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Direct-fuelled fuel cells

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Abstract

Fuel supply is one important problem to be solved for commercial application of fuel cell technology. Conventional fuel-cell types require hydrogen as the fuel, which has to be free from impurities when operated at temperatures below 100 °C. The storage and distribution of this explosive and extremely fugitive gas is one of the open questions in the context of a customer-orientated broad commercial market. The direct-fuelled fuel cells (DMFCs) overcome the hydrogen specific restrictions. They are capable of directly using natural gas or fuels which are liquid under ambient conditions. In this paper the different options from direct-fuelled systems are described and their general aspects discussed. The state-of-the-art at Siemens in this field, and also the remaining technical questions are outlined as a basis for assessing future applications.

Keywords: Fuel cells; Direct-fuelled systems

1. Introduction

Fuel supply is one important problem to be solved for commercial application of fuel cell technology. Different conceivable applications of fuel cells, especially those with discontinuous operation (such as electrotraction or small (trans-)portable power supplies) can preferably be realized by 'low-temperature' systems. However, those systems require clean hydrogen, especially when operated at temperatures below 100 °C.

The generation of hydrogen is a well-established process practised in large stationary chemical plants. But the storage of this explosive and extremely fugitive gas is one of the open questions in the context of a customer-oriented broad commercial market. The problem is most crucial in the case of mobile applications where the on-board storage of hydrogen has to fulfil additional requirements with respect to weight and volume. A fuel that is liquid under ambient conditions would be more attractive. But also the generation of hydrogen from liquid fuels such as methanol in compact reformers has limitations in downscaling the systems and, hence, is a big challenge for technical engineering.

Moreover, the supply and distribution of hydrogen will be difficult. It is questionable whether a corresponding widespread infrastructure can be created on a mid-term timescale. Due to the obstacles to a hydrogen technology above-mentioned direct-fuelled systems gain special interest. The expression 'direct fuelled' is potentially misleading. In the

following, it will be defined as 'using hydrogen-alternative fuels'.

2. Benefits of direct-fuelled systems

From the technical point of view, hydrogen is the most favourable fuel for fuel cells. It provides excellent kinetics for the oxidation reaction. The reaction occurs in a simple one-step route with no poisoning intermediates or by-products. Moreover, the electrochemical oxidation of carbon-containing fuels is mostly difficult due to metastable intermediates (such as R-CO-R') or undesired by-products (such as R-CHO, C).

However, direct-fuelled systems are expected to bring fundamental advantage over the hydrogen-operated versions. The main arguments in their favour can be summarized as follows:

- 'simple' system setup
- no additional fuel processing/cleaning necessary
- a consequence may be: lower volume, lower weight, and lower costs
- existing infrastructure for fuel supply and distribution can be utilized
- high energy density of the fuel per unit volume and weight, and
- low costs of the fuel

The basic simplicity of the system setup is illustrated here for the example of a mobile or independent application

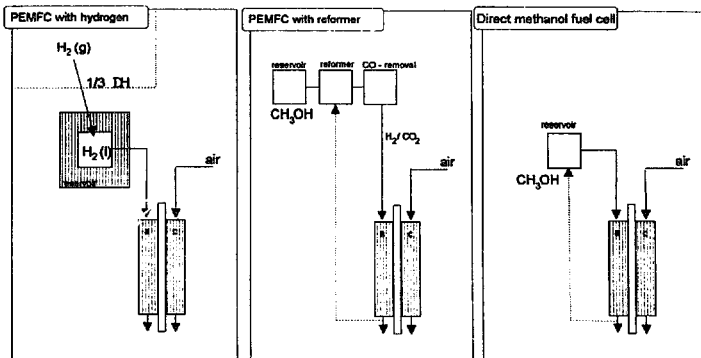


Fig. 1. Concepts of fuel supply for mobile or independent operation.

(Fig. 1). In this case, a direct methanol fuel cell (DMFC) is compared with a hydrogen-operated or reformate-operated proton-exchange membrane fuel cell (PEMFC).

When hydrogen is used as the fuel, its storage will be the key item. The highest energy density is obtained by using the liquid phase. But the liquefaction needs roughly one third of the specific energy. In addition, the thermal insulation markedly increases the volume of the reservoir. On using compressed gas or hydrides the specific energy density is lowered and the weight of the reservoir becomes dominant due to its required pressure stability.

