

FUEL CELLS: STATE OF THE ART AND FUTURE DEVELOPMENTS

Holger Apfel, Carsten Cremers and Ulrich Stimming

TU Munich, Department E19

Garching near Munich

1. Introduction

Energy conversion systems are the principal source of pollution on our planet. In the industrialized countries, the electric power plants that convert chemical energy in electrical energy are the main producers of CO₂ emissions, private cars, on the other hand, are the principal producers of CO and NO_x emissions. Figure 1 illustrates this situation for an industrialized country such as Germany (given for the year 2001) [1].

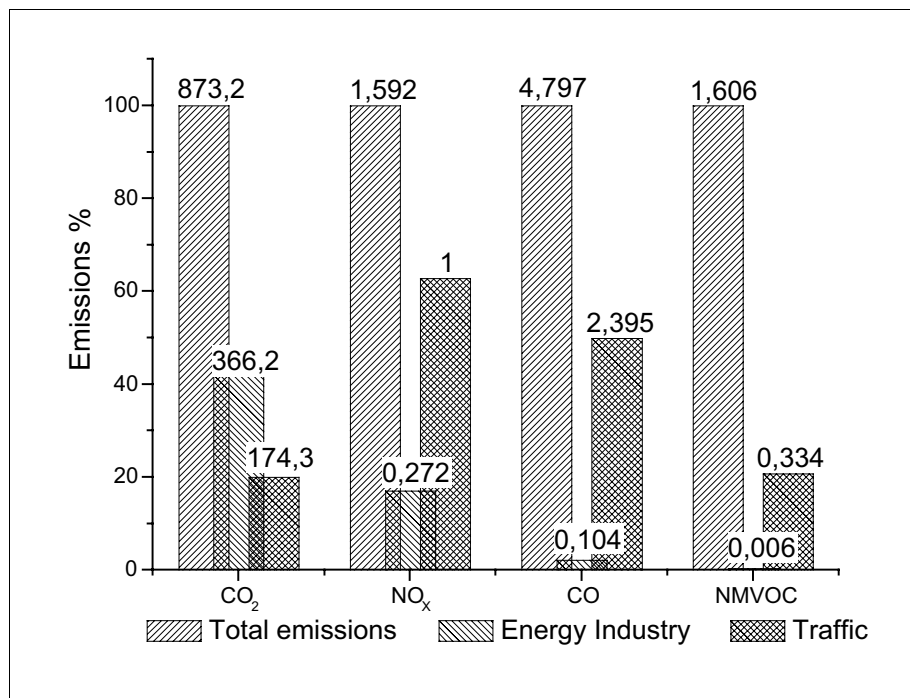


Fig. 1: Emissions generated in Western Germany in 2001 with emphasis on power plants and road traffic in relation to overall emissions [1]. All numbers in million tons. NMVOC = Non-methane volatile organic compounds.

The concentration of CO₂ in the earth's atmosphere has increased considerably since the last century as a consequence of industrialization [2,3] (Fig. 2) and is considered the main reason for the greenhouse effect leading to an increase of the earth's surface temperature. Furthermore, power plants and cars are important consumers of mineral oils and natural hydrocarbons, both of which have a higher potential as a raw material for the chemical industry than as fuel for, e.g., the production of electricity. Nowadays the air pollution and the diminution of the earth's resources of hydrocarbons are two main topics in politics and economics and regenerative energy sources are sought after. A better energy conversion technology would be very attractive, as it would reduce both the air pollution and the indiscriminate destruction of precious chemicals.

