interrupt device. The curve marked 'IR free' relates to pure polarization at the electrode, whereas that marked 'not IR free' contains all other partial polarizations between the tip of the Haber–Luggin capillary and the active zone of the gas-diffusion electrode.
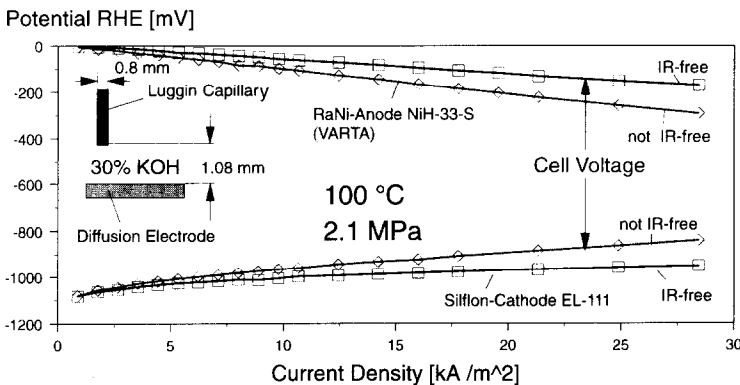

Fig. 1. Half-cell measurements.

This largely consists of the ohmic drop between the tip of the capillary and the macroscopic surface of the electrode. This ohmic drop is independent of current density, and is roughly the same for the anode and cathode. Even at current densities higher than 40 kA/m², no diffusion limitations have been observed. The best results were obtained using a Silflon® electrode developed by Hoechst. It contains essentially silver and Hostaflon®. Several types of electrodes with Raney nickel, platinum–carbon, as well as commercially available electrodes with unknown catalysts were tested. The differences found were small.

If we assume that the ohmic drop between the Haber–Luggin capillaries equals the ohmic drop between the electrodes of the falling-film cell with a 0.5 mm interelectrode gap, the overall polarization curve shown in Fig. 2 may be drawn. Any error caused by this simplification is not great, especially in the current-density range between 5 and 10 kA/m².

Figure 3 shows projected performance data for the complete cell. For central power plants, the conditions of high efficiency are of special interest, whereas for transportation applications high power density (up to 6 kW/l) is important. We should emphasize that, so far, no other type of fuel cell has demonstrated such high performance.

Figure 4 depicts the degradation of a standard Silflon® cathode, which had been operated for three years in a chlor-alkali membrane cell pressure free at 3 kA/m² in 80 °C NaOH. The measured degradation over this period is ~20 mV at 2.6 MPa, a
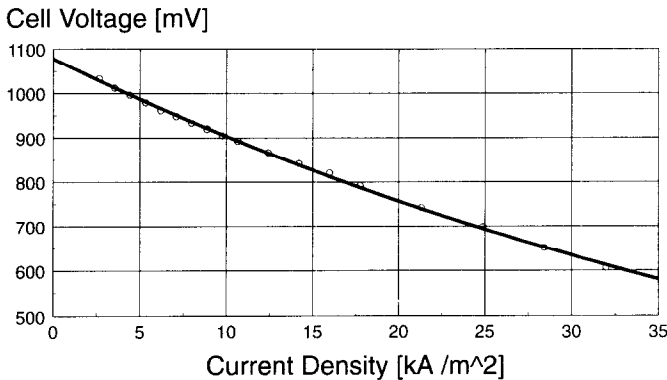
Cell Voltage [mV]

Current Density [kA /m^2]