In principle, the hydrogen required can be also produced on-board by reforming a liquid fuel such as methanol. However, due to the CO sensitivity of platinum, an additional CO removal unit has to be placed between the reformer and the fuel cell. Moreover, the dynamic behaviour and load range (at tolerable efficiencies) of a miniaturized reformer are questionable and introduce a lot of risks.

At a first glance, the system setup of a DMFC looks very simple compared with these two options. This fact is the main driving force for the development of DMFCs. Their benefits, state-of-the-art and technical obstacles will be discussed in more detail in Section 4.

3. Direct-fuelled options

In principle, a number of electrochemically active molecules can be considered as a fuel for a direct-fuelled fuel cell [1]. In this context, experiments are described in the literature where cells were operated with hydrazine, aldehydes, formic acid and other organic compounds [2-4]. However, technical or commercial applications set additional requirements on the fuel, e.g. availability, handling, safety and last but not least cost. This fact diminishes the variety of conceivable fuels to a very low number.

The main routes for direct-fuelled options are through the primary energy carrier, natural gas and coal. Hydrocarbons (natural or by coal gasification) can be effectively converted into electrical energy at temperatures higher than 600 °C, e.g. in MCFC or solid oxide fuel cell (SOFC) systems. Fuels with improved electrochemical activities, such as alcohols (preferably methanol) can be oxidized even at temperatures below 100 °C. The DMFC based on a polymer electrolyte fuel cell concept is the most popular representative of this kind.

An interesting supplement to the fossil fuels, natural gas and coal is represented by the 'regenerative' fuels, e.g. biomass. They will probably not be able to provide a major part of the whole demand for energy (especially in the near-term future) but illustrate the principal possibility of a 'green' solution for energy conversion (owing to the scope for CO₂ recycling). The biomass can be converted into methanol or hydrocarbons for further technical use.

4. Direct methanol fuel cell

The DMFC overcomes the hydrogen-specific restrictions. It is based on the direct electrochemical conversion of methanol [5] without an intermediate reforming step (Fig. 2). The principle is known for decades, but until now nobody could demonstrate any commercialization and it did not exceed the laboratory scale of small demonstrators in the sub-kW range.

One of the reasons for the fruitless efforts was the insufficient current density (about 50 mA/cm² at 0.4 V) and the poor faradaic efficiency (< 60%) obtained by the direct oxidation of methanol. But recent experiments, performed at Siemens, yielded current densities up to 400 mA/cm² at 0.5 V and faradaic efficiencies > 90% [6]. These values approached technical interest, especially when they have to compete with those of a PEMFC that is combined with a

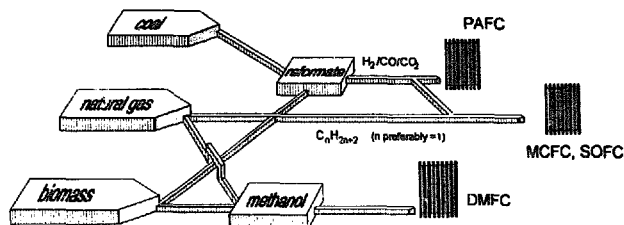


Fig. 2. Direct-fueled options (main routes).

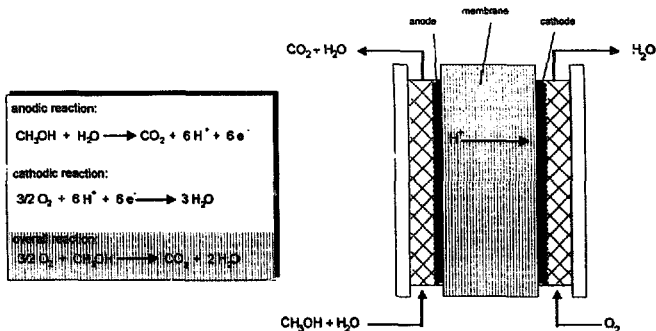


Fig. 3. Schematic principle of a DMFC.

methanol reformer. For this reason the commercialization of the DMFC gains renewed interest.

The schematic principle of the DMFC, followed by Siemens, is shown in Fig. 3. It is based on a PEMFC-type construction with similar materials except the anode catalyst: Pt/Ru alloys are used instead of pure Pt.

The initial concept used liquid methanol/water mixtures. Operational temperature was 80 °C. Characteristic performance data were about 100 mA/cm² at 0.5 V. The technical feasibility of a DMFC stack was demonstrated by the assembly and running of a 12-cell battery (active electrode area: 250 cm²).