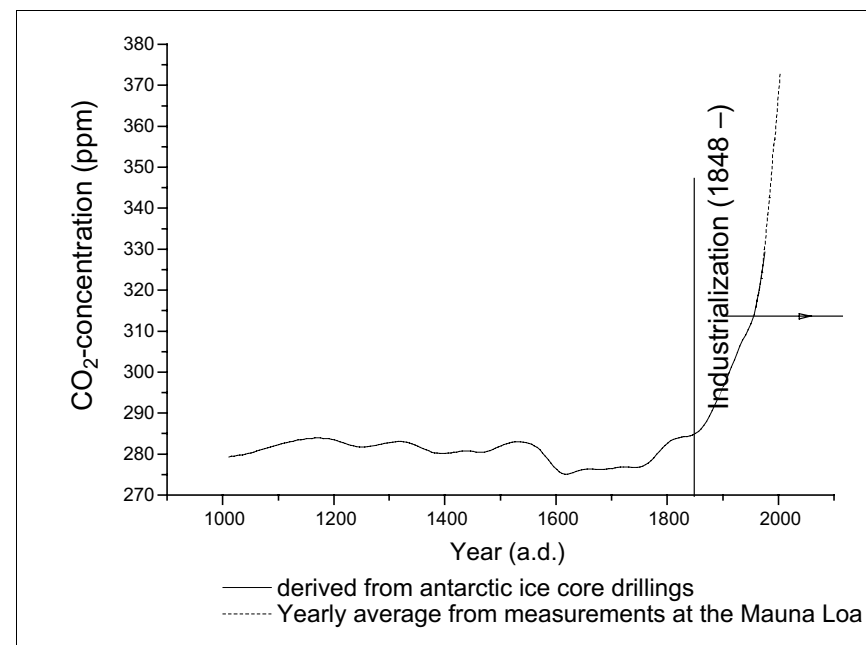


Fig. 2: CO₂ concentration in the earth's atmosphere as a function of time [2].

One possible technology to achieve this are fuel cells. Fuel cells convert the chemical energy of a fuel such as methane directly into electrical energy with a better yield and much lower emission levels than any other energy conversion system [4,5]. Although the principal operation of a fuel cell is known since the last century, the necessary technology for producing fuel cell systems of high efficiency, acceptable costs and at an industrial level has only been developed in the last few decades.

2. Fuel Cells

2.1 Functions

The principle operation of a fuel cell (Fig. 3) is comparable to that of a battery. In contrast to batteries – where the chemical energy is stored in substances inside the battery – fuel cells are just devices where the conversion takes place. The reagents are stored externally and have to be supplied continuously to the fuel cell in order to obtain electricity. Thus, fuel cells are systems that convert chemical energy directly into electricity in an invariant electrochemical set-up.

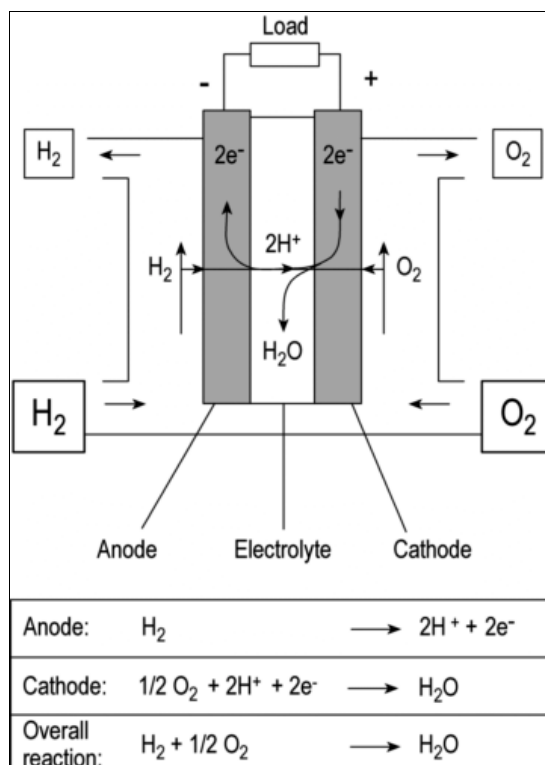


Fig. 3: Sketch of the principal operation of a fuel cell: Two electrodes are separated by a gas tight electrolyte. The fuel (H_2) is supplied at the anode, where it is oxidized releasing electrons. The oxidant (O_2) is supplied at the cathode, where it is reduced consuming electrons.

