

R &D OF ENERGY TECHNOLOGIES

ANNEX A

V FUEL CELLS



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AV 1 Low Temperature Fuel Cells: Development Status and Future Perspectives

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This report is intended to give an overview of the current state of the art in low temperature fuel cell technology. After a brief general introduction into the fuel cell technology, a more detailed description of the two major types of low temperature fuel cells, polymer electrolyte membrane fuel cell and direct methanol fuel, and their current and potential applications will be given. Subsequently, the deficiencies of these fuel cells will be summarised and some suggestions for future developments in this field will be given.

AV 1.1 Introduction

Energy conversion from fossil fuels today is both a major source of air pollution and a major consumer of these valuable resources. Systems which allow performing this conversion with a higher efficiency or using regenerative resources are therefore sought after. Fuel cells are a very promising technique in this field. As the chemical energy of the fuel is here directly converted into electrical energy without an intermediate heat cycle the maximum achievable efficiency is not bound to the Carnot limit. Fuel cells can therefore be much more efficient than conventional heat cycle systems (cf. Figure 1). In this calculation the heat cycle efficiency becomes only higher than that of the fuel cell operate with hydrogen / oxygen if the temperature of its higher reservoir largely exceeds 1000 K keeping the lower reservoir at 300 K at the same time, a situation which is very difficult to realise in a real world system. Fuel cells operating with methane / oxygen have a higher thermodynamic efficiency at all temperatures.

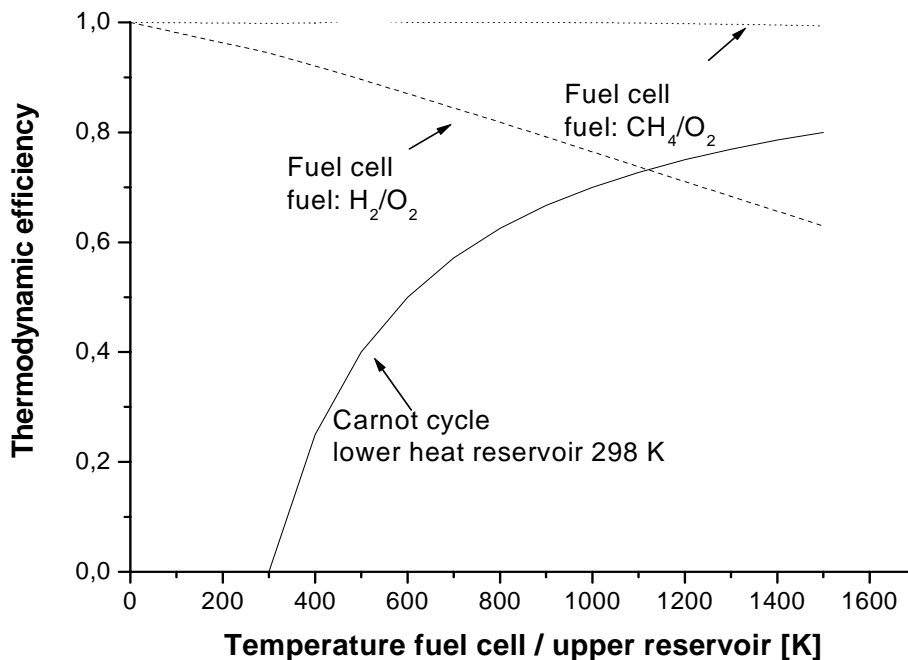


Figure 1- Thermodynamic efficiency of a fuel cell operated with pure hydrogen and oxygen compared to a Carnot cycle with lower reservoir at 300 K as a function of operation temperature

As systems operating at low temperatures offer a number of advantages e.g. shorter start up time, reduced material strain, reduced expenses on thermal insulation and security it is natural that they receive high attention especially for those applications which do not allow for a sensible use of waste heat like in the automotive or portable sector.

In addition to their high conversion efficiency fuel cells also have much lower emissions of pollutants such as NO_x or SO₂ than conventional motors. Furthermore at least the cell itself does not contain any moving parts leading to a reduced emission of noise and potentially reduced costs for maintenance.

AV-1.1.1 Principle of operation

The principle design of a fuel cell resembles that of a battery. Two electrodes are separated by a suitable electrolyte that permits the transport of ions but isolates electrons. The latter must run over an external circuit delivering the electrical work. But unlike with batteries the fuel which is converted is not stored inside the fuel cell. This is advantageous as the amount of fuel needed may be varied independently from the design power of the cell and, even more important, the fuel cell system may be “re charged” during operation. A sketch of the principal set up of a fuel cell for the example of a fuel cell with proton conducting electrolyte is shown in Figure 2. Because the fuels converted in most fuel cell systems are gases and the catalysts used in the electrodes are regularly not selective towards the reduction or oxidation reaction another important function of the electrolyte

is to separate the reactants as pronounced mixing of them would lead to a chemical short circuit of the cell and strongly reduced efficiencies (cf. section 0).

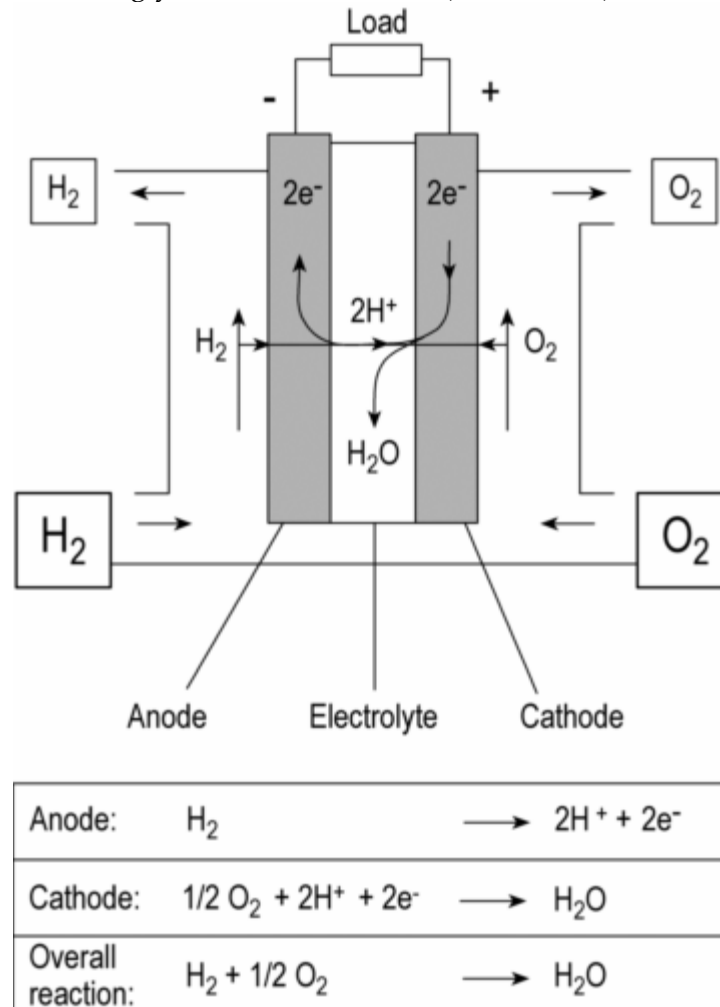


Figure 2-Sketch of the principal operation of a fuel cell

AV-1.1.2 Types of fuel cells

Although most fuel cells have a similar set up they do strongly differ in their operation conditions e.g. operating temperature and usable fuels. In principle fuel cells are divided into low temperature and high temperature types. Low temperature fuel cells operate below approx. 200 °C and high temperature fuel cells above 600 °C. In the intermediate temperature range no fuel cell systems do yet exist due to the lack of suitable electrolytes. But first developments towards this end have been made and two electrolytes have been proposed based on polybenzimidazole (PBI) and ortho phosphoric acid by Celanese¹ and based on ammonia polyphosphate by Kenyo et al² and Cappadonia et al³. As the electrolyte is the most important difference between the different types of fuel cells they are typically classified after the electrolyte. In the following tables the currently available type of fuel cells are listed with the materials which are typically used and characteristic data of operation:

Table 1- Materials and components for different types of fuel cells

Fuel cell	Electrolyte	Electrodes (anode/cathode)	Interconnector	Construction materials
Alkaline fuel cell (AFC)	conc. KOH in porous matrix	Ni/Ag (Pt/Pt) on porous Ni	Nickel	graphite, Inconel
Proton exchange membrane fuel cell (PEMFC)	proton exchange membrane	Pt on graphite	graphite sheet metal (stainless steel)	steel
Phosphoric acid fuel cell (PAFC)	conc. phosphoric acid in porous matrix	Pt/Pt	graphite	Inconel
Molten carbonate fuel cell (MCFC)	molten Li and K carbonate in porous matrix	Ni/NiO	Inconel	Inconel, Ni, ceramic
Solid Oxide fuel cell (SOFC)	yttrium stabilized zirconia $ZrO_2 (Y_2O_3)$	Ni cermet, $SrLaMnO_3$, other perovskites	chromium based alloys or chromium based ceramics	ceramic, Ni and Fe alloys

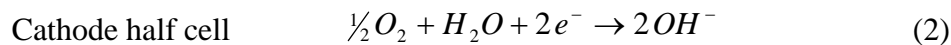
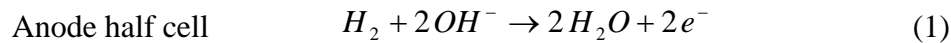
Table 2- Operation parameters for different types of fuel cells

Characteristic	AFC	PEMFC	PAFC	MCFC	SOFC
Temperature	60 – 90 °C	50 – 90 °C	160 – 220 °C	620 – 660 °C	800 – 1000 °C
Fuel	pure hydrogen	pure hydrogen, reformat [*] , methanol	pure hydrogen, reformat	natural gas, reformed or directly fed, biogas, coal gas	natural gas, reformed or directly fed, biogas, coal gas
Oxidant	pure oxygen	pure oxygen or air	Air	air	air
Application	space and military	space, military, automotive, and stationary	cogeneration power plant	cogeneration or combined cycle power plants, depending on size	
System power at present		50 kW – 250 kW	11 MW	2 MW demonstration plant	100 kW demonstration plant
Electrical efficiency					
Stack	69 – 70 %	50 – 68 %	55 %	65 %	60 – 65 %
System	62 %	43 – 58 %	40 %	54 % (cogeneration) 60 – 65 % (combined cycle)	> 50 % (cogeneration) 65 – 70 % (combined cycle)

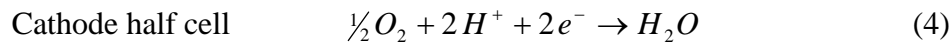
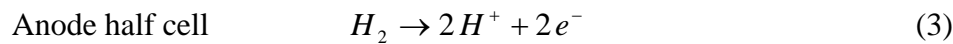
As can be seen the properties of the cell strongly influence the potential field of application. One important factor is the compatibility with carbon based fuels. Those fuels are today in general subject to a reforming process before entering the fuel cell as will be shown later. As a side product of this process CO is formed which acts as a catalyst poison for most noble metal catalyst and especially for platinum in the temperature region below

200 °C. Therefore the use of reformed fuels in low temperature fuel cells requires a complex gas clean up. Some carbon based fuel may also be fed directly to appropriate fuel cells e.g. the direct use of methane or natural gas in solid oxide fuels cells (SOFC) is currently under investigation . But the most prominent representative of this group of *direct fuel cells* is the direct methanol fuel cell DMFC. As will be shown later DMFC usually are especially adapted polymer electrolyte fuel cells (PEMFC) and operate with aqueous solutions of methanol.

Two other types of low temperature fuel cells are currently commercialised with some success, the alkaline fuel cell (AFC) and the phosphoric acid fuel cell (PAFC). Both use electrolytes consisting of a liquid which has been immobilised in an appropriate matrix. The base material of the electrolyte in the case of the AFC is usually aqueous potassium hydroxide solution whereas in the PAFC ortho phosphoric acid is employed. The half cell reactions are the following for the AFC



and for the PACF



The major obstacle for the use of the AFC is its sensitivity to carbon dioxide. This does not only limit the usable fuels to pure hydrogen, ammonia and hydrazine but in most cases even prevents the use of air as oxidant. For those applications where pure oxygen and hydrogen are available, especially onboard of space crafts and submarines, AFC's are quite successful e.g. onboard of NASA's space shuttle where the AFC stack has recently been improved .

PAFC operate at temperatures up to 250 °C. At these temperatures the sensitivity of the platinum electro catalysts towards CO poisoning is strongly reduced. Thus this type of cells can operate with CO concentrations in the feed gas up to 1% which accords to the CO concentration of reformed natural gas after a two step shift conversion. Today PAFC are used in larger facilities of some 100 kW for stationary co generation and operate with reformed natural gas. Their major draw back is the comparatively low conversion efficiency of only 40%.

AV-1.1.3 Efficiency of conversion

The high conversion efficiency of fuel cells is one of their most respected advantages. The increase of the conversion efficiency still is and also will be in future a major topic in fuel cell research. It is therefore important for the further discussion to regard it in some more detail.