However, the successful operation of a stack revealed problems too. The main obstacle that became apparent was the electroosmotic water transport through the membrane. The measured rate of about 60 ml/h (each cell of 250 cm²) is intolerably high and effective water removal becomes difficult. Due to this basic unavoidable effect a concept with a gaseous fuel supply was used in further experiments. In this manner, the concentration of water could be kept low in an appropriate stoichiometric range.

By using methanol/water vapour and raising the temperature to 130-140 °C, current densities could be increased to about 400 mA/cm² at 0.5 V (4 bar_{abs.}, O₂ mode). Measured voltage-current characteristics are illustrated in Fig. 4.

Faradaic efficiencies $\geq 94\%$ could be realized by adjusting the methanol concentration around 2 mol/l.

However, in spite of these promising results, a number of technical problems have still to be solved. They can be easily deduced from Fig. 5 which shows the long-term operation of a DMFC. The observed degradation of cell voltage was in the range of 0.3 mV/h. This means that a loss in performance of 10% will be reached in less than 200 h. A comparison of this value with the required life time for mobile (2000 h) or stationary (40 000 h) applications makes it clear that the actual degradation is still restrictive to any commercial application. Furthermore, operation with air instead of oxygen is essential for most conceivable applications. Performance loss of 30 to 50% is the consequence and will be further increased on reducing the cathode pressure (air operation near ambient pressure is essential for a high overall efficiency).

As a consequence of the results obtained and the basic requirements imposed, future efforts will have to focus on these technical items.

5. Transportation applications

The most attractive applications for such direct-fueled systems are those in which storage or generation of hydrogen

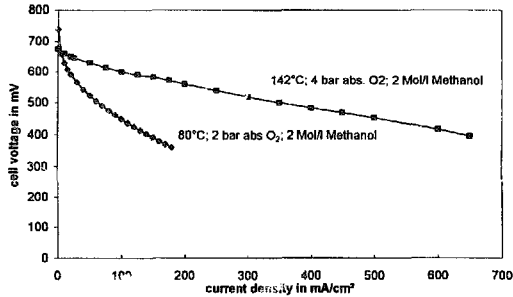


Fig. 4. Voltage-current characteristics of a DMFC (single cell of 25 cm²): O₂ mode; curve measured at 80 °C: concept with liquid fuel supply; curve measured at 142 °C: vapour concept.

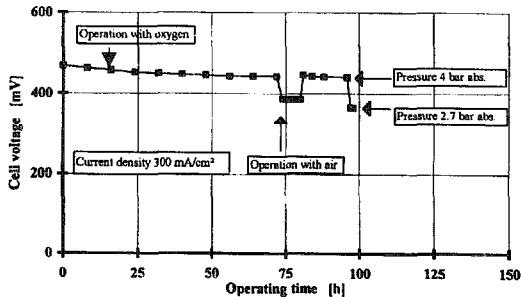


Fig. 5. Long-term operation of a DMFC (single cell of 25 cm²) at 120 °C; O₂ mode.

causes significant effort and has a negative impact on the volume and weight of the system. This is especially valid for the electrotraction of road vehicles as already mentioned.

The discussion of conceivable applications becomes more effective when a realistic set of requirements is drawn up. For instance, a propulsion system for a passenger car has to fulfil the following requirements in order to be competitive with a conventional combustion engine:

- fast start-up behaviour (< 60 s)
- low volume and weight: power/volume ≤ 2.5 l/kW, power weight ≤ 2.5 kg/kW
- quick response/dynamic behaviour (10% to 90% P_{max} in less or equal 100 ms)
- safe fuel concept (preferably a liquid fuel)
- simple design/mass producible concept
- system costs \leq US \$150/kW
- system efficiency at least comparable to existing technologies

The main challenge for the application of a DMFC in this field will be a short start-up time. While a hydrogen-operated fuel cell provides already about 50% of its power at 20 °C, the electrochemical oxidation of methanol yields power characteristics which are strongly dependent on the working temperature

The traction and electric supply of trains and ships will be probably easier to realize. But the combined electricity and heat supply of private households may also be potential markets for the DMFC. Ultimately, the market penetration will depend on the complexity of the fuel cell system, its performance and its costs and general acceptance.