Fig. 2. Battery curve of falling-film fuel cell, 100 °C, 2.1 MPa.
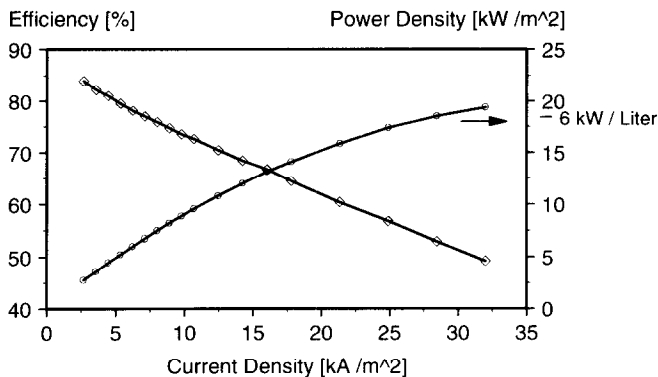
Fig. 3. Performance data of falling-film fuel cell, 100 °C, 2.1 MPa.

Polarization [mV]

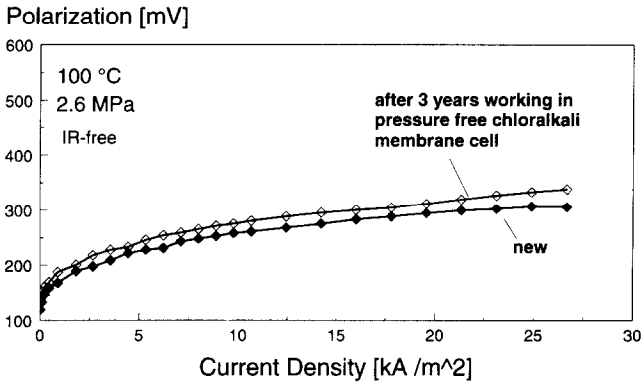Fig. 4. Degradation of Silflon® cathode, operated three years in a chlor-alkali membrane cell and tested at high pressure.

very small value. This results from high-pressure operation, since the same electrode shows a typical degradation of 50 to 100 mV when operated under pressure-free conditions. This degradation is almost nearly equal to the polarization in the membrane cell over the first 100 days. After this period of time, polarization remains more or less constant for several years.

A Silflon® cathode with no special long-term dopant additives in a chlor-alkali membrane cell shows the same polarization as the standard cathode after three years, but no long-term degradation has been observed. When tested under high-pressure conditions, this type of electrode showed the same polarization as standard electrodes. If these results are confirmed under the new operating conditions with complete laboratory cells in long-term experiments, proven stability will be more than sufficient. After several years of study, we consider that the Silflon® cathode is sufficiently robust for industrial use. Compared with other cathodes containing silver, the Silflon® cathode can withstand very high- or low-current densities, as well as current interruption, without damage.

Technical concepts for a fuel cell power station

Figure 5 displays a design concept for a fuel cell power plant. The bipolar stack of several hundred cells should be placed inside a pressure container. The cells, of ~3 to 5 mm thickness, are supplied by a main manifold. The electrolyte is sprayed on to the top of the block, and flows as a falling film through the cell, exciting by dripping over a sluice. Every cell is therefore galvanically separated from both its neighbour and the manifold, which is important in avoiding corrosion due to shunt currents. The cells may be of a lightweight construction, since they are contained in a pressure vessel. Sealing problems are thereby also greatly reduced. For large central power plants, a cell stack volume of 1 to 2 m^3 should be sufficient to provide enough electrical power for a small town.