The overall efficiency of a fuel cell system is given by:

$$\eta_{sys} = \eta_{td} \cdot \eta_U \cdot \eta_F \cdot U_f \cdot \eta_p \quad (5)$$

Herein η_{td} is the thermodynamic efficiency of the fuel cell which is determined by the ratio of the Gibbs free enthalpy ΔG and the heating value ΔH

$$\eta_{td} = \frac{\Delta G}{\Delta H} \quad (6)$$

The voltage efficiency is the ratio of the actual cell voltage U_{cell} and the cell voltage U_{eq} as determined by the thermodynamic equilibrium:

$$\eta_U = \frac{U_{cell}}{U_{eq}} \quad (7)$$

Major contributions to reduced voltage efficiency are given in order of their significance with increasing current density: kinetic losses at the electrodes, ohmic losses and diffusion limitations. The first is in many cases the most important source of efficiency loss. It is related to inadequate kinetics of the reaction at the used catalyst and thus may be reduced by finding better catalysts. The ohmic losses are typically caused by the electrolyte and thus may be reduced by improving the ionic conductivity of the electrolyte or by reducing its thickness. Last not least improving the gas diffusion electrodes (GDE) with respect to the structure of the catalyst layer and the gas diffusion layer (GDL) may avoid diffusion limitations

The Faraday efficiency is the ratio of the current drawn from the cell and the current which equals the amount of converted fuel according to Faraday's law

$$I_F = \dot{n}_{fuel}^{conv.} \cdot \nu_{fuel} \cdot F \quad (8)$$

with ν_{fuel} the electrochemical order of the fuel oxidation e.g. $\nu_{H_2} = 2$ and the Faraday constant $F = 96485 \text{ C/mol}$

$$\eta_F = \frac{I_{cell}}{I_F} \quad (9)$$

The Faraday efficiency becomes less than one if fuel is converted in side reactions e.g. by the cross over to the cathode compartment and subsequent direct oxidation, a situation often encountered in direct methanol fuel cells (DMFC) where the lack of an appropriate membrane material is still a major obstacle for their commercialisation.

The fuel utilisation U_f on the other side considers the fact that not all fuel entering the cell is converted. This is necessary as a complete depletion of fuel would lead to a strong potential gradient over the electrode from the entrance to the exhaust. Furthermore it is often desirable to keep a certain flux in the cell in order to remove impurities and reaction products.

$$U_f = \frac{\dot{n}_{fuel}^{in} - \dot{n}_{fuel}^{out}}{\dot{n}_{fuel}^{in}} \quad (10)$$

Beneath energy losses during the electrochemical conversion itself the conversion efficiency of the fuel cell system is further reduced by losses in its peripheral components.

These losses e.g. by the parasitic power consumption of auxiliary devices like blowers or pumps are included in the peripheral efficiency η_p .

$$\eta_p = \frac{P_{sys}^{out}}{P_{stack}^{out}} \quad (11)$$

Fuel utilisation and peripheral efficiency are strongly affected by the system design.

AV 1.2 State of the art low temperature fuel cell systems and their applications

AV-1.2.1 Polymer Electrolyte Membrane Fuel Cells (PEMFC)

This type of cell is characterised by the use of a proton conductive polymer membrane as electrolyte. The best known material of this kind is Nafion® by DuPont™. It consists of polytetrafluoroethylene as hydrophobic backbone and perfluoro sulphonic acid as hydrophilic side chains.

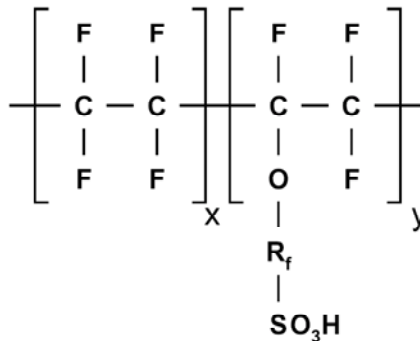


Figure 3- Structure of DuPont Nafion (source DuPont)

Similar membranes are produced by e.g. W.C. Gore (Primea) and Asahi Glass (Flemion). In contact with water, water is inserted into the hydrophilic regions of the polymers forming micelles filled with an aqueous acid and protons can cross the membrane via these pathways. The advantage of this conduction principle is the high conductivity the draw back lies in the difficulty of maintaining the correct humidification. The reactions taking place at the electrodes are the same as for the PAFC see equations (11) and (12). Thus water is formed at the cathode. Furthermore protons crossing the membrane are always accompanied by water molecules. This mechanism called “*electro-osmotic drag*” transfers about 2.5 water molecules per proton through the membrane. As a consequence of these two effects a situation is encountered where larger amounts of water need to be removed from the cathode to avoid it being flooded whereas the anode shows the tendency of drying out. Both, flooding of the cathode and drying out of the anode must be avoided in order to prevent major losses in efficiency: The drying of the anode would cause a strong increase of the ohmic resistance and a flooding of the cathode would prevent oxygen to reach the cathode in sufficient quantities leading to diffusion over potentials. One possible solution is the integration of a water management system into the fuel cell system. As this adds to the system complexity, weight and costs it is an

undesirable measure especially in automotive applications. An alternative way to resolve the problem is the exploitation of the back diffusion of water along the concentration gradient between cathode and anode. As according to Fick's first law the diffusion rate is proportional to the concentration gradient:

$$\frac{d H_2O}{dt} = -D \frac{d C_{H_2O}}{dz} \quad (12)$$

and since the difference in water concentration should be kept small it follows that very thin membranes are required. This is in agreement with attempts to reduce ohmic losses in the cell by a reduced membrane thickness. As a consequence all manufacturers of PE membranes have proposed thinner membranes during the last years. The thinnest Nafion membrane NE 111 available today has a thickness of only 1 mil (25.4 μm).

Nevertheless, today's PEMFC show best performance if run at temperatures between 70 °C and 80 °C and with the anode fed with humidified hydrogen saturated at the operation temperature. The operation temperature of a PEMFC is limited by a number of factors. First of all the glass transition of Nafion or similar membranes in their protonated form lies between 120 °C and 140 °C. Temperatures exceeding the glass transition temperature could cause damages to them. Secondly temperatures above 100 °C can lead to a drying out of the cell if not operated with overpressure. Temperatures below 0 °C are equally difficult as during normal operation most parts of a fuel cell system get wetted and freezing becomes an issue especially for automotive applications.

The catalysts used in typical state of the art PEMFC are carbon supported platinum for oxygen reduction reaction and supported platinum or platinum alloys for the anodic oxidation depending on whether pure hydrogen or reformed gas is used as anode feed. Typical loadings are 0.5 mg/cm². Even lower loadings are under investigation. The catalyst is applied to the membrane either directly using various printing processes or by hot pressing of gas diffusion electrodes formed by applying the catalyst to appropriate gas diffusion medias e.g. Toray paper or SGL Sigracet materials. The thus formed membrane electrode assemblies (MEA) are the core of any PEM fuel cell. With state of the art MEAs power densities of 0.5 W/cm² and more at 0.7 V are possible (cf. Figure 4).

AV-1.2.2 Operation of PEMFC with reformed fuels

Though the simplest and most efficient systems could be designed using hydrogen as fuel the still lacking infrastructure for hydrogen distribution and storage forces the use of other more readily available fuels also in PEMFC systems both in stationary and mobile application. To allow for a stable operation of PEMFC with reformed fuels both an appropriate gas clean up and improved anode catalysts are necessary.

In order to improve the CO tolerance of the anode catalysts the use of binary or ternary alloys is under investigation. Highest performance today is obtained using platinum ruthenium alloys having equal atomic ratios of both metals. Due to improved synthesis methods supported platinum ruthenium catalysts with high weight percentages of 60 %

noble metal or even higher (especially important for the DMFC) with a high metal dispersion are commercially available today.

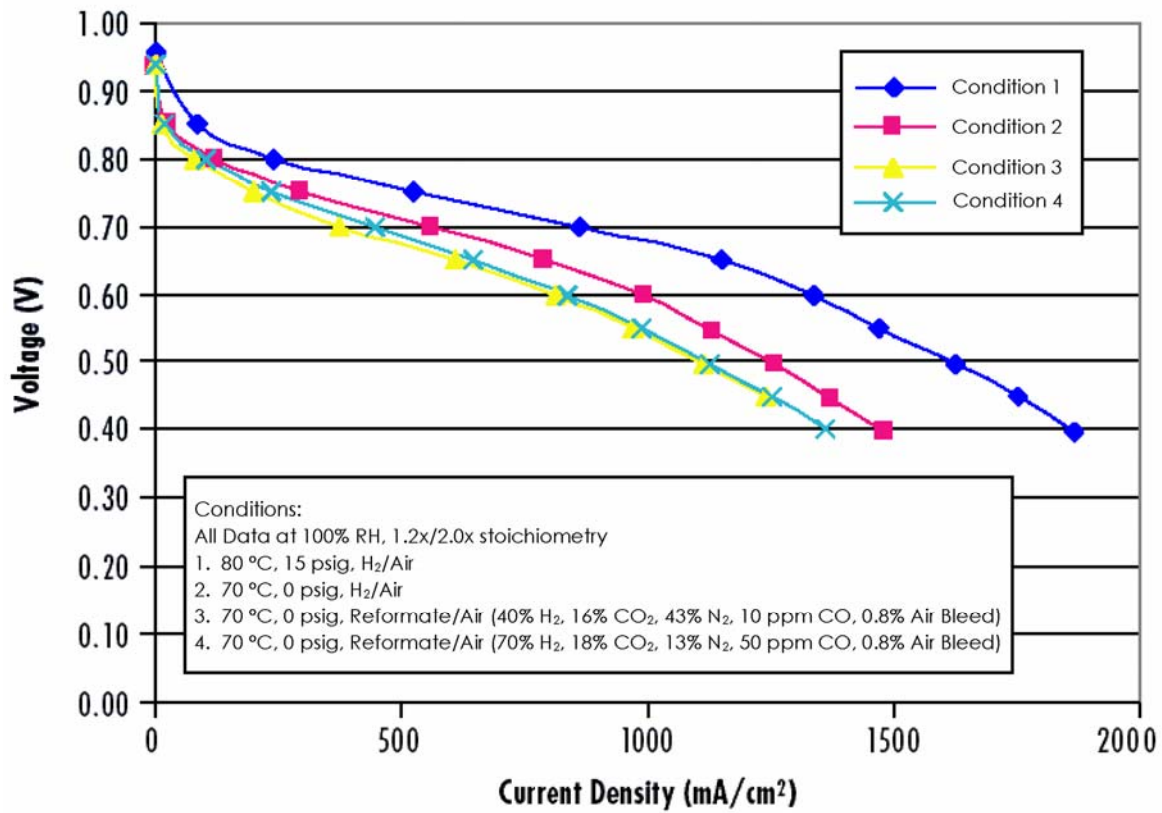


Figure 4- Voltage current characteristic of a W.C. Gore Primea 56 MEA under different operation conditions⁵

The mechanism via which the accelerated oxidation of CO proceeds has yet not been completely understood. A frequently discussed model is that of an increased availability of surface oxygen as depicted below.

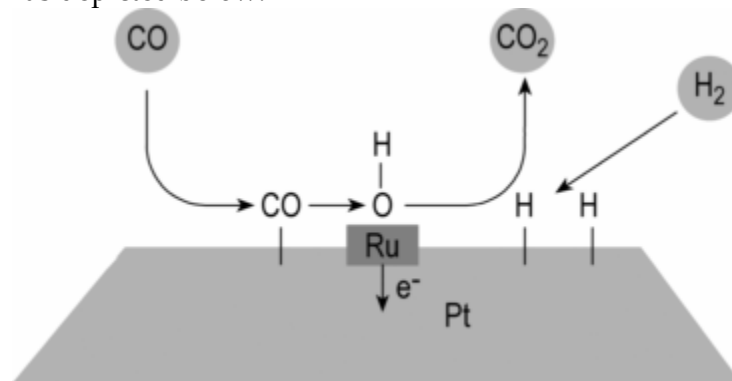
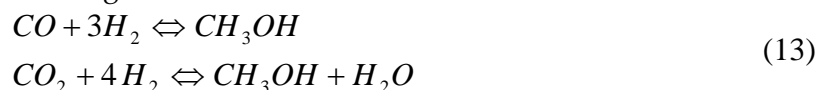


Figure 5- Sketch of a possible reaction mechanism for CO oxidation at Pt Ru catalysts

With respect to the reformer one of the major topics the reduction of the size and the weight of these components. This is of high importance for mobile applications but also stationary applications can profit from improved load change behaviour due to reduced thermal masses. Therefore the use of micro reaction technology for these components has been investigated by a number of groups during the last decade. In the course of these studies it was found that the potential of optimisation using micro reaction technology is quite different for different reformer systems as well as for the different stages in the reformer. Whereas reformers both for steam reforming and partial oxidation have been successfully realised by a number of groups as micro structured reactors the reports on working shift converters are much fewer. The Pacific North Western National Laboratories (PNNL) recently reported the realisation of a shift converter in micro structure design working with a temperature gradient from about 400 °C to 200 °C along the reactor thus including high and low temperature shift conversion in a single reactor. With an extrapolated size of approximately 3 litres for a 50 kWe PEMFC systems this shift reactor also would be rather small¹. The final step in the process chain, the selective oxidation of the remaining CO again has been realised in micro structured components quite successfully. Overall the goal of a compact fuel processor for automotive applications still seems to be feasible. But regarding the difficulties encountered at least for automotive applications a clear tendency towards using pure hydrogen is imposed by industry. Thus (steam) reforming of methane is rather a topic for stationary co generation applications.

AV-1.2.3 Direct Methanol Fuel Cells

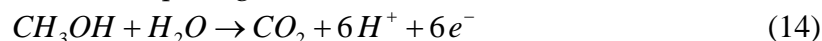
Methanol is a rather suitable fuel for fuel cell applications. Methanol can easily be obtained from synthesis gas.



Synthesis gas itself can be obtained via reforming of virtually any carbon based fuel. Most commonly natural gas is used as feed stock but biomass as a regenerative fuel is also possible.

As the processes in the methanol synthesis (13) are reversible and only slightly exothermic their reversion is an easy way to obtain hydrogen for fuel cells. Especially the low reaction temperature of less than 250 °C and the resulting low CO concentrations can render such systems comparatively simple. But still the additional weight and space for the reformer unit make these systems less suitable for e.g. portable application.

As an alternative the direct electrochemical conversion of methanol is known since 1920¹¹. In a typical PEMFC like set up the gross anodic reaction is as follows:



With a thermodynamic anode potential of $U_{eq} = 0.02 \text{ V}$ vs. NHE the cell should have a similar open circuit voltage as the PEMFC of about 1.2 V.