6. Solid oxide fuel cells

Finally, the solid oxide fuel cell (SOFC) also belongs to the class of 'direct-fuelled' systems. A promising field for this fuel cell type is decentralized power supply in the MW range, where the SOFC gains interest due to its capability to convert natural gas without external reforming.

Operating in the 900–1000 °C temperature range, the SOFC allows even the direct electrochemical conversion of CO. In addition, the heat released by the cell reaction at high temperature can be used to drive the endothermic steam-reforming reaction of methane. It implies that it is possible to steam reform natural gas mainly within the stack, and thus to reduce the flow of heat which has to be carried away by a cooling cycle. The efficiency of the system increases as the power of the compressor driving this cycle is reduced.

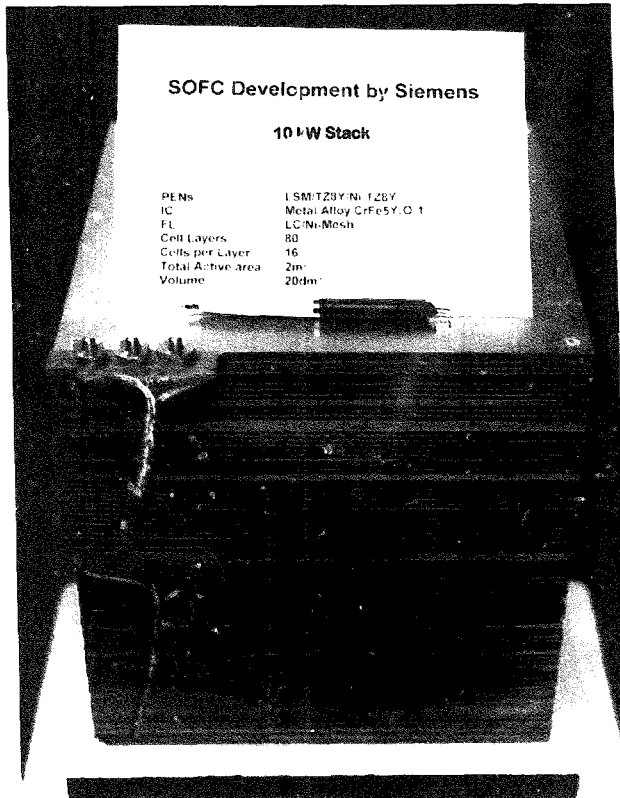


Fig. 6. 10 kW SOFC stack of Siemens (80 layers of 16 cells; 16 cm² each; volume 20 l).

In the range of one to some tenths of a MW, the predicted benefits in electrical efficiency of SOFC-based power plants over conventional methods of electricity generation from natural gas can only be achieved by an internal-reforming SOFC. So internal reforming is a major target of present worldwide SOFC development.

At Siemens, the state of SOFC development [7] is characterized by an 80-level stack, each level consisting of 16 cells with an active area of 16 cm² each (Fig. 6). The stack has an overall size of 26 cm × 26 cm × 30 cm. Cells were made from conventional components, that means 150 μm thick electrolyte of yttrium stabilised zirconia (YSZ), anodes of nickel-YSZ-cermet and cathodes of lanthanum-strontium-manganite. Metallic current collector plates of a high-temperature corrosion-resistant chromium-based alloy were used.

Fed with pure hydrogen and oxygen at 950 °C, this stack could be loaded with a current density of 0.7 A/cm² at a voltage of 0.75 V per level (Fig. 7), which corresponds to a total power output of 10.7 kW (Fig. 8) and a power density of 0.5 W/cm². The values for fuel and oxygen utilization under these conditions were 48 and 24%, respectively. Changing from oxygen to air caused the current density to decrease to 0.3 A/cm². Lowering the temperature to 850 °C resulted in a 30% drop of the current density.

For a technical application, it is necessary to operate stacks on natural gas with a 70-80% fuel utilization and air as the oxidant. In addition, at least parts of the stack should be able to run at temperatures of 800 °C, and lower, since a larger temperature span within the stack allows for a reduced power consumption of the cooling cycle and the application of conventional heat exchangers.