Integrating the fuel cell into 'down-to-earth' hydrogen technology

Hydrogen and oxygen gas-generation units must also be a part of a fuel cell power plant. The most economical way to provide pure oxygen is by means of liquid air
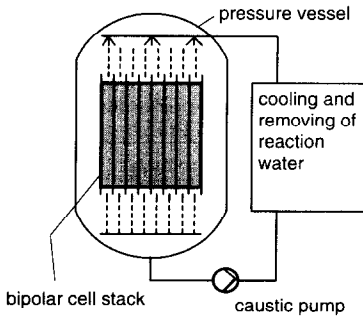
Fig. 5. Technical concept for a power station with falling film and dripping gaps.
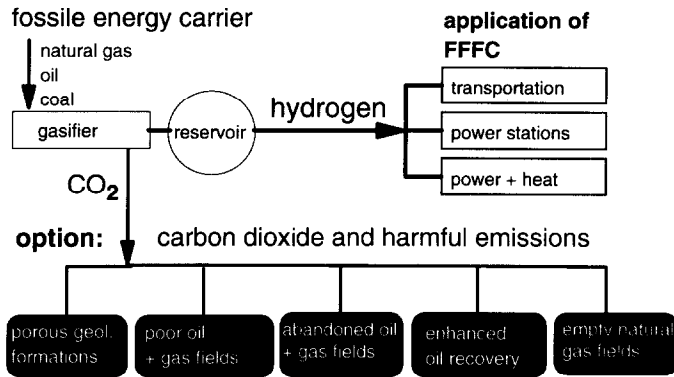

Fig. 6. Integration of the falling-film fuel cell into a 'down-to-earth' hydrogen technology.

distillation. The energy requirement of oxygen plant is more than compensated by the lower polarization of the electrodes, which results from a higher pressure operation. The most practical way to supply hydrogen is by steam reforming of natural gas. Due to the incompatibility of the alkaline fuel cell with CO_2, the shifted reformate must be scrubbed using a pressure-swing-adsorption (PSA) device. At the first glance, its use may appear to be a handicap, but it also represents an opportunity to provide a CO_2-free source of energy, since PSA produces concentrated CO_2 which can be sequestered in suitable geological formations. Disused oil and gas fields are best suited for this option, since their gas-tight quality has been demonstrated over millions of years (Fig. 6). Other geological formations will required proof of their gas tightness. Additional costs for underground deposition of CO_2 may be 0.003 DM/kWh for power generation and 0.06 DM/100 km for transportation applications. The quoted cost is for a 600 MW power plant with a 100 km distribution system pressurized up to 20 MPa [3]. For producing oil wells, these costs are countered by higher oil yields, which can exceed 100%. In the USA, CO_2 injection is commercially used for enhanced oil recovery (EOR) [4]. Although this is aimed at a reduction in oil recovery costs, more carbon may be sequestered underground than is recovered as oil. In the USA, natural subterranean lakes of CO_2 are used for this purpose. Other pollutants may also be sequestered with CO_2, but their fraction should remain lower than 10% in the case that CO_2 is to be used for enhanced oil recovery. The external environmental damage costs avoided by this option will result in a net gain to the national economy.
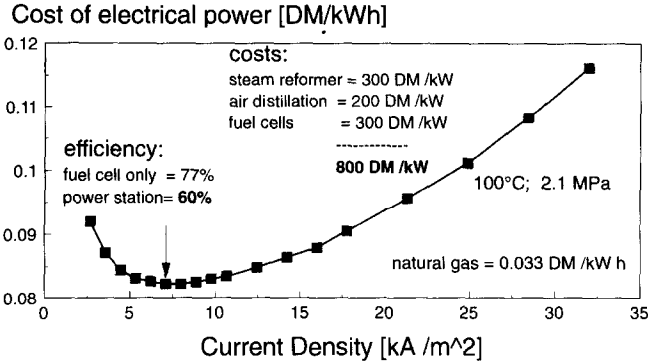
Cost of electrical power [DM/kWh]

Fig. 7. Cost of power generation for a 700 MW fuel cell power station based on natural gas 0.033 DM/kWh; overall efficiency = 60% (LHV); overal cost = 800 DM/kW.