In reality the reaction proceeds in a multi step process with CO as an important intermediate. The formation of CO as intermediate causes the same problems as CO in reformed gas so that a number of results obtained in developing CO tolerant catalyst for reformed gas can be used here as well. Especially the use of Pt Ru catalyst has been quite successful. Nevertheless, the turnover frequency of methanol remains quite low so that quite large amounts of catalyst are required to obtain reasonable power densities per geometrical surface area. Typical loadings are currently¹² around 5 mg/cm^2 . Such large amounts of catalyst can only be used if the catalyst is applied without further support in form of metal blacks. Supported carbon catalysts have shown higher performance per mass of noble metal but only for comparatively low loadings. At higher loadings the support leads to strongly increased thickness of the catalyst layer and thus to increased ohmic resistance, e.g. for layers with 4 mg/cm^2 noble metal formed with a 40% PtRu / C catalyst an average thickness of about $300 \mu\text{m}$ has been measured whereas a 5 mg/cm^2 layer of Pt Ru black has only an average thickness of about $20 \mu\text{m}$. The limits for the advantageous use of supported catalyst varies in literature between about¹³ 0.5 mg/cm^2 and¹² 1 mg/cm^2 . A possible solution could be the use of supports exhibiting higher proton conductivity. To this respect carbon nano tubes are currently under investigation.

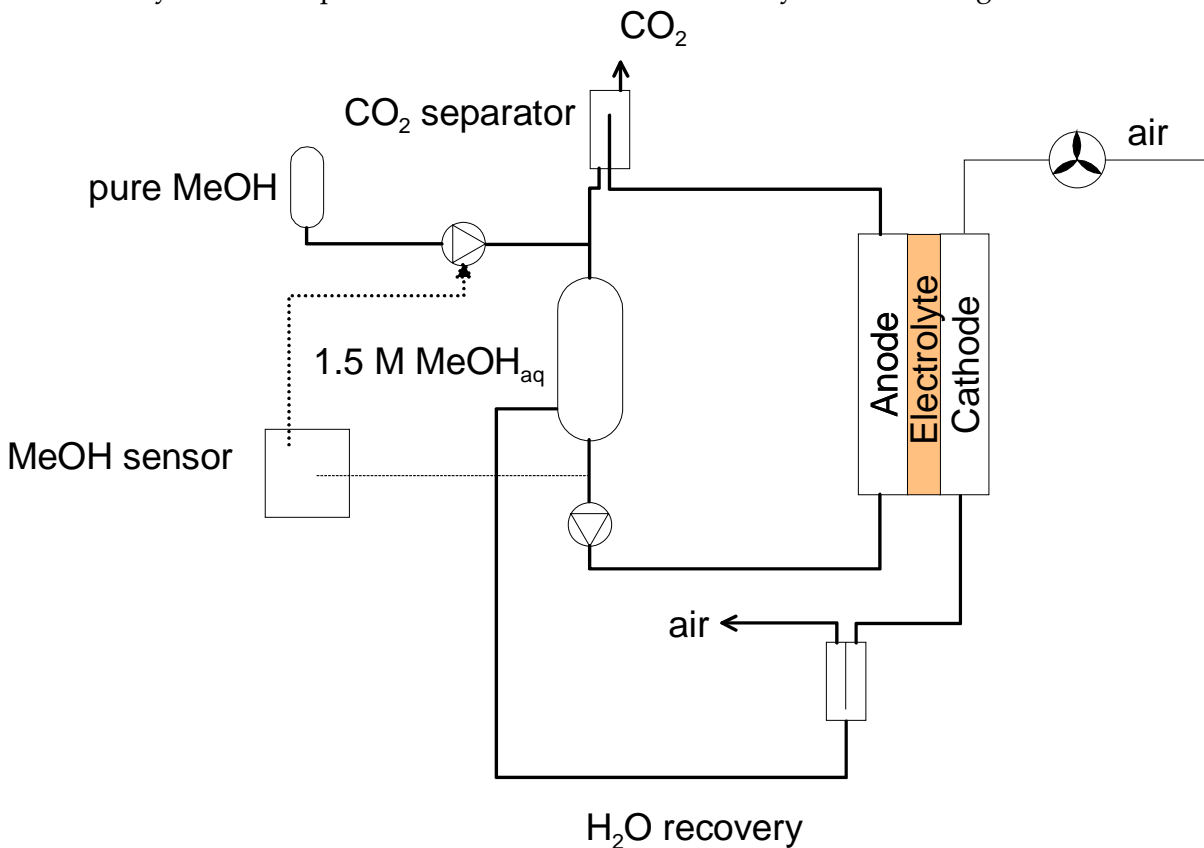


Figure 6-Typical set-up of a liquid fed DMFC

Conventional DMFC systems are operated with a liquid aqueous solution of methanol. Typical concentrations are between 1 and 2 mol/l. Though it is apparent from (14) that water is necessary for the reaction the use of such diluted solution is due to some other issues. Most important factor is the insufficient stability of Nafion against methanol; in contact with more concentrated methanol solution a strong swelling of the membrane is observed. Another issue is the cross over rate of methanol which drastically increases with concentration also increasing the Faraday losses. The latter can reach up to 50% under unfavourable conditions¹². Improved membrane materials are therefore sought after¹.

In a standard set up as shown in Figure 6 methanol solution is circulated because of the very low fuel utilization of less than 10% with each passage. This is necessary in order to force the formed CO₂ out of the cell.

To minimize the fuel storage DMFC systems should be designed such that pure methanol can be used for the refueling. This requires that most of the water which is removed from the cathode is recovered and that the methanol concentration can be measured in the anode circuit.

For smaller power demands a simpler set up has been proposed by mti micro fuel cells. Here pure methanol is fed to the anode passively via the capillary forces of a metal foam which acts as gas diffusion media and current collector. The necessary water is recovered from the cathode via back diffusion. The cathode itself works with air in a self breathing mode¹.

AV.1.2.4 Stationary low temperature fuel cell systems

The standard fuel for stationary fuel cell applications is natural gas. As this fuel cannot be converted directly in low temperature fuel cells with any reasonable performance stationary low temperature fuel cell systems do require a reforming unit as depicted in Figure 7. The problem of coupling a methane reformer to a low temperature fuel cell is that the reforming of methane proceeds at quite high temperatures of about 800 °C leading to quite high CO concentrations in the product gas of more than 10%. As a consequence a multi step gas clean up is required to generate hydrogen of suitable purity for the use in the fuel cell. Furthermore the heat of the product gases needs to be recovered to keep the overall system efficiency at an acceptable value. Thus reformer systems for low temperature fuel cells become a quite sophisticated network of reactors and heat exchangers (cf. Figure 8).

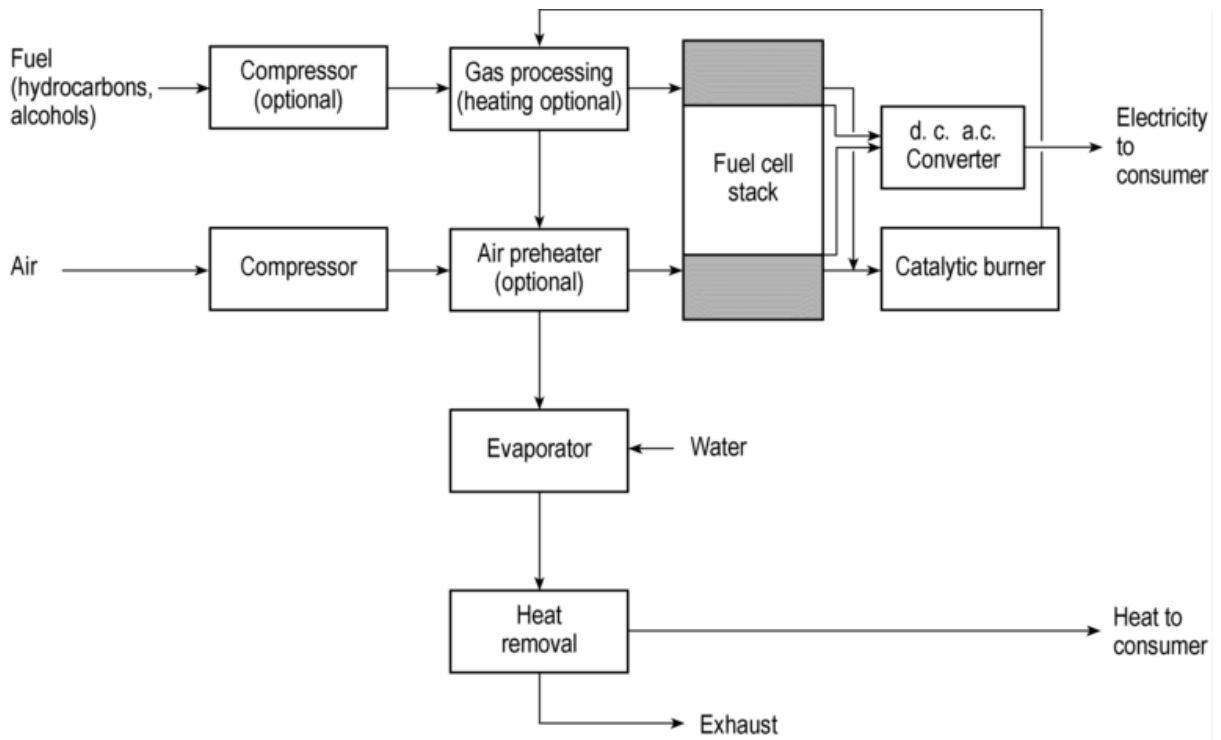


Figure 7-General set-up of a low temperature fuel cell based stationary CHP facility

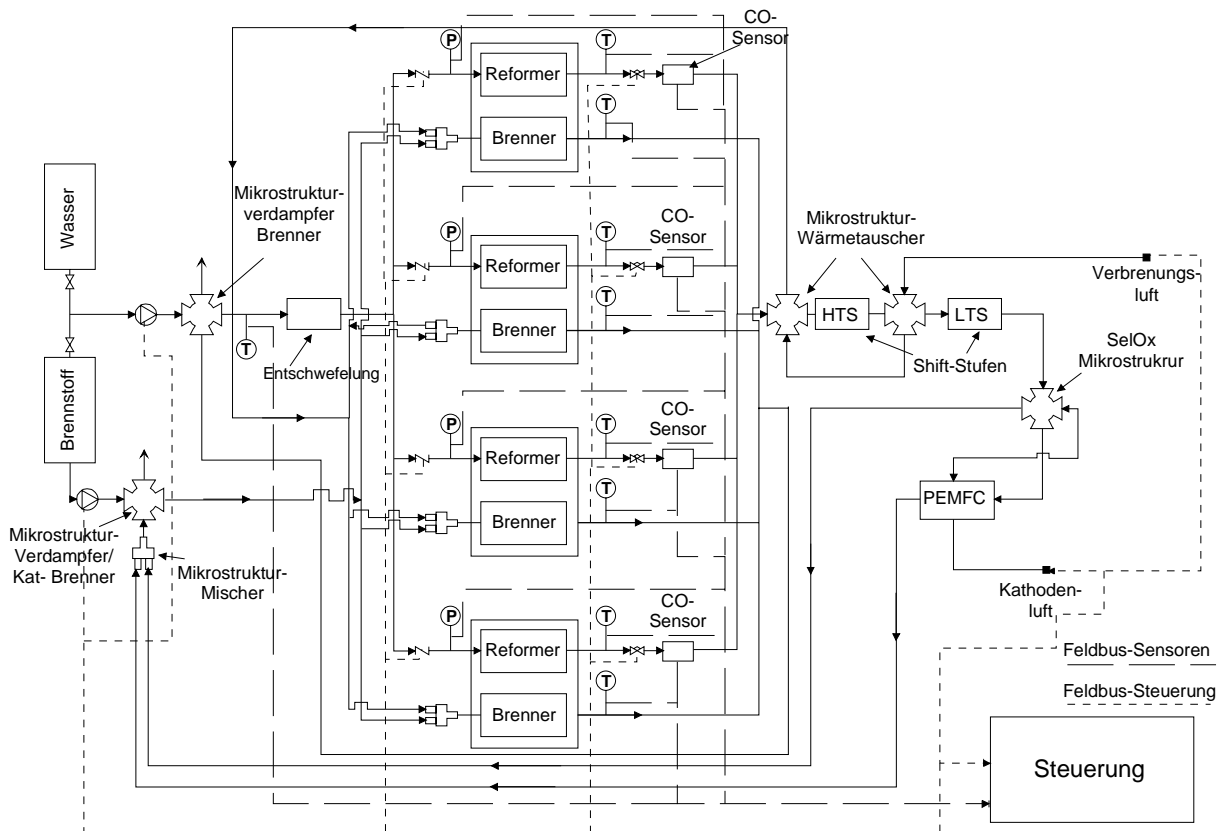


Figure 8-Sketch of a micro-reactor based PEMFC systems fed with hydrocarbons

Another characteristic of most stationary applications is that in addition to electricity also heat is demanded. The temperature at which the heat needs to be provided is different for different applications. For industrial applications temperatures well above 200 °C are required as the heat regularly is used to produce process steam. This field today is clearly a domain of conventional systems and the future of high temperature fuel cells.

The situation becomes different if the heat is used for residential heating purposes or the set up of a small district heat network. In the former case temperatures of 60 °C to 70 °C are sufficient for the latter case temperatures of 70 °C to 90 °C are required. Comparing this to the fuel cell data the temperature level of PEMFC are just sufficient for the use in these systems. First prototypes of such systems have been realised e.g. by Vaillant and Plugpower¹.

A problem of the residential co generation of heat and power arises from the fact that the heat and electricity demand vary throughout the year in quite different ways. In particular during the summer season heat demand becomes quite low whereas the demand for electricity can strongly increase if electricity is used for chilling. In order to achieve higher system efficiencies throughout the year motor engines and gas turbine co generation facilities may be coupled to sorption chillers. These devices can use the reject heat of the motors at a temperature level between 80 °C and 100 °C in order to produce usable cold reducing the demand for electricity at the same time. A comprehensive review of these

devices may be found in¹. In the case of low temperature fuel cell systems standard sorption chillers can scarcely be used due to the required temperature of the driving heat. Here either a more complex two stage sorption cycle as described e.g. in¹ is required or the parameters of the chilled water loop have to be adjusted. The latter option seems to allow for economic installations in small scale systems (10 kW to 100 kW) as has been demonstrated in¹ for solar heat systems with parameters very similar to those of PEMFC systems.