Figure 3 schematically shows the principle of a fuel cell with a proton conducting electrolyte, hydrogen as fuel and oxygen as oxidant. Hydrogen and oxygen are supplied to porous electrodes; the gases diffuse through the electrode to the electrode - electrolyte interface. This is

the reaction zone where the gases are consumed. The oxygen ions on the cathode react with the hydrogen ions, which permeates the electrolyte and form water. The electrons stripped off the hydrogen during ionization cannot permeate the electrolyte; for them the only way to reach the cathode is by an external electron-conducting path. Work is performed as soon as a suitable load is introduced into this path.

2.2 Efficiency

Because of the direct energy conversion fuel cells work at a higher efficiency than energy conversion processes which involve a conventional heating cycle as the latter are limited by the Carnot cycle efficiency. This is illustrated in Fig. 4, which compares the theoretical efficiencies as a function of temperature of a fuel cell and a Carnot process operating between T and 300K.

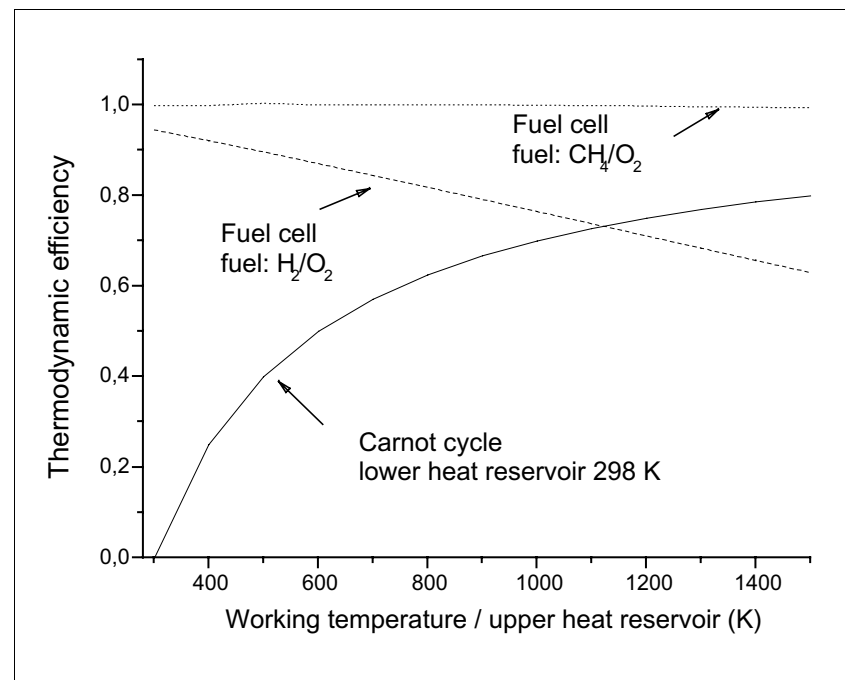


Fig. 4: Thermal efficiency as a function of temperature of the energy conversion of a fuel cell and a conversion process limited by the Carnot factor.

The figure shows two things: first that the efficiency of the fuel cell depends on the type of fuel used. And second that the thermal efficiency of a fuel cell is higher than that of a Carnot process unless the upper temperature of the process largely exceeds 1000K.

But just as with combustion engines, the thermodynamic efficiency represents the upper limit for the cell rather than the actual performance. There are several factors that reduce the efficiency of a real fuel cell system:

First, there are the losses that occur inside the fuel cell. The factor describing those is called the *electrical efficiency* and is given by the product

$$\eta_{el} = \eta_{id} \eta_U \eta_F U_f \quad (1)$$

where the *ideal or theoretical efficiency* $\eta_{id} = \Delta G / \Delta H$ is the thermodynamic efficiency. η_{id} is the value plotted in Figs. 4 and 6.

The *voltage efficiency* $\eta_U = \Delta U_{cell} / \Delta U_{theoretical}$ reflects voltage losses due to polarization phenomena at the electrodes and ohmic potential drops at the interfaces, in the electrolyte and in the interconnectors (the theoretical cell voltage for water production is 1.23 V at standard conditions, cell voltages in real systems vary between 0.6 and 1.1 V depending on current densities). The voltage efficiency is the target of most of the research today. Details are discussed in Section 2.5.2.