Central power generation

Figure 7 shows d.c. power generation costs for a 700 MW fuel cell power plant. The overall efficiency is 60% based on the lower heating value of methane at the current density giving the lowest costs for power generation. Approximately 7% of the cell efficiency of 77% is consumed by the oxygen plant, 85% of the chemical energy is transferred from methane to hydrogen. This high value is achieved by using waste heat from cells and oxygen plant, because steam reformer fed with cold water exceed not 83%, today. The capital costs for the complete plant are ~800 DM/kW, which include those of the steam reformer (~300 DM/kW), and of the oxygen plant (~ 200 DM/kW). These costs may be determined with relative certainty, since they represent parts of the Hoechst product spectrum. Half of the 300 DM/kW for the fuel cell plants is a conventional chemical process equipment, which limits the cost risk. The cost estimation had been done by a specialist of the Hoechst group [5]. Any error in these costs will have only a small effect on the costs of the generated power. With the present cost of natural gas equal to 0.033 DM/kW, the cost of electric power will be 0.082 DM/kW, assuming fixed costs to be 25% per year. The generating cost would be 0.085 DM/kW for operation at 80 °C, and would fall to 0.080 DM/kW for operation at 120 °C. The sale of any byproducts, such as nitrogen, carbon dioxide, rare gases, and low temperature waste heat are not considered in determining the cost. Costs as low as these cannot be attained with other fuel cell power plants, nor with power plants of any other type. This general statement is also true for the use of coal, since any additional costs for the gasifier plant are counterbalanced by lower feedstock costs. Figure 7 also demonstrates that the system can be operated at twice-rated power without significantly raising generating costs. A reserve capacity for peaking requirements and power outage is therefore not required. Capital costs equal to significantly more than 800 DM/kW could be permitted without changing the cost advantages of those of competing technologies.

Decentralized power generation

If fuel cell power plants are competitive for central station use, then this becomes even more evident for decentralized plants. To allow low capital costs, the gas-generation

units should be big. The CO_2 produced can then be collected and disposed of more efficiently. Combined heat and power (cogeneration) must be assumed in decentralized applications, since heat distribution costs are small. This combined unit is preferably electrical power controlled in a stand-alone manner and not heat controlled as usually done by internal combustion engines working on the power line. The fuel cell does not require costly, high-technology materials, so stack sizes down to 1 l volume to provide energy for single-family dwellings are feasible. Hydrogen for heating applications produced at a central location instead of natural gas is not extravagant. The energy losses for the conversion of hydrogen to natural gas are partly made up by the ability to use almost 100% of the higher heating value of hydrogen by using a catalytic burner for heating.

Transportation

Falling-film fuel cells (FFFC) may be applied in transportation facilities. The lack of infrastructure for hydrogen production and transportation via pipeline is often cited as a major obstacle. However, the fact that the fuel cell can use energy four times more efficiently than the conventional energy sources [6] diminishes these inconvenients. An investment of ~8 billion DM would be required in Germany for generating the necessary hydrogen and oxygen. If decentralized power generation were simultaneously introduced, the costs of connection of service stations to the pipelines would be negligible. Assuming a total cost of 15 billion DM, the cost per vehicle would be only 400 DM. At natural gas prices of 0.033 DM/kWh, pre-tax fuel costs would be 1.30 DM/100 km. Including capital recovery on the infrastructure investment, the total costs would be 1.50 DM/100 km. The cost of the investment infrastructure would be equal to the cost of gasoline saved in the first year of operation. The infrastructure may initially be built up in islands, with pipeline transport of pressurized gas. The 100 km long hydrogen and oxygen pipeline system in the Rhine-Rhur area, Germany, could also be used.

Figure 8 shows a schematic of a passenger car containing an 80 kW FFFC cell with a volume of 17 l. The stack would contain approximately 0.5 kg of silver with a market price of ~100 DM. The stack weight may be 15 kg. It is difficult for a company specializing in the production of chemicals to give an estimation of the manufacturing cost for the production of cells, in millions of items, which will be
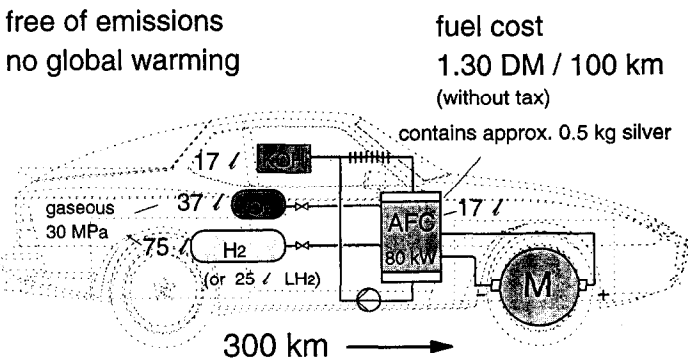