AV-1.2.5 Low temperature fuel cells in mobile applications

Currently two applications for fuel cells on board of automobiles are under discussion. First of all fuel cells as power sources for an electrical drive train and secondly as an auxiliary power unit (APU) delivering electrical energy independently from the main engine. The two applications strongly differ in the size of the system, about 50 kWe for propulsion compared to 2 kWe to 5 kWe for APU, and the usable fuels. With respect to the existing fuel infrastructure and the high energy density and easy handling of liquid fuels a combination of reformer and PEMFC has been favored by the automotive industry for a long time. As fuels gasoline / diesel or methanol as an easier to reform alternative were considered. In recent times more and more companies changed their opinion and today a solution with hydrogen stored on board either under high pressure (up to 700 bars) or cryogenic is preferred as it allows for a much simpler and potentially less expensive system.

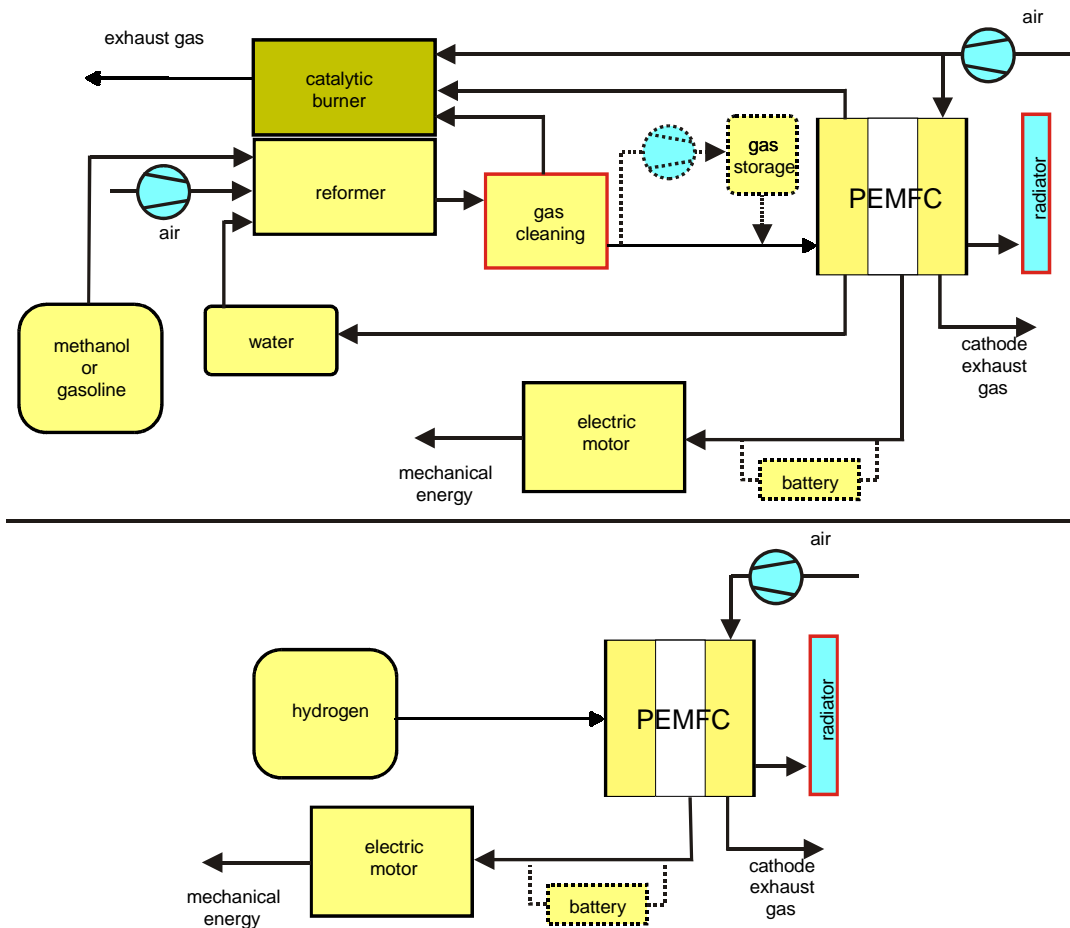


Figure 9-Mobile fuel cell systems operating either on reformed fuel (upper) or pure hydrogen (lower)

To keep the fuel cell systems as small as possible it is further requested that the PEMFC operates at higher temperatures of at least 120 to 130 °C to reduce the size of the radiators needed for the exchange of the waste heat. Further on, the cell should operate without external humidification. To fulfil these requirements improved membrane materials are required.

For APU application it is in general required that the fuel cell operates on the same fuel as the main engine, today this means gasoline or diesel. On the other hand the APU should help save energy in situations where otherwise the main engine running under low partial load would have provided the necessary electrical energy in combination with an alternator. This applies in particular for parked lorries.

Besides in automobiles, the use of fuel cells in other mobile applications is also under discussion. One important field might be the generation of electricity for on the ground airplanes. Here a fuel cell APU may offer an increased efficiency in spite of the necessary kerosene reformer because of the very low efficiency of the turbine APU's used today. As

further advantage the in flight production of water is under investigation e.g. by Airbus Deutschland.

AV-1.2.6 Fuel cells for portable applications

In these applications fuel cells are expected to replace conventional batteries making the higher storage capacity of the fuel the most important advantage. Conversion efficiencies are of lower importance as long as they do not restrict operation time. Furthermore, typical batteries used today like lithium ion batteries are quite expensive themselves so that the market barrier for the introduction of fuel cells is lower than in other applications. On the other hand some additional requirements need to be observed. The operation temperature of portable systems regularly should not exceed 50 °C to 60 °C. This does not allow for a reformer. Further, it is important that the fuel storage must achieve a high level of security (for laptop computers e.g. clearance by IATA in general is necessary).

In this field PEMFC with chemical hydrogen storage (or possibly pressurized storage) are competing with DMFC. The advantage of the PEMFC is their much higher power density. Their disadvantage is that today's hydrogen storage systems are still not satisfying and that the missing hydrogen infrastructure prevents an easy refill of the hydrogen storage. Methanol is easier to handle but the low power density of today's DMFC especially if operated at low temperatures and the peripheral components for the water management result in larger systems. Nevertheless, portable DMFC systems have been first demonstrated by Toshiba, Smart Fuel Cells and mti micro fuel cells.

AV 1.3 Deficiencies of today's low temperature fuel cell system

The level of performance achieved with today's low temperature fuel cell and especially the PEMFC is quite high if hydrogen can be used as fuel. And this is also the most apparent deficiency of this technology with the dependence on a fuel which is not readily available. Further problems are found depending on the intended application.

AV-1.3.1 Deficiencies of PEMFC

In the mobile sector the efficiency of today's PEM fuel cells is still not high enough as the disposal of the generated waste heat still causes problems. A PEMFC stack with 50 kW power operating at an average cell voltage of 0.7 V has a voltage efficiency of 58%. It follows that at least 36 kW of thermal power need to be removed. The problem becomes even more severe as the operation temperature of today's PEMFC is quite low and often stacks are operated at higher power densities, i.e. low voltages and high currents.

A second problem is the high demand on membrane humidification. The water management significantly adds to the system complexity, weight, size and costs.

A further minus is a still insufficient long term stability of the PEMFC caused by chemical degradation of the MEA as well as its inappropriate resistance to the mechanical stress in the stack.

AV-1.3.2 Deficiencies of DMFC

The central problem of today's DMFC is their low area related and volume related power density. Two major deficiencies are responsible for this, the high cross over rates of methanol and water through the Nafion membrane and the low activity of today's catalyst for the methanol oxidation leading also to an inappropriate demand on noble metals.

Further deficiencies concern the systems design. So far no convincing solutions for methanol dosage into the anode circuit and for the removal of the formed CO₂ from the anode circuit without additional methanol losses have been found.

With respect to sustainable development the DMFC suffers from the fact that methanol today is almost entirely produced from fossil resources. But it may be accessible in the future by regenerative sources.

AV-1.3.3 Deficiencies in oxygen reduction reaction

The oxygen reduction reaction is the main source of over potentials with today's PEMFC. It is likewise a source of efficiency loss in the DMFC were the parasitic oxidation of the methanol crossing the membrane adds to the problem. Improved catalyst for the oxygen reduction and oxidation reaction are therefore an important issue even beyond fuel cells in electrolyser systems or air batteries.

AV 1.4 Future research and development needs for improved low temperature fuel cells

In the previous sections it has been shown that the fuel cell technology has reached a fairly good level of development. Nevertheless, a number of problems remain which need to be addressed by future research in order to better use the potential of the technology for a sustainable development.

AV-1.4.1 Improved membrane materials for higher operation temperatures

Both stationary and mobile applications can profit if the operation temperature of the fuel cells could be raised to temperatures between 200 °C and 300 °C. The profits of such a higher temperature would be:

- conduction mechanism not relying on liquid water
- no electro osmotic drag
- no flooding of the cathode
- no drying out of the anode
- no sensitivity to CO poisoning at T > 250 °C
- simplified exchange of waste heat
- more options of using waste heat

ability for internal reforming of lower alcohols

To achieve this goal, new materials will need to be developed because this target temperature is not in accord with the conduction mechanism of the membrane material used today relying on liquid water. In developing such new materials it should be avoided using any starting materials which are exceptionally expensive, scarcely available or doubtful with respect to a sustainable development, conditions which apply to the fluoro polymers used today at least to some extent. To this end, it is worthwhile also to consider inorganic alternatives like the ammonia polyphosphate composites which have been proposed previously^{2 3}.

AV-1.4.2 Increased conversion efficiency

Especially for mobile and portable application where reject heat can rarely be used a further increase of the conversion efficiency is necessary. A specific power output of 0.5 W/cm^2 at an average cell voltage between 0.8 V (target 1) and 0.9 V (target 2) corresponding to voltages efficiencies higher than 66% should be aimed at. In order to achieve this goal a number of improvements will need to be made. A key role will be played by improved electro catalyst as the initial voltage drop which can be attributed to the reaction over potential must be reduced drastically to reach the target. A second problem is the low open circuit voltage with less than 1.0 V compared to 1.2 V according to thermodynamics. Beneath catalyst properties here also the small but present cross over of hydrogen is responsible so that an improved less permeable membrane material is also required. Reduced permeability should therefore become a further issue in the development of new membrane materials.

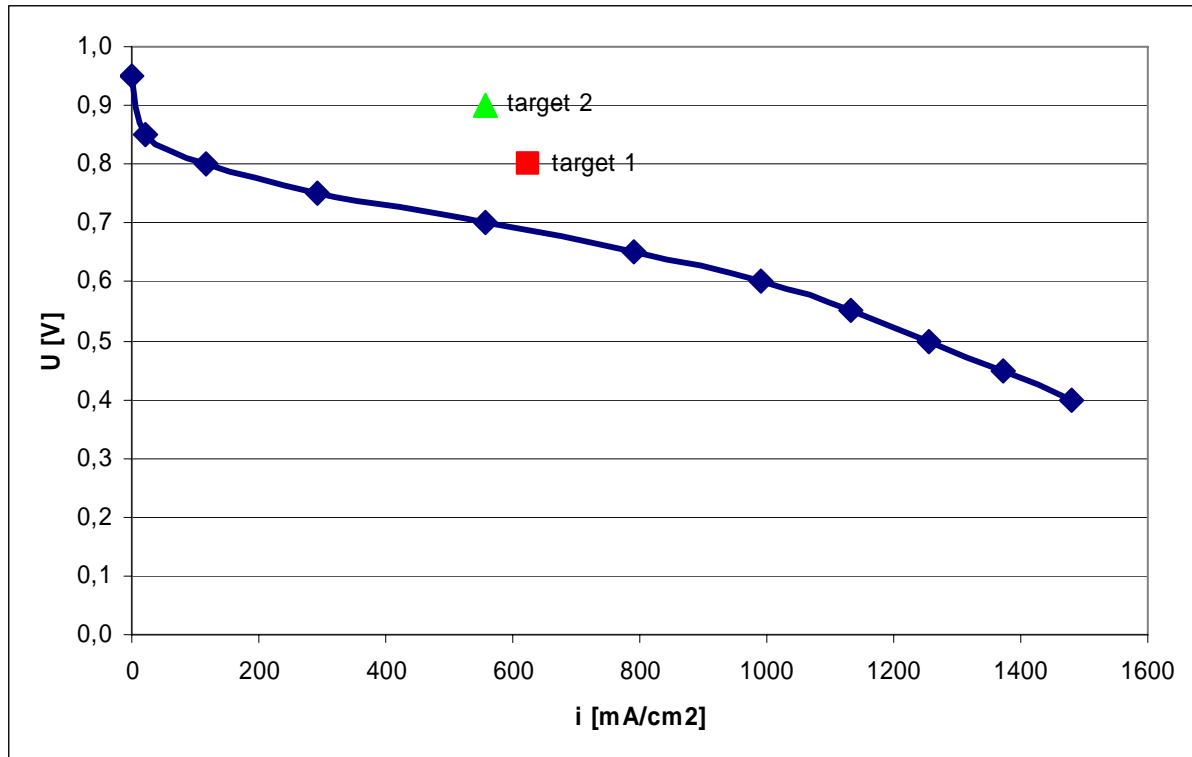


Figure 10-State of the art PEMFC U-i curve (condition 2 of Figure 4) and possible development targets (see text)

As the major source of electrode over potentials can be found at the cathode the development of improved oxygen reduction catalyst must be the first goal. Nevertheless it should also be considered to further improve the anode catalyst e.g. by use of better carbon supports.

AV-1.4.3 Improved system designs

As a consequence of the raised stack temperature also the temperature of the stack off gases will increase. Heat released at this elevated temperatures is much more usable than heat released at the low temperatures of today's PEMFC. In mobile application the major advantage will be drawn from a reduced size of radiators for recooling the cooling liquid. For stationary systems the loss of efficiency still would be too important. Here an appropriate use of the heat must be found. Here further research concerning the thermodynamics of fuel cell systems is required and especially thorough simulation of potential co or tri generation systems will have to be performed.