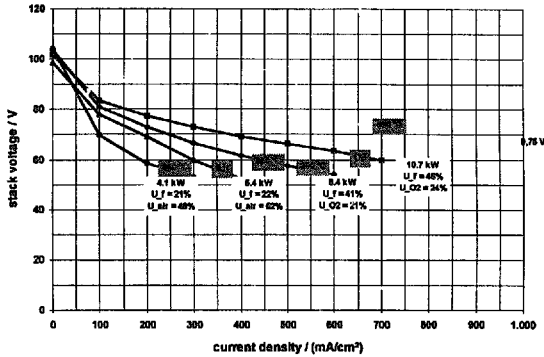


Fig. 7. Measured voltage-current characteristics of the 10 kW SOFC stack developed at Siemens; fuel: H₂; oxidant: O₂ or air at atmospheric pressure.

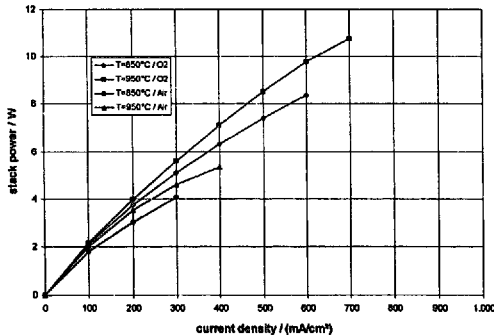


Fig. 8. Measured power profile of the 80 layered SOFC stack developed at Siemens; fuel: H₂; oxidant: O₂ or air at atmospheric pressure.

Operation of an SOFC at temperatures below 800 °C will be possible only when new materials and structures for the active cell components are applied. For instance gadolinium-doped ceria is a candidate for an electrolyte under reduced temperature due to high ionic conductivity ($2 \Omega^{-1} \text{ m}^{-1}$ at 650 °C). Unfortunately the electronic conductivity under reducing conditions as encountered on the fuel side is 20 times higher. With fuel on one and air on the other side of such an 'electrolyte', the chemical potential of oxygen changes continuously from the anode to the cathode side. The change occurs in such a manner that nearly the whole thickness of the material is maintained under reducing conditions and is thus a good electronic conductor.

Fig. 9 shows the results of model calculations for a cell where the polarization of the electrodes has been neglected. Though the Nernst voltage derived from the composition of the gases is 0.99 V the open-circuit voltage is only 0.75 V which is in excellent agreement with the measured value. This is due to an electronic short-circuit current of 0.3 A/cm². For technical applications at least 0.7 V under load

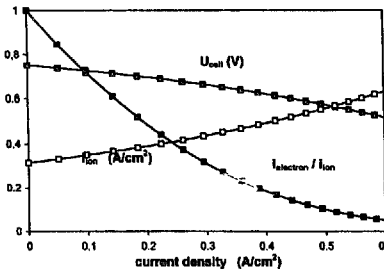


Fig. 9. Calculated voltage-current characteristic and ionic current contribution of an SOFC with gadolinium-doped electrolyte operated with H₂/air at 650 °C (30% H₂, 50% H₂O).

have to be realized, but in this range still over 50% of the ionic current is short circuited. This could only be avoided by applying a thin ($\approx \mu\text{m}$) layer of YSZ on the anode side, thus blocking the parasitic electronic current without increas-

ing considerably the ionic resistivity of the compound. Obviously, electrodes compatible with this electrolyte structure have to be developed.

7. Summary and outlook

It is obvious that the broad commercialization of fuel cells will require a related infrastructure for the fuel supply. This fact and the fundamental simplicity of fuel cells are a clear vote for direct-fuelled systems, e.g. based on methanol or natural gas as the fuel. Though their technical realization is more ambitious compared with hydrogen operation they are an interesting option for energy conversion on a long-term time scale.

On the other hand hydrogen systems are more mature and therefore closer to market. Most of the problems, such as cost reduction, efficient air operation can be dealt with.

For this reason, a strategy of parallel development of hydrogen and direct-fuelled versions looks most promising to the commercialization of the fuel cell technology. In order to solve all technical and cost problems (which are mostly also relevant to direct-fuelled cells), the hydrogen-fuelled systems should be thoroughly examined to derive adequate

knowledge. This data can be used and transferred to concentrate on the specific technical problems in the development of direct-fuelled stacks.

The goal of the current project at Siemens is the concept evaluation of a DMFC system and to prove it by the development of a demonstration plant. A number of technical problems have still to be solved. The operation of a stack will provide knowledge on system efficiency and fundamental technical problems to get a sound basis in assessing future technical applications. These will depend on the complexity of the system, the performance and the costs.

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