free of emissions
no global warming

fuel cost
1.30 DM / 100 km
(without tax)

contains approx. 0.5 kg silver

17 l

gaseous   37 l
30 MPa
75 l   H2   17 l
(or 25 l LH2)   AFC 80 kW

M

300 km ⟶

Fig. 8. Proposal of a falling-film fuel cell car; cost of production and distribution equipment for hydrogen and oxygen will be ~400 DM/car.

decisive in determining the final cost of the vehicle. The system in the vehicle consists of tanks, a small pump for electrolyte recirculation, and a radiator. In order to simplify the system, it was decided not to remove product water out of the vehicle, so that the latent heat could be used for interior heating. The high efficiency of the cell means that waste heat is limited, and this consideration will be important in winter, especially during short trips. Dilute electrolyte may be exchanged for concentrated electrolyte at a service station. Hydrogen and oxygen are most effectively stored under pressure. The pressure vessel size required for an average range of 300 km will be similar to that for a gasoline-powered vehicle. Today, these vessels are in general made from high-performance polymers. It is possible to double the range by simply cooling the vessel with liquid nitrogen [6]. Instead of gaseous hydrogen, liquid hydrogen may also be used. However, the advantages of a smaller vessel are accompanied by certain disadvantages. These include the loss of the energy required for liquefaction, and the time required for filling the vessel. Similar cases exist already for the use of pressurized hydrogen, since more than one million passenger cars operate on pressurized natural gas used in Otto-cycle engines. The three-tank arrangement in Fig. 3 is subject to future modification, as required. Development of such a vehicle and its infrastructure must consider such factors as global warming, protection of the environment, energy conservation, together with vehicle dynamics, safety, and cost.

In contrast to the proposed vehicle with a proton-exchange membrane fuel cell operating on reformed methanol carried on board, which is favour in today's US Department of Energy programme, the alkaline fuel cell vehicle, proposed in this paper, is technically very simple, has a zero-emission level, and with a CO_2 sequestration that is also free from global warming emissions. In regard to the source of the primary energy consumed, the alkaline fuel cell has significant advantages, because steam reforming requires only one chemical conversion, from natural gas to hydrogen. The proposed methanol system requires natural gas reforming, methanol synthesis, and a second on-board steam reformer.

Discussion

The authors are aware that very broad future technical concepts and projections have been deduced from a rather limited data base. However, the novel technical characteristics of the alkaline FFFC are required in the context of the today's energy and environmental situation. Compared with these considerations, it is not significant if cell performance characteristics differ by 10%, or so, from those assumed, or if the cell capital cost is a factor of two higher than the estimates given here. The option fuel technology with no CO_2 emissions is valid for other types of fuel cell, but for these, costs would be higher. If the FFFC is used in transportation applications, our present dependence on oil will be drastically reduced by reducing primary energy requirements by approximately 60% and by the substitution of natural gas or coal for oil.

Summary

The FFFC technology will allow:
(i) protection against global warming;
(ii) protection of the environment;
(iii) energy conservation;

(iv) enhance oil and gas recovery by the use of CO_2, and

(v) lower electricity and transportation energy costs.

The proposed 'down-to-earth' hydrogen technology has the same attributes as the solar–hydrogen economy. The practical acceptance of either, or both, systems will be a question of economical considerations.

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