AV-1.4.4 Enlarged choice of usable fuels

As has been said before, the dependence of today's low temperature fuel cell technology on hydrogen as fuel is one of its major drawbacks. Further research is necessary to enlarge the choice of suitable fuels. Thereby the direct conversion in the fuel cell should be

preferred. Nevertheless improved reforming techniques will remain an issue in the short to midterm future for stationary applications.

Due to their thermodynamic properties alcohols and other oxygenated fuels are most suitable for the conversion in direct fuel cells.

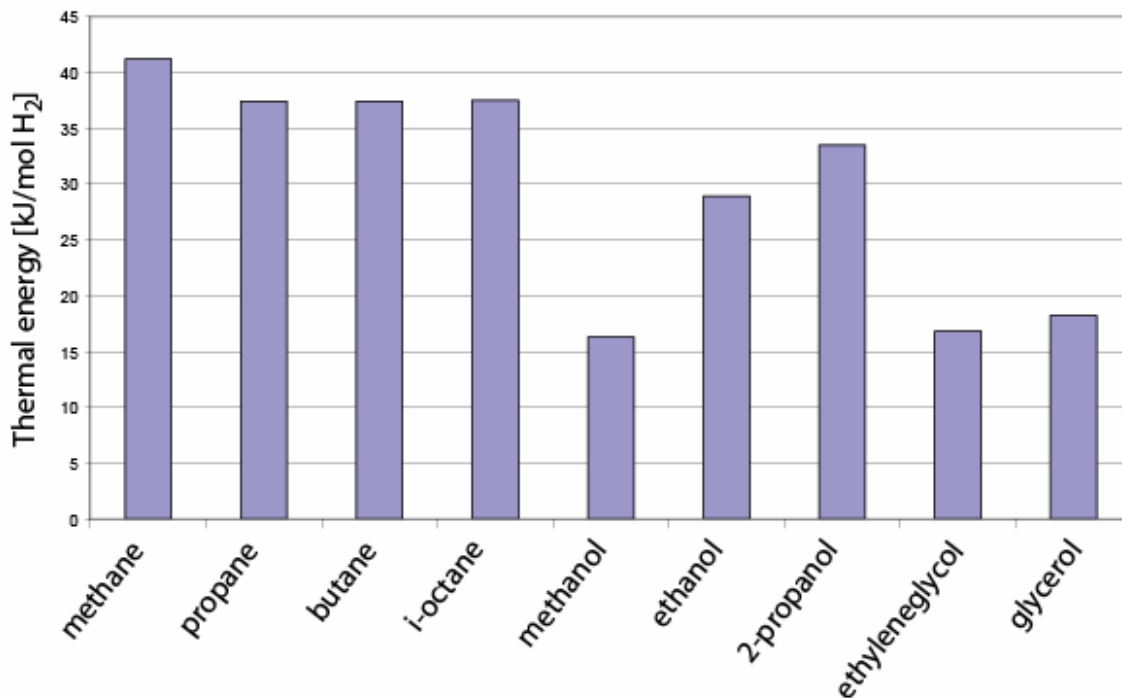


Figure 11- Thermal Energy demand for the production of 1 mol H₂ by steam reforming of different fuels

This type of fuels is also of high interest as they may be obtained from biomass even much easier than methanol e.g. via fermentation processes. A further potential advantage for the use in Nafion based fuel cells could be the reduced cross over rate.

The major challenge in converting fuels like ethanol, ethyleneglycol or glycerol in fuel cells will be to find catalysts which are able to induce the rupture of the C–C bond at an acceptable rate at these low temperatures. First experiments have revealed that the performance of a standard DMFC cell which is fed with aqueous ethanol solutions is drastically decreased².

In spite of this difficulty such fuel cells could be feasible especially if the operation temperature could be increased as shown above. Even the direct conversion of hydrocarbons might be possible as some unpublished results of the group of Prof. Stimming have shown²¹

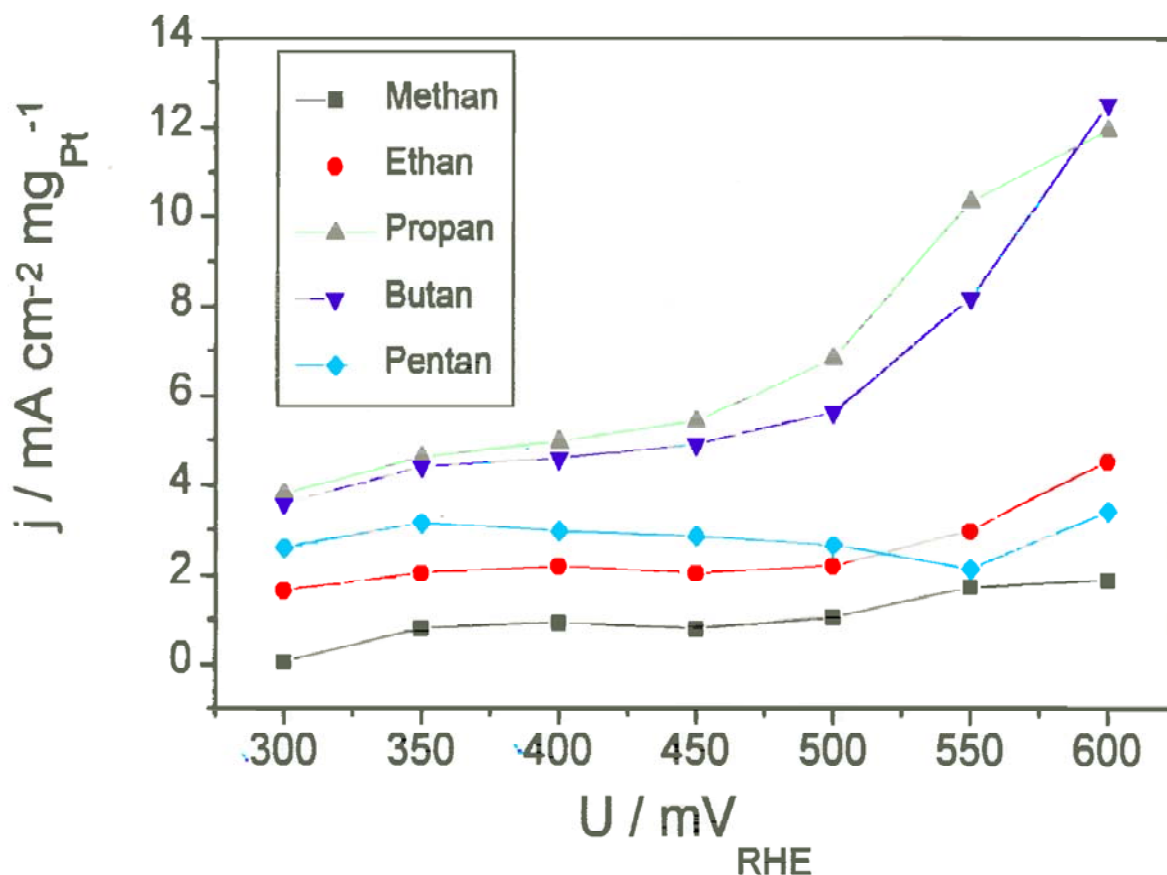


Figure 12-Polarisation curves for the anodic oxidation of short chained hydrocarbons at PEMFC like gas diffusion electrodes; feed contains stoichiometric amounts of water²¹

AV-1.4.5 Bio-electrochemical fuel cells

In this entirely new class of fuel cells enzymes are used as catalysts. This can offer a number of advantages. As virtually every biological substance can be biodegraded in nature by biological processes employing enzymes the choice of fuels which can be converted in these cells should be rather large. Furthermore, the pronounced selectivity of enzymes for their substrates would allow for membrane free cells simplifying the system design. On the other hand this high selectivity may also cause further problems. In many cases the oxidation of a substance like glucose in biological cells proceeds via a cascaded process involving a number of different enzymes each specific for a special step of the process. To arrange for such a process in a technical cell will be quite challenging. But the major challenge is to attach the enzyme in a suitable way to an electrode in order to set up an external electric circuit.

In spite of all difficulties bio electrochemical fuel cells are a most promising technology as they would also allow for complete new application for fuel cells especially in medicine

where they could become a compatible energy sources for implanted sensors which are currently developed.

AV-1.4.6 Summary of research need

In summary it can be stated that materials research will be the major task in future fuel cell developments. Herein two aspects deserve highest attention

Improved membrane materials allowing for higher operation temperature at a reduced cross over rate of water and fuel and an easier exchange of waste heat in automotive applications

Improved electro catalyst for

- . Better kinetic of the oxygen reduction reaction
- . Anodic oxidation of fuels having C–C bonds

Beneath materials research also the engineering aspects must not be forgotten. Especially for stationary applications suitable ways to use the waste heat and the integration of fuel cells with existing co or tri generation facilities especially such working on regenerative resources should be considered. Here thorough thermodynamic analyses and system simulations are required.

AV 1.5 Conclusions

Today's low temperature fuel cell technology has achieved a quite high level. Efficient fuel cells for different applications can be realised if hydrogen is available as fuel. As the availability of hydrogen is doubtful even in future, future fuel cell research should focus on enlarging the choice of fuels suitable for the conversion in fuel cells. Beneath new membrane materials allowing for moderately raised operation temperatures new catalyst need to be looked for. On the other hand the system aspect must be observed and a better understanding of the thermodynamic properties of whole fuel cell systems aimed at.

References

- [1] C. Ewen, C. Henschel "The Fuel Cell – Innovation for Sustainability" study published by IFOK GmbH and Celanese AG
- [2] T. Kenyo, Y. Ogawa *Solid State Ionics* 76 (1995), 29–34
- [3] M. Cappadonia, O. Niemzig, U. Stimming, *Solid State Ionics* 125 (1999), 333–337
- [4] K. Sasaki, Y. Teraoka *J. Electrochemical Society* 150(7) (2003), A878
- [5] K. Poast, M. Burghardt, L. Mustin, H. DeRonck, "Space Shuttle Fuel Cell Life Extension Program", Fuel Cell Seminar 2003, 3rd – 7th November 2003, Miami Beach, FL
- [6] Brochure Gore™ Series 56 MEA for Stationary Power
- [7] G.A. Whyatt, W.E. TeGrotenhuis, J.G.H. Geeting, J.M. Davis, R.S. Wegeng, L.R. Pedersen Demonstration of Energy Efficient Steam Reforming in Microchannels for Automotive Fuel Processing in M. Matlosz, W. Ehrfeld, J.P. Baselt (Eds.) Proceedings of the 5th International Conference on Microreaction Technology (IMRET 5), 27th to 30th May 2001, Strasbourg (France), Springer Verlag Berlin (2002), pp 303–312

- [8] P.Pfeifer, L. Bohn, O. Görke, K. Haas Santo Wasserstoffherzeugung aus Kohlenwasserstoffen mit Mikrostrukturkomponenten Wissenschaftliche Berichte des Forschungszentrums Karlsruhe FZKA 6990 (2004), 213 214
- [9]. C. Cremers, U. Stimming, J. Find, J.A. Lercher, P. Reuse, A. Renken, O. Kurtz, K. Crämer, K. Haas Santo, O. Görke, K. Schubert Micro Structured Steam Reformers as Flexible Hydrogen Generators for Fuel Cell Systems Fuel Cell Seminar 2003, Miami Beach, FL (USA), 3rd 7th November 2003
- [10] W.E. TeGrotenhuis et al. "Progress in Developing a Microchannel Based Fuel Processor for Automotive PEM Fuel Cell Power Systems", 7th International Conference on Microreaction Technology (IMRET 7), 7th to 10th September 2003, Lausanne, Switzerland
- [11] E. Müller, Z. Electrochem. 28 (1992) 101
- [12] V. Gogle et al. J. Power Sources 127(1 2) (2004), 172 180
- [13] L. Liu et al. Electrochimica Acta 43(24) (1998), 3657 3663
- [14] J. Kerres et al. J. New Materials for Electrochemical Systems 5 (2002), 97 107
- [15] S. Gottesfeld, Keynote Lecture, Fuel Cell Seminar 2003, 7th to 10th November 2003, Miami, FL (USA)
- [16] Vaillant GmbH Informationsbericht Brennstoffzellen Heizgerät 2003
- [17] F. Ziegler, Int. J. Therm. Sci. 38 (1999), 191 208
- [18] C. Schweigler, VDI Fortschrittsberichte, Reihe 19, Band 121 (1999)
- [19] F. Storkenmaier et al. "Small capacity Water / LiBr absorption chiller for Solar Cooling and Waste Heat driven Cooling" 21st International Copngess of Refrigeration, Washington, DC (USA), Proceedings
- [20] F. Vigier, C. Coutanceau, A. Perrad, E.M. Belgsir, C. Lamy, J. Appl. Electrochemistry 34(4) (2004), 439 446
- [21] Diplomarbeit]

AV 2 SOLID OXIDE FUEL CELLS

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AV 2.1 Characteristic features of SOFC in comparison with other fuel cells

The major characteristic features of fuel cells are deeply related with the electrolyte so that fuel cells are categorized in terms of the electrolytes to be used. The solid oxide fuel cells are built by using solid oxides such as yttria stabilized zirconia (YSZ) as electrolyte. This, therefore, has quite different features from the molten carbonate fuel cells or from the phosphoric acid fuel cells based on liquid electrolytes. In SOFCs, there is no need to manage the liquid electrolyte nor to manage the corrosion of materials in contact with corrosive liquids. Instead, the ionic conductivity is not high compared with those in liquid electrolytes so that this requires the handling of thin films with sophisticated layered structure. Furthermore, gaseous sealing and interface contact resistance become technological important issues.