The *faradaic efficiency* $\eta_F = I / I_m$ is defined as the ratio between the observed current and the theoretically expected current calculated on the basis of complete reaction. The faradaic efficiency is lower than 1 if a parallel reaction takes place. A prominent example, the DMFC, is discussed later in Section 3.2.2.

U_F is the utilization of the fuel in the cell or stack. U_F is smaller than 1 if a part of the fuel leaves the stack without taking part in the reaction.

The electrical efficiency of the complete fuel cell system comprises also the efficiency of the periphery and is given by

$$\eta_{el}^{system} = \eta_{el}^{stack} \eta_p, \quad (2)$$

where the *periphery efficiency* η_p is defined as the ratio between the usable energy delivered by the system and the energy output of the cell. This factor considers losses by blowers, feed pumps, control equipment and other peripheral components. If a reformer is needed this may be another major factor of loss in the system (in case of a POX reformation the system efficiency may decrease by 20 % or more).

The resulting electrical efficiencies are shown in Fig. 5 where known or projected efficiencies of the different energy conversion systems are compared for different sizes of plants. The efficiencies of two types of fuel cell systems shown in the diagram are higher than those of engines and conventional power plants of comparable size and, in the case of the SOFC, are higher than the maximum achievable efficiency of Carnot-type units.

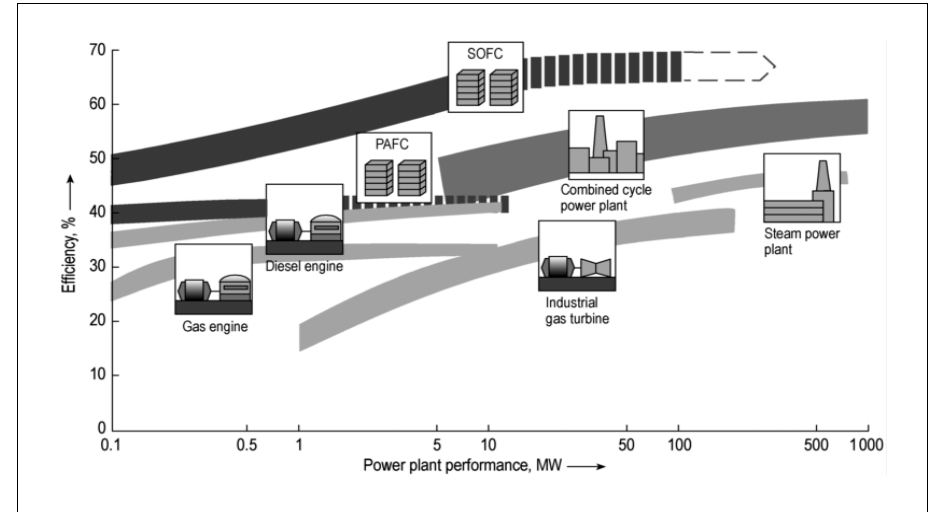


Fig. 5: Efficiency of energy conversion as a function of the size of the power plant. Conventional systems are compared with projected fuel cell systems such as PAFC and SOFC [6].

The efficiencies shown in Fig. 5 consider only the electric efficiencies of the plants. If the heat produced by the fuel cell can be used, e.g. in plants for combined generation of heat and power (CHP), the total conversion efficiency can reach 90% or more while the electric efficiency remains at 45% or more. In those cases the heat generated by the fuel cell can be used for producing hot water or steam.

In addition to the high efficiency, fuel cells also exhibit emission levels that are notably lower than present legal requirements (in Germany, for instance, stipulated by "TA Luft"). Several factors contribute to this: Firstly, fuel cells work continuously, so that there are no problems with pulsating combustions as they are encountered in gas and diesel engines. Secondly, sulphur is a catalyst poison for all types of fuel cells used today so it has to be removed before entering the stack, which results in a strongly reduced SO₂ emission. Furthermore, the temperatures reached by the highest temperature fuel cells are about 1000 °C – and thus much lower than the temperatures within gas turbines and diesel engines, reducing NO_x emissions to levels well below the limits specified by the law. Finally, fuel cells do not have moving mechanical parts, so they are virtually soundless.