SOFCs are operated around 1000 °C; this gives rise to merits of SOFCs in utilization of heats generated from fuel cells and demerits of additional requirements for overcoming thermal stresses. Another important feature of SOFCs comes from the fact that oxidant related species (oxide ions) are transported through the electrolyte instead of protons in PEFCs. This leads to very important differences in fuel flexibilities between the high temperature and the low temperature fuel cells. The high temperature operation is important in the following senses:

- (1) Heat required in the endothermic reforming reaction of hydrocarbons to carbon monoxide and hydrogen can be supplied from the output heat from the high temperature fuel cells.
- (2) The remaining fuels can be burned and used in the combined gas turbines. In turbine systems, the combustion process does not contribute to the energy conversion, whereas the fuel cells can generate electricity during the oxidation process but it is not easy to utilize fuel until 100%. It is attractive to combine fuel cells and thermal engines

AV 2.2 Historical Survey

To develop SOFC stacks, it is needed to develop materials, material processing techniques and stack design at the same time; these three technological issues are closely related with other so that sequential development from materials, through materials processing, stacking technology to system development does not work well for SOFCs. This implies that, since the beginning, sophisticated R&D efforts are needed.

The first success was obtained by Westinghouse PC in 1980s, in the US. They adopted a sealless tubular type design with electrochemical vapor deposition (EVD) technique that is

based on a clever way of fabricating dense films on porous substrates. They used yttria stabilized zirconia as electrolyte, lanthanum strontium manganite as cathode, nickel as anode and lanthanum magnesium chromite as interconnect. High conversion efficiency of fuels into electricity and long lifetime (over 70,000 h) were achieved in this stack. This was an epoch making success. In particular, its long lifetime confirmed that degradation in SOFCs can be expected to be quite small, when the severe chemical reactivity at 1000 °C can be appropriately avoided by proper materials selection from the equilibrium thermodynamics point of view.

This success led to a worldwide enthusiasm for developing SOFC stacks with recognition that the sealless tubular SOFC stacks by WHPC had some weak points in the sense that the power density was small and the fabrication cost high. To overcome the low power density of tubular stacks, many groups started to construct planar stacks that need gas sealing at edges and good contact across the interfaces. In particular, the Argonne National Laboratory proposed in 1980s, the monolithic cells that have high power density and can be fabricated with wet process. Even so, the technology associated with developing planar SOFC stacks, is highly sophisticated so that only a few developers succeeded in making progress so far.

In US, the SOFC system investigations have been well advanced on the basis of successfully constructed tubular stacks. In Japan, the major achievement has been made in adopting the low cost fabrication methods based on ceramic technology for both tubular and planar stacks. Particularly, the technology associated with oxide interconnect has been well developed in Japan. In Europe, on the other hand, the planar SOFCs with metal interconnects have been built to increase the power density compared to the tubular cells and to reduce the materials cost by using Cr based alloys or ferritic alloys instead of expensive (LaCrO₃ based) oxide interconnects.

The operation temperature of SOFC stacks depends on the interconnect materials adopted for respective stacks. When oxide interconnect is adopted, the operational temperature is set around 1000°C, whereas a lower temperature is needed when the metal interconnect is used; this is done to avoid the degradation originating from the use of metals at high temperatures. To operate SOFCs at lower temperature, further development is required to improve the oxide ion conductivity of the electrolyte and the electrode activities. As a result, investigations on new electrolytes and electrodes have been made extensively. Typical new materials are scandia stabilized zirconia, lanthanum strontium gallium magnesium oxides as electrolyte, lanthanum strontium ferrite cobaltite as cathode.

AV 2.3 Applications

The primary application of SOFCs has been regarded as the large stationary power generation. For this purpose, efforts have been made to increase the conversion efficiency by combining them with Gas Turbines in MW size system. First test on operating SOFC

GT combined system was made by Siemens Westinghouse PC. The use of SOFC as cogeneration of heat and power is also regarded as standard applications for north Europe, Canada and northern parts of US.

In recent years, there has been a growing interest in developing a smaller system in the range of several kW to several ten kW. This is for stationary use as well as for automotive use. Particularly, proposal of utilizing SOFC as Auxiliary Power Unit gives rise to more general considerations on how to use SOFCs in transportation fields. As a result, APU systems for tracks, ships, trains are now under considerations in various sizes (from several kW to several 100 kW).

DoE and DoD, in the US, started in 2000 a new 10 year SOFC project called Solid State Energy Conversion Alliance.

AV 2.4 Current Issues

Cost, reliability and conversion efficiency are the important parameters for fuel cells. For SOFCs, reduction of cost can be made in three ways: 1) first one has to reduce the amount of expensive elements such as Y, Sc, Ga, La. 2) it is necessary to adopt an inexpensive processing technique for the ceramics (a wet method with a small number of sintering steps) and for the metals (coating, surface treatments....) 3) it is necessary to increase the power density per area or volume.

Reliability depends on the materials to be used in the stacks. The EVD cells fabricated by WHPC exhibited a long stability for more than 70,000 h. Even so, the other stacks fabricated by different methods should be examined carefully because diffusion properties leading to degradation may be different. When metal interconnect or sealing materials are used, it is important to confirm whether the long stability can be achieved. Particularly, the chromium vapor emitted from oxide scale of metal interconnect may cause severe degradation because those vapors attack the electrochemical active site in the electrolyte/cathode/gas three phase boundaries. This phenomenon is peculiar in the sense that the degradation becomes large when the temperature is lowered. This implies that the overpotential which increases with decreasing temperature is a key driving force for this degradation.

Conversion efficiency of SOFCs is expected to be very high, although the theoretically predicted thermodynamic efficiency is lowered with increasing temperature. This is mainly because of the low overpotentials for the cathode and the anode reactions and also because the heats evolved from the fuel cells can be utilized in the reforming process around 700 800°C.

Recently, there has been some interest in those SOFCs which can be fabricated in a simple manner even though the conversion efficiency is lowered. A typical example is the micro tube SOFCs; here, no interconnect materials are used for high temperature cell to cell

connection, but the interconnection is made at low temperature outside the stacks. This makes the fabrication easier to the detriment of the electrical loss along the long electrical path. In turn, this implies that the interconnect technology is crucial to determine whether the construction of SOFC stacks can be successful or not.

AV 2.5 Perspective

For the stack developments, the following points are important;

for the high temperature stacks with oxide interconnects, once an inexpensive fabrication method is successfully adopted, the increase of the power density will be the most important issue to reduce costs and lead to the commercialization.

For the intermediate temperature stacks with metal interconnects, an inexpensive fabrication method of coating on the metal interconnect is needed. In addition, the use of expensive elements such as Sc or Ga should be reduced

In addition, the following research topics will be focused in the near future:

Development of new electrolyte: the discovery of the lanthanum gallate based oxide as a new electrolyte in 1995 opened a new era of developing lower temperature solid oxide electrolyte to bridge the so called conductivity gap between the low temperature proton conductive material and the intermediate temperature solid oxide material.

New electrode reactions: direct hydrocarbon SOFC or one chamber SOFC without using interconnects will be of great interest in view of the new aspects associated with the electrochemical reactions. There is some indication that water vapor which can be dissolved into ceria based oxides may affect the electrode reaction mechanisms.

Fuel flexibility is one of the characteristic features of SOFCs when compared with other fuel cells. In particular, there can be a variety of methods in utilizing hydrocarbons, biomass, ammonia etc. In contrast to the PEFC (which has a close relationship with the hydrogen technology), the utilization of hydrocarbon fuels is the most important aspect of the high temperature fuel cells. The current nickel anode suffers from carbon deposition. Even so, an impressive work was made using Ni/ScSZ cermet anode for only 3% humidified methane. This anode was able to operate more than 100 h under a high current density. This leads to new motivations to investigate nickel anodes for hydrocarbon fuels. Furthermore, anodes tolerable against redox cycles or sulfur impurities are also highly desired. For this purpose, oxide anodes without metals are currently investigated extensively.

Small scale SOFC less than 1KW: Requirements for mobile applications will be strengthened. For this purpose, new technology of fabricating fine structures will be needed in addition to the development of new materials.

AV 3 TECHNOLOGICAL STATUS OF THE MOLTEN CARBONATE FUEL CELL

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AV 3.1. Introduction

A molten carbonate fuel cell (MCFC) has been developed to ramp up distributed power generation from several hundreds of kilowatts to the megawatt range. The MCFC, operating at 600–650 °C, presents several advantages: high efficiency, low emissions, and capacity to utilize various fuels such as coal, natural gas, petroleum and hydrogen. Electrochemical reactions in high temperature fuel cells proceed easily. Since the MCFC operating temperature is higher than 600 °C, the exhaust gas can be converted to electricity. The combined energy efficiency thus achieved is more than 50–60%. From the several hundreds of kilowatts needed for a dispersed power generating system, waste heat, with an average temperature of 200–300 °C, can be used for heating. Therefore, the total energy efficiency of the MCFC is estimated as more than 80%.

AV 3.2. Principle of operation of the MCFC

Figure 1 presents a diagram illustrating the principle by which the MCFC operates. The cell structure consists of an anode, a cathode and electrolyte. The anodic and cathodic reactions in the fuel cell can be formulated as follows:

Cathode reaction:



Anode reaction:



The overall reaction is:



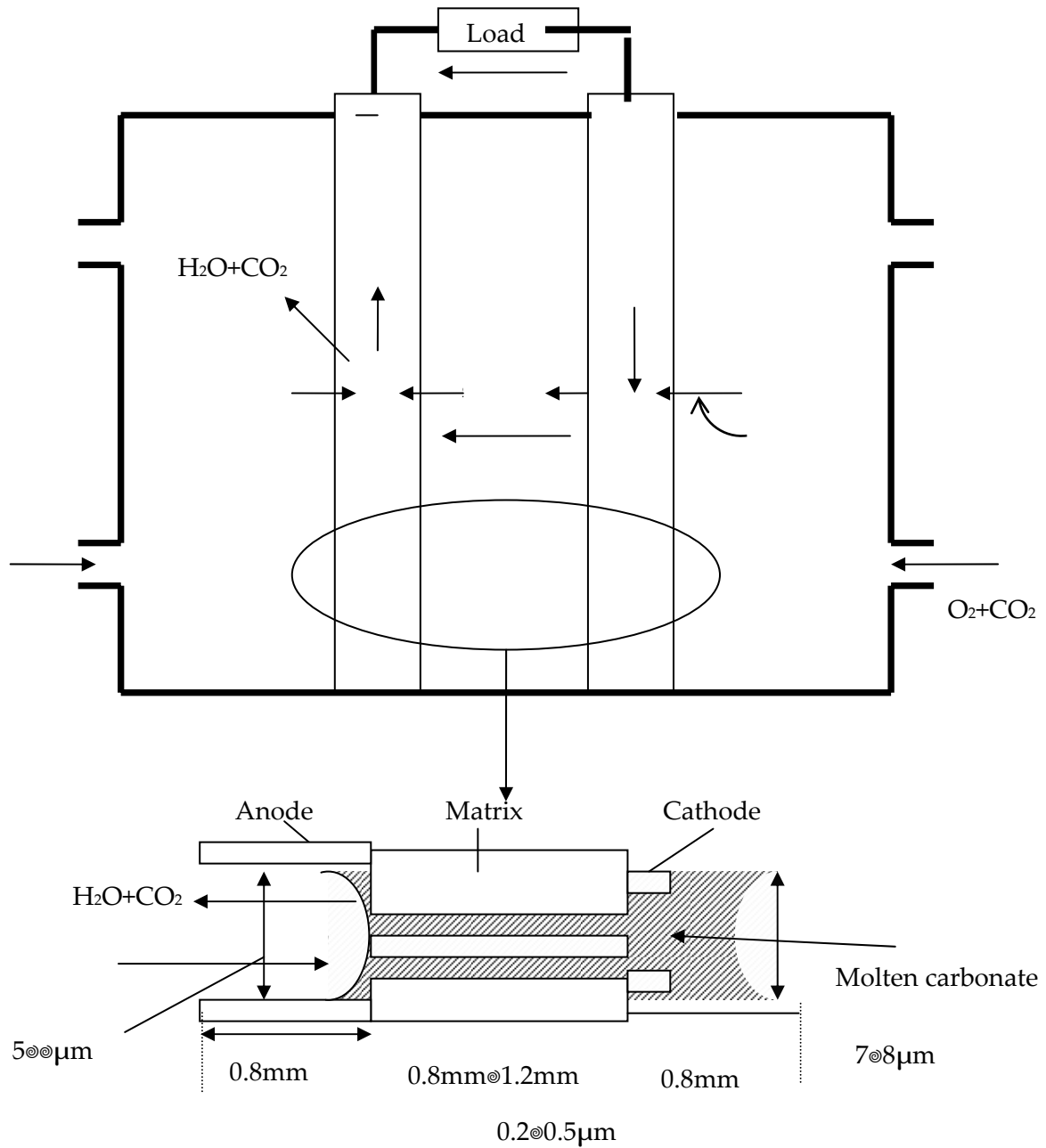


Figure 1- Principle of MCFC construction and the microstructure of the electrodes

In the MCFC, the carbonate anion in the molten carbonate serves as an electrolyte under the operating temperatures of 600-650 C. Although there are many kinds of carbonates available, those which are stable at the MCFC's operating temperature are shown in Figure 2.

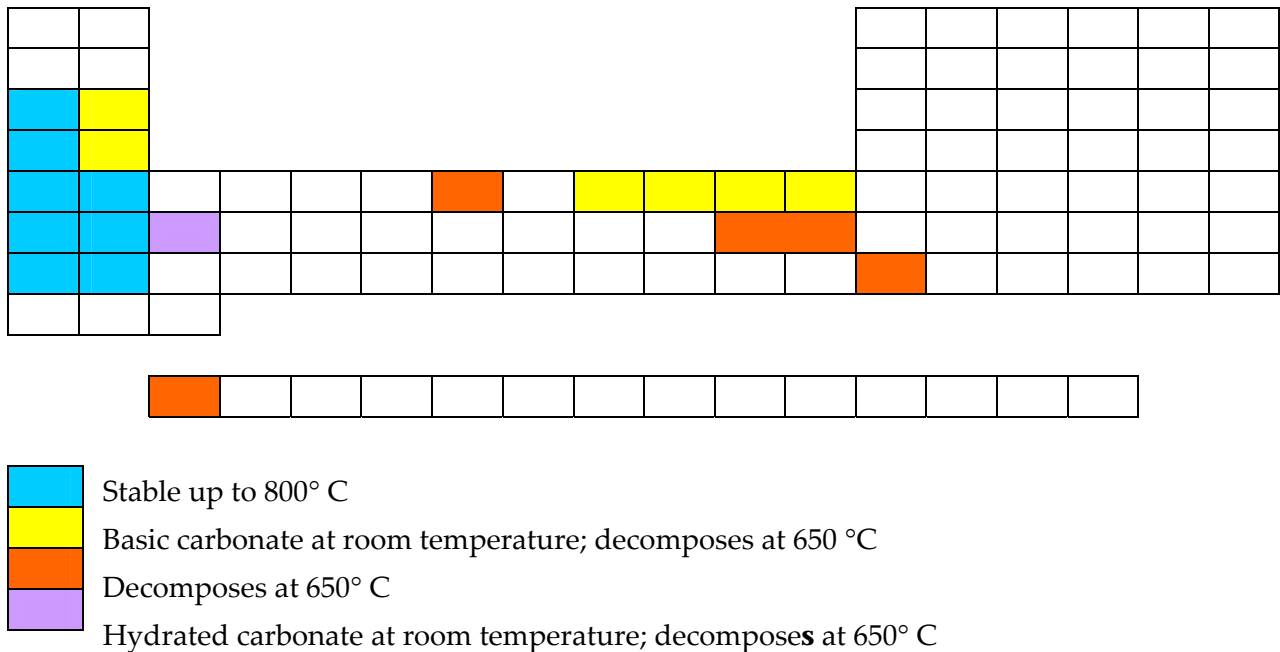


Figure 2- Stable candidate carbonates for use in a MCFC

To effectively promote the above gas reactions, a working fuel cell employs a porous electrode to increase the rate of gas diffusion. An electrode is easily fabricated from porous nickel which is stable in the carbonate and is stable up to a maximum temperature of 600 650 °C. It is this electrode stability that limits the MCFC’s operating temperature to 600 650 °C.

No single carbonate melts in the range of 550 700 °C. However, some eutectic mixtures of carbonates do melt at such temperatures. A phase diagram of the ternary mixture of lithium carbonate sodium carbonate potassium carbonate is provided in Figure 3. There are four eutectic compositions of the ternary mixture. One of the eutectic points is of a 62 mol% lithium potassium carbonate mixture melted at 488 °C. Since the electrical conductivity of a light element carbonate is high and the melting point is low, lithium carbonate is preferred for the electrolyte for the MCFC. Since the 1970’s, a mixed lithium carbonate potassium carbonate electrolyte system has typically been used.

The open circuit voltage (OCV) of the MCFC is formulated as follows:

$$E_T^0 = E_{0,T} + \frac{RT}{2F} \log \frac{P(H_2)}{P(CO_2)P(H_2O)} + \frac{RT}{2F} \log P(O_2)^{1/2} P(CO_2) \quad (4)$$

The first term is the standard potential of water formation at T. The second term is the anodic reaction from equation (2), and the third is the cathodic reaction. When the electrode reaction yields the product gas and consumes the reactant gas, the OCV depends on the partial pressure of the gases in equation (4).

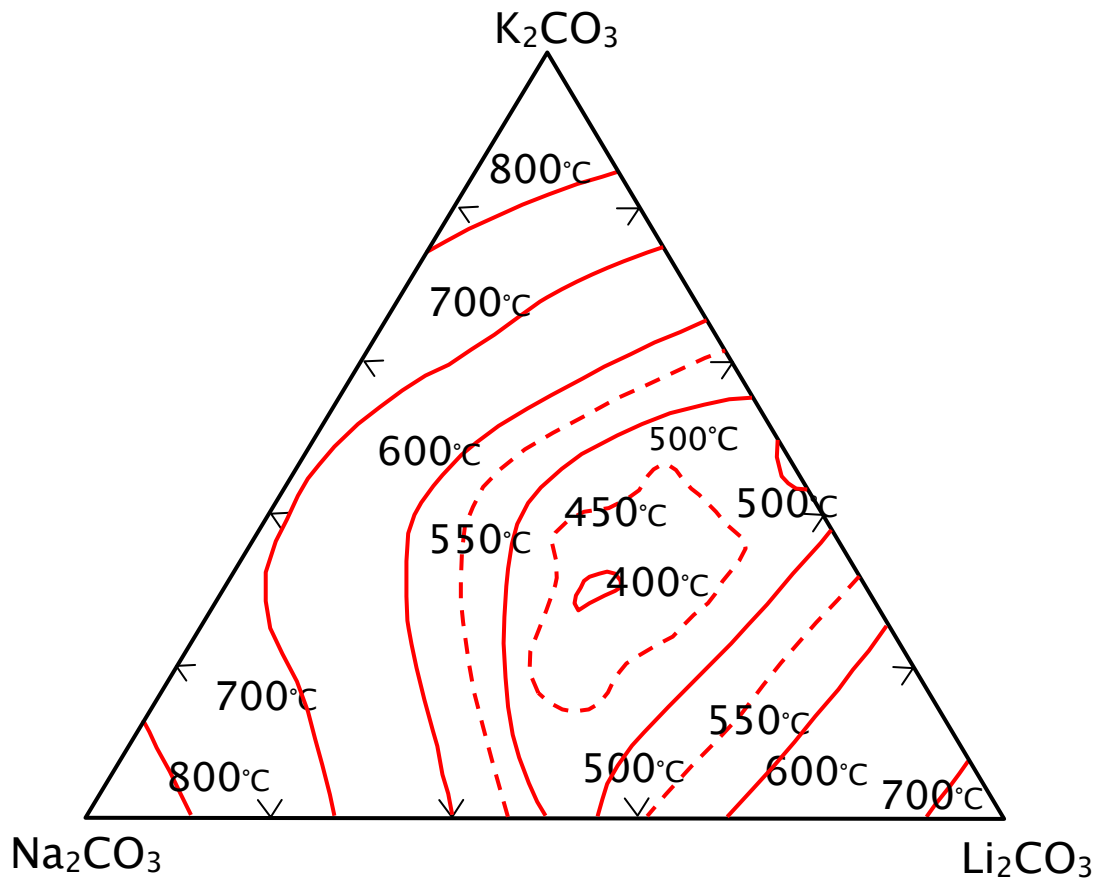


Figure 3- Phase diagram of molten $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ ternary system

In a fuel cell power generation system, the fuel gas utilization has to rise to attain a high energy efficiency. The difference of inlet and outlet gas compositions at the anode lowers the cell voltage. This change in the OCV is a Nernst loss and varies according to the gas utilization. In the power generating state, an electrochemical reaction proceeds, and the cell potentials are formulated as follows;

$$E_T = E_T^0 - \eta_{\text{nernst}} - (R_{\text{cathode}} + R_{\text{anode}} + R_{\text{ir}})I \quad (5)$$

The variable E_T^0 is the OCV, as stated above; η_{nernst} is the Nernst loss; R_{cathode} is the cathodic polarization, and R_{anode} the anodic polarization. The variable R_{ir} is the iR polarization.

AV 3.3 MCFC Gas reactions

AV-3.3.1 Electrode reactions and output power

As previously stated, in the MCFC, hydrogen, carbonate anion, oxygen, and carbon dioxide react as shown in (1) and (2). The porous electrode is valuable for an effective electrochemical reaction, because the reactant gas can quickly diffuse to the electrochemical reaction site, and because, as illustrated in Figure 1, the surface area of the electrode can be enlarged to assist the reaction.

The MCFC output power is the product of the voltage and the current. The cell voltage is stated in Section 2; the cell current depends on the kinetics of the electrode reaction.

The current density i is formulated as follows:

$$i = I/A \quad (6)$$

where I represents the current, and A the electrode surface area.

In the anodic MCFC reaction, the transport of the carbonate anions in the electrolyte and the cathodic current are equal. Generally, the chemical reaction velocity v and the chemical potential of chemical species C_i are related as follows:

$$v = kC_1^{l_1} C_2^{l_2} \dots C_m^{l_m} \quad (7)$$

In the above reaction, $l_1 \otimes l_2 \dots$ is the reaction order for each chemical species. The reaction velocity, v , and the current density, i , are related by:

$$i = \frac{nFv}{A} \quad (8)$$

in which n stands for the electron number of the reaction, and F represents the Faraday constant. On the porous electrode, C_x in (7) corresponds to the partial pressure of the reactant gas. Thus, the current density of i and the partial pressure of the reactant gas can be derived as follows:

$$i = \frac{nF}{A} kP_1^{l_1} P_2^{l_2} \dots P_m^{l_m} \quad (9)$$

where $l_1 \otimes l_2 \dots$ is the reaction order of each chemical species, in the same manner as in (7). In the equation

$$i_0 = \frac{nF}{A} k \quad (10)$$

the variable i_0 is defined as the exchange current density. It is the index of reactivity of the electrochemical reaction. Since the anodic and cathodic reactions in the fuel cell are different electrochemical reactions, each reaction will be discussed separately.

AV-3.3.1 Cathodic reaction

The mechanism of the oxygen reduction reaction has been investigated in detail. In the cathodic reaction in the MCFC, oxygen and carbon dioxide are the chemical species in equations (1). Since the discussion of the electrochemical process is complicated by the reaction occurring in the porous electrode, the mechanism of oxygen reduction on a flat gold electrode to remove such factors has been examined. In the first step of the chemical reaction, oxygen gas dissolves into the molten carbonate. Two processes then take place:

Peroxide path: e



Super Oxide path:



The dissolution behavior of the oxygen into the carbonate depends on the temperature, and the partial pressure of oxygen on that of the carbon dioxide and the carbonate composition. Appleby and Nicholson^{1,2,3} reported that the peroxide path was dominant in the range of 800 to 750 °C. In contrast, Uchida^{4,5,6} and Selman⁷ individually reported that oxygen reduction in the MCFC at an operating temperature below 650 °C proceeds via the superoxide path. In addition, they investigated the mechanism of oxygen reduction by comparing the experimental reaction order with the theoretical one based on equations (11) and (12) above. They concluded that the final step of both the peroxide path and superoxide path, in which the oxide anion and the carbon dioxide yield a carbonate anion, constituted the rate determining step. By appropriate parameter fitting to experimental data, it may be possible to extend these results to a mixed process, including both the superoxide path and the diffusion of carbon dioxide.

The electrode reaction rate may be formulated as follows, provided that the superoxide path at MCFC operating temperature is the rate determining factor.

$$i = i_0 \left\{ \exp(\alpha F / RT \cdot \eta) - \exp(-\alpha F / RT \cdot \eta) \right\} \quad (13)$$

$$i_0 = nFk \quad (14)$$

In these equations, k is the rate constant. By examining the exchange current density, i_0 in relation to its dependency on partial pressure, we can evaluate the mechanism of oxygen reduction. In Table 1, the value of i_0 is higher than that of a low temperature fuel cell and is independent of the electrode materials. Therefore, the oxygen reduction process in the MCFC does not depend on the electrode materials but on the porous structure.

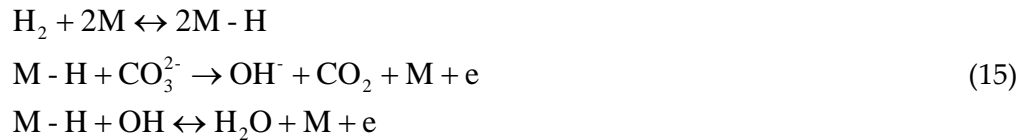
Table 1-Exchange current density of the oxygen reduction process on various MCFC cathodes

Carbonate	Exchange current density	Temperature	Electrode	Method
Li/K	11 mA/cm ²	650	Planar Au	PS
Li/Na	10 20 mA/cm ²	650	NiO,SnO @RuO	AC QS
Li/K	2.8 mA/cm ²	650	Porous NiO	Steady state
Li/K	2.8 mA/cm ²	650	Porous NiO	AC

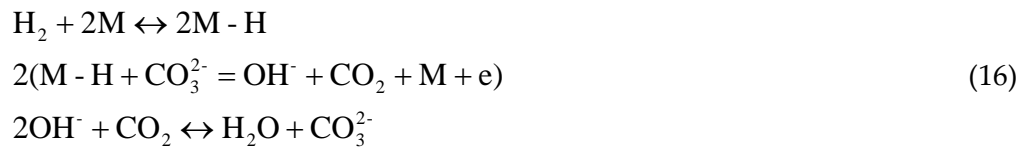
PS: Method of Potential step, AC: Impedance method, QS: method of Qulostatt

AV-3.3.3 Anodic reaction

The hydrogen oxidation process in the MCFC proceeds quickly compared with the oxygen reduction process. Ang and Sammells⁸ reported that the hydrogen oxidation process was that given by the equation set (15). e



On the other hand, Jewulski and Suski⁹ reported that absorbed hydrogen on a nickel electrode is oxidized in a parallel reaction.



Although both of the reaction orders are two, the stoichiometric coefficients related to the hydrogen oxidation is two and one for (15) and (16), respectively. The experimental data indicated that the chemical coefficient was less than one. Hence, the hydrogen oxidation process was thought to have taken place as in equation (16).

We examined the exchange current density of the hydrogen oxidation reaction by means of a planar electrode. The results, shown in Table 2, reveal i_0 values that are one order higher than those of the cathode reaction. The anode reaction proceeds quickly, and is not influenced by the electrode materials.

Table 2 -Exchange current density of hydrogen oxidation on planar electrodes

Carbonate	i_0 mA/cm ²	Electrode material	Method
L/K 650	100	Ni,Co	PS
L/ 650	70	Cu	PS
L/K 550	69	Au,Ni,Cu	AC
L/K 650	10 300	Au,Ni,Cu	AC

AV 3.4 Materials and structure of MCFC

AV-3.4.1 Cell design and stacking

The structure of a single cell is shown in Figure 4. The MCFC power generation system is installed by stacking of ten to several hundreds of cells, a component called the stack. The power output density is *ca.* 120 mW/cm², 0.8 to 0.85 V at 150 mA/cm². With a cell area of *ca.* 1 m², a single commercial cell can generate 1.2 kW of output. A stack of two hundred and fifty cells can produce 300 KW.