2.3 Different Types of Fuel Cells

Today's fuel cells can be divided into two groups depending on their operation temperature. Low temperature fuel cells operate at a temperature typically lower than 200 °C, while high temperature fuel cells operate at a temperature above 600 °C. The fuel cells are usually classi-

fied and named after the electrolyte present in the cell, with the exception of the direct methanol fuel cell (DMFC), which is identified by the fuel used. Except for some alkaline fuel cells, a common characteristic of fuel cells is the use of an immobilized electrolyte, which means that the electrolyte is solid or consists of a liquid retained in a solid matrix. Immobilized electrolytes offer many practical advantages such as fewer corrosion problems, no leakage of the liquid, easier design, planning and construction. An overview of the materials used for the components of the different fuel cell systems is given in Table 1.

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 1: Materials and components for different types of fuel cells

The other parameters such as reagents, temperature, pressure and application of the fuel cell system depend on the electrolyte in the cell. Table 2 lists these 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 – 50 kW	11 MW	2 MW demonstration plant	100 kW demonstration plant
Electrical efficiency					
Stack	69 – 70 %	50 – 68 %	50 %	60 %	60 – 65 %
System	62 %	43 – 58 %	40 %	44 % (plant) 60 – 65 % (combined cycle)	53 % (plant) 65 – 70 % (20 MW)

Table 2: Operation parameters for different types of fuel cells

Several fuels can be used. Depending on the type of systems they can be directly supplied to the anode or first undergo a reforming reaction. The thermodynamic efficiencies of the conversion of different fuels are given in Fig. 6.

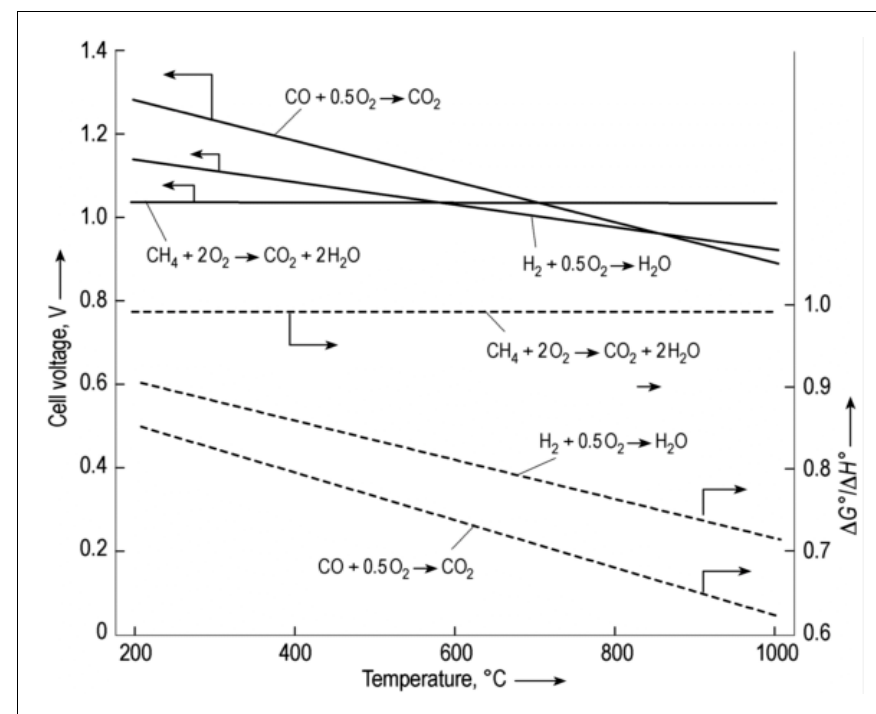


Fig. 6: Thermodynamic equilibrium voltages and theoretical efficiencies for the conversion of different fuels in a solid oxide fuel cell. The temperature dependences of the theoretical efficiencies $\Delta G^\circ/\Delta H^\circ$ of various reactions are plotted on the right scale. The corresponding cell voltages, calculated from the Nernst equation, are shown on the left scale.

2.4 Stack

Figure 3 shows only the electrochemical core of a fuel cell. However, a single electrode-electrolyte assembly is not sufficient for electricity generation, since the typical voltage of a single cell is below 1 V. In order to obtain suitable voltages a number of cells are connected in series. Thus, in addition to the electrochemical components, a fuel cell needs interconnector plates, which electrically connect two adjacent electrochemical units and usually also act as reactant distributors. Several fuel cells connected by interconnectors form a stack. Such a stack is shown in Fig. 7 for a fuel cell with polymer electrolyte.

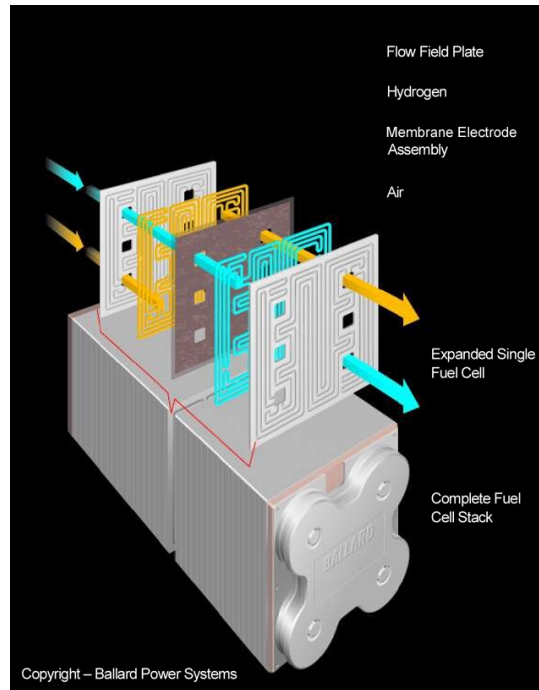


Fig. 7: Ballard PEMFC-Stack [7].

Regardless of the actual type of fuel cell there are certain demands on the properties of the materials involved:

The *electrolyte* has to have a high conductivity at operating temperature, i.e. it should cause a low ohmic drop ($< 0.15 \Omega \text{ cm}^2$). Furthermore, it should have negligible electronic conductivity, be gas impermeable, and chemically stable in an oxidative and reductive environment (1.2 V and 0.0 V, respectively).

The *electrodes* must have a high electro-catalytic activity for fuel oxidation or oxidant reduction, a high electrical conductivity (electronic or mixed ionic and electronic), and must be chemically stable to reduction or oxidation and be gas permeable.

The *interconnector* must have a high electronic conductivity and must be stable in oxidative environment on the cathode side and reductive environment on the anode side.

The *electrochemical system* interconnector-anode-electrolyte-cathode must exhibit high thermal stability to sufficiently withstand frequent thermal cycles, have a long operation life

(5000-150,000 h, depending on application), be light, compact, not expensive, and easy to produce.

In order to reach these targets, the design of the cell is of crucial importance, in fact, it can strongly affect the production costs and the efficiency of a fuel cell system. An important factor for the design is the dimension of the three-phase zones, where the electrochemical reactions take place. The three-phase zone has a thickness of just a few micrometers, therefore cell designs have to consider the design of the components (electrodes, electrolytes, and interconnectors) in such a way that the specific power density is increased by minimizing the volume of the stack for the same volume of the reaction zone.

2.5 System

2.5.1 Mobile Systems

Drive-train

In mobile applications, size is at a premium, followed by instant availability - nobody wants to wait a prolonged time before driving away. Up to now the focus therefore was on PEMFC's, which have been developed to power densities approaching 0,3 kW/l [8] and can start at ambient temperature. By now (2003) every major car manufacturer has shown at least some demonstration car powered by a fuel cell. Some, as Daimler-Chrysler or Toyota, have small numbers of fuel cell vehicles in everyday use already. Driving tests with those vehicles demonstrated a system efficiency not reached by internal combustion engines (ICE) (Fig. 8).

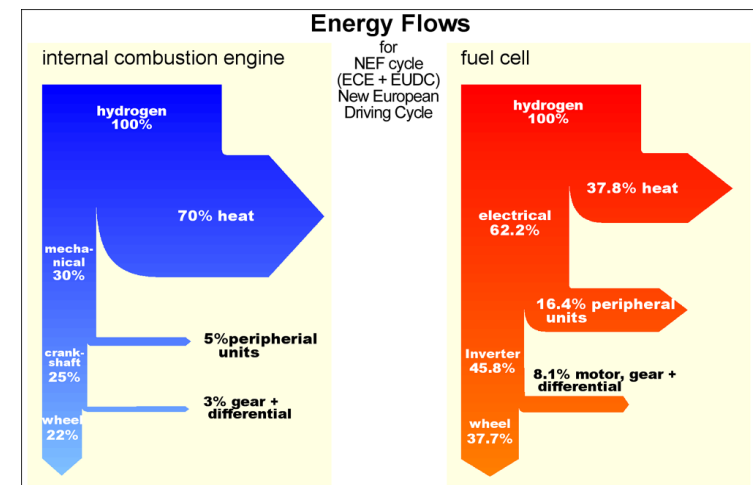


Fig. 8: Comparison of fuel to wheel efficiencies of an internal combustion engine and a fuel cell engine driven vehicle [9].

However, the use of a PEM type cell has also drawbacks:

Firstly, the low working temperature of the cell of some 70 °C means that the temperature of the coolant will not exceed 65 °C, which leaves a mere 25 °C temperature difference to the surrounding at a hot summer day compared with a conventional vehicle with its upper coolant temperature of some 90 °C as well as a 50% loss of thermal energy with the off-gas. This translates directly into a fourfold increase of the thermal load on the cooling equipment, which in turn increases size, price and power demands of the components involved.

Secondly PEMFC's today are based on sulfonated PTFE and therefore have a low CO-tolerance of less than 100 ppm. The cell therefore has to be fuelled either by pure hydrogen stored on board or by a CO-depleted gas which can only be generated by further refining the reformate derived from methanol or gasoline (Fig. 9).

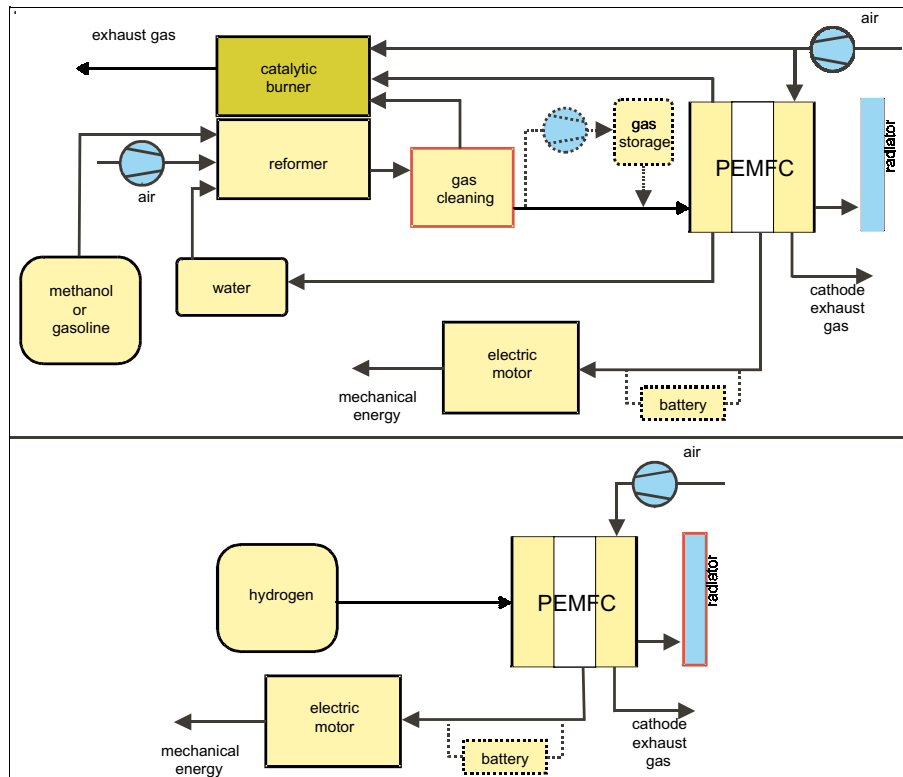


Fig. 9: Hydrocarbon and hydrogen fuelled PEM system.

Gasoline would be the ideal fuel for fuel cells as the infrastructure is available already. Yet PEMFC's need not only reforming and post-reforming processes to generate PEM-compatible fuel out of gasoline or diesel; the process is further complicated by the frequent load changes of car drive trains with the associated flow and heat transients. This way of generating fuel gas out of an existing liquid has therefore been abandoned by all car manufacturers.

Methanol would be a more suitable liquid fuel from the PEMFC's view: the need for reforming remains but the process itself is simpler and needs lower temperatures (250 °C vs. 800 °C); post-reforming the gas is easier as well. Methanol-driven fuel cell vehicles have driving ranges comparable to those of ICE-driven vehicles. Switching gas stations from gasoline to methanol merely means cleaning the piping and recalibrating the measuring equipment. DaimlerChrysler has built several demonstration vehicles (NECAR 3, NECAR 5) with driving ranges of more than 400 km. But during the last 3 years the line was abandoned in favor of vehicles fuelled by hydrogen.

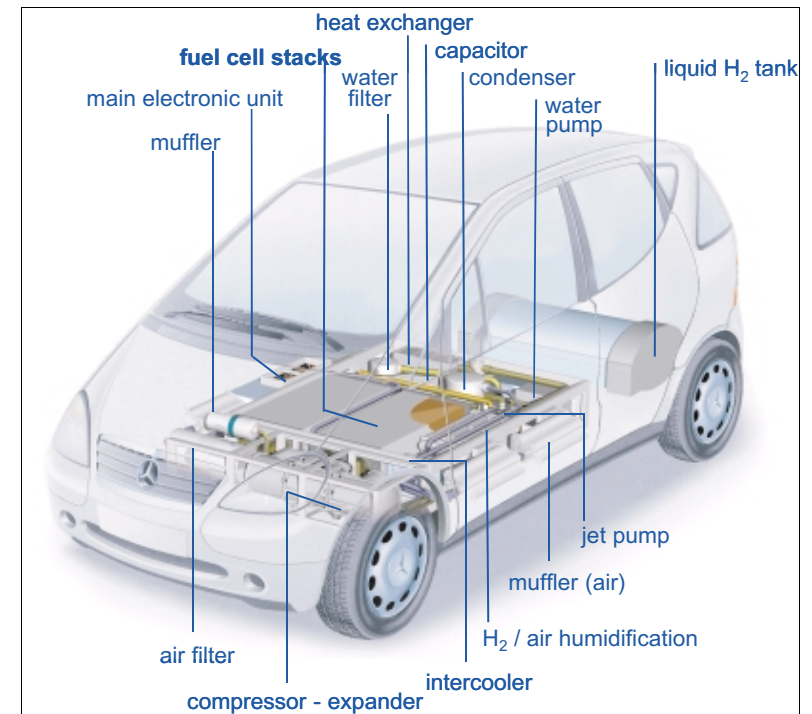


Fig. 10: NECAR 4 packaging of components [11].

The fuel cell vehicles envisioned by the manufacturers today are directly fuelled by hydrogen. Design advanced considerably so that the fuel cell system fits into a small car without reduc-

ing the passenger or freight space (example: NECAR 4 by Daimler Chrysler shown in Fig. 10). While the use of hydrogen results in a fairly simple system (Fig. 9) and adequate driving range (400 - 500 km once higher pressurized storage tanks are available), unfortunately hydrogen as an energy source is not available as a primary energy carrier - the gas has to be generated first, usually out of hydrocarbons. Using hydrogen as the energy source for driving cars therefore would only add another conversion step into the chain, reducing the overall efficiency of the system. But even if we would limit the use of hydrogen to the amount generated by regenerative energies, such as wind, solar or – yet to be developed – biochemical plants, there would still remain the problem of delivery: in 2003 there exist just some 70 hydrogen filling stations throughout the world [10]. Installing the 60,000 stations necessary to provide a worldwide