When the cells are stacked as in Figure 4, a separator plate made of metal, plays the same role in an MCFC as in the technology of a Polymer Electrolyte Fuel Cell and a Phosphoric Acid Fuel Cell. That role is to divide the electrochemically active components, the anode, cathode and electrolyte. This plate is used to electrically connect the cells in series. In addition, it distributes fuel and oxidant gas and supplies them to each electrode effectively. And it also exhausts the produced gas, which is water and carbon dioxide in the MCFC out of cell. As a cell connector, the separator plate should be electrically conductive. In the MCFC, the anode atmosphere is reducing, while that of the cathode is oxidizing. No single material can perform all the functions of a separator plate. A typical separator plate is made of clad plate, one side of which is stainless steel for oxidizing conditions, and the other nickel for a reducing atmosphere. The dimensions of such a plate should accommodate the size of the gas path used to distribute the gas. In operating a large stack, the cell stack temperature should be controlled by the cooling of the oxidant gas. Thus, the gas distribution design is related to the stack temperature, and depends on the number of cells, the stack dimension, the fuel type and system design.

The external manifold design is shown in Figure 4. Four manifolds are placed in each lateral side for an inlet and outlet for both the fuel and oxidant gas. Each manifold is mechanically pressed against the lateral side with a gas sealer. This type of manifold has a cross flow pattern for the fuel and oxidant. Although the external manifold structure is simple, some problems exist: the gas sealer material may corrode, and the electrolyte may migrate through the sealer, a situation permitting stray current to flow. In a large cell with a cross flow structure, some temperature variation may occur as well.

In the MCFC, the electrolyte plate consists of a molten carbonate impregnated in an electrolyte supporting material which is made of porous ceramic. Since the plate contains the molten carbonate, it is a soft structure that can be used for gas sealing. A diagram of the other manifold structure, an internal manifold, is presented in Figure 5.

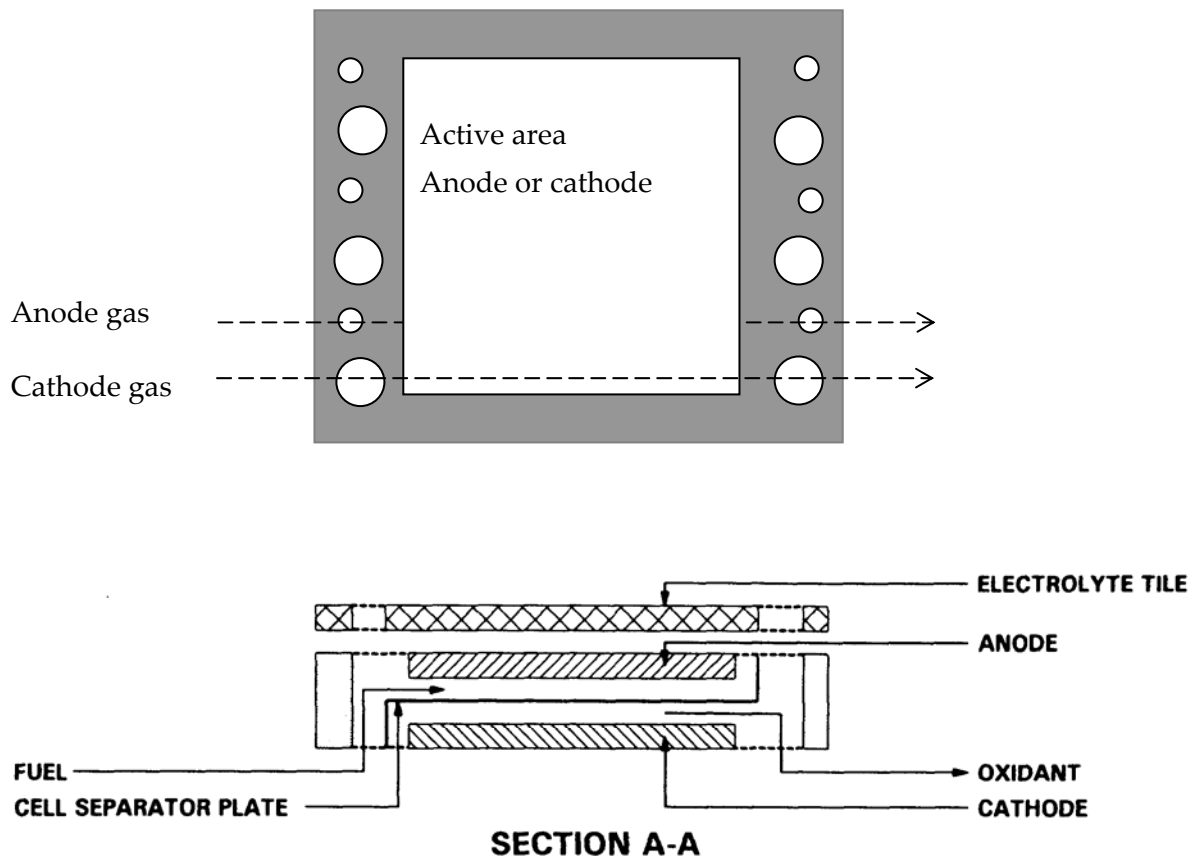


Figure 5- Gas flow of internal manifold MCFC

AV-3.4.2 Component materials

The materials used in the MCFC components are provided in Table 3.

Table 3- Typical MCFC components

Component	Material
Anode	Ni Al, Ni Cr
Cathode	NiO(Li+2 3 mol%)
Electrolyte	62 mol%Li CO 38 mol%K CO
Matrix	LiAlO
Current collector	Anode: Ni, Cathode: SUS310S, SUS316L
Separator	SUS310S, SUS316L/Ni

AV 3.5. System

The basic system of the MCFC power generation is shown in Figure 6. The fossil fuel(coal, oil, or natural gas) is converted to a hydrogen rich fuel gas by a steam reforming process. Since the MCFC can accept carbon monoxide as a fuel gas, an extra peripheral device to remove CO is not required. The design of the power generation system takes into account the dimensions of the power plant, the fuel type and the structure of heat the recovery system.

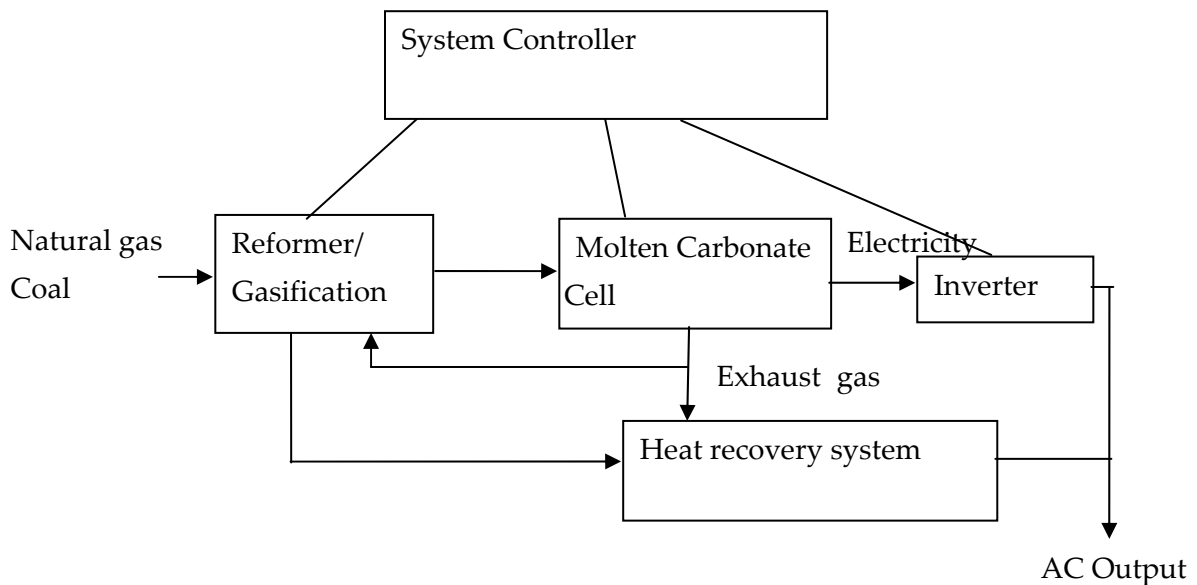


Figure 6- MCFC power generation system

AV 3.6 Research and Development of MCFC in Japan

The MCFC technology presently available can provide in situ power generation and/or a 200 300 kW distributed power supply system. This plate type system includes a cell structure up to 1 m² in size, assembled with porous nickel electrode plaques, a ceramic electrolyte supporting plaque, and a stainless steel separator plate. The separator plate is provided with a gas supply and an electrical connection. Since the manufacturing technology for the electrodes and the electrolyte supporting plaque can uniformly fabricate components up to ca. 1 m², this area is typically used. Up to 250 of these 1 m² sized cells are stacked to a height of 3 4 meters in an electrical serial connection. This stack typically generates 250 to 350 kW depending on the operating pressure. To demonstrate the distributed power generation system in electrical utilities, Fuel Cell Energy (FCE) in the U.S. and Ishikawajima harima Heavy Industry (IHI) in Japan, have been developing and manufacturing MCFC stacks. An FCE 250 kW class stack and

has been operated for 10,000 hours at ambient pressure. IHI is developing a pressurized 0.5 MPa and 1.2 MPa 10 kW class of MCFC and has successfully operated such systems for 10,000 hours in 2002 and for 3,000 hours in 2003, respectively. The MCFC power system must meet a durability target of 10 % power degradation in a 40,000 hour operation to be of practical use. The technological issue involved in reaching the durability standard is nickel shorting with concomitant electrolyte loss.

A severe nickel shorting problem causes a reduction of cell voltage in long term operations and a failure to attain a highly efficient power generation system. To assess the nickel shorting mechanism, investigators have dissolved nickel oxide as a cathode material into molten carbonate as an electrolyte during the operation of the system; under these conditions, the diffused hydrogen of the fuel gas from the anode side reduced the dissolved nickel cation in the electrolyte, so that nickel metal particles were deposited in the electrolyte. When these particles grouped together like a chain, they formed an electrical path between the anode and the cathode. The resultant nickel shorting happens after an operating period of more than 10,000 hours.

During a long period of operation, the electrolyte carbonate mixture was lost in the cell because of creepage, corrosion, and evaporation. The corrosive nature of molten carbonate is well known and needs to be taken in account for optimal cell design. The molten carbonate is kept in the cell by supporting lithium aluminate (LiAlO_2) which is a stable ceramic under these operating conditions. However, investigators have reported that the particles of lithium aluminate enlarged in the molten carbonate during lengthy operation periods. The particle growth reduces the supporting force, which comes from the capillary force generated in the fine pores in the lithium aluminates. The overall behaviour of lithium aluminates in molten carbonate is still not understood. Although the amount of evaporated carbonate is negligible for cell performance, the evaporated chemical species, alkali oxide, may influence peripheral devices such as a gas turbine.

The Fuel Cell Energy company in the U.S. has been developing an internal reforming MCFC which can be directly fed as fuel methane, natural gas or bio gas. This system can be simplified by removing the reformer. This company demonstrated their 250 kW power system at 14 sites in the United States and at three sites in Japan. The MTU (Motoren und Turbinen Union) company, which has experience in power system design, manufactures the MCFC power system in partnership with FuelCell Energy, and has demonstrated a 250 kW distributed power system at more than 10 sites in Europe.

The Ishikawajima Harima Heavy Industry company has been developing 1.2 MPa 750 kW MCFC modules made up of two 375 kW stacks and a reformer for electrical utilities, through a

subsidy provided by the Japanese government until the 2004 fiscal year. A number of Japanese companies plan to demonstrate 0.4 0.5 MPa pressurized 300 kW distributed power systems constructed on the basis of IHI technology.

The installation of MCF power generation into plants has begun in 2003 at an on site bio gas production plant. The public announcement stated that the installed cost of MCFC power generation is one million yen, or \$80,000 U.S. per kW. However, after the process and control operation tests required and the coordination to the conditions existing in the individual plants where the units were placed, the actual installed cost was one to two million yen per kW. In Japan, the installed cost of thermal power generation is 20,000 300,000 yen per kW, or \$18,000 25,000 U.S. per kW. Attempts to reduce costs are focused on the engineering and processing of the MCFC plant. When the yearly production exceeds 100 units of the 200 300 kW class, the installed cost will fall to 300,000 400,000 yen per kW. The market for dispersed power generation, in the 100 500 kW class, is potentially large when the efficiency of the given power generator is more than 45% higher than that of a grid power plant. In the future, increases in durability and performance should enable the MCFC to be utilized in many applications.

References

- [1] A. J. Appleby and S. B. Nicholson, *J. Electroanal. Chem.*, **53**, 105(1974).
- [2] A. J. Appleby and S. B. Nicholson, *J. Electroanal. Chem.*, **83**, 309(1977).
- [3] A. J. Appleby and S. B. Nicholson, *J. Electroanal. Chem.*, **112**, 71(1980).
- [4] I. Uchida, T. Nishisna, Y. Mugikura, and K. Itaya, *J. Electroanal. Chem.*, **206**, 229(1986).
- [5] I. Uchida, Y. Mugikura, T. Nishisna, and K. Itaya, *J. Electroanal. Chem.*, **206**, 241(1986).
- [6] I. Uchida, T. Nishisna, Y. Mugikura, and K. Itaya, *J. Electroanal. Chem.*, **209**, 125(1986).
- [7] C. Y. Yuh and J. R. Selman, *J. Electrochem. Soc.* **131**, 262(1984).
- [8] P. G. P. Ang and A. F. Sammells, *J. Electrochem. Soc.* **127**, 1287(1980).
- [9] J. Jewulski and L. Suski, *J. Applied electrochem.*, **14**, 135(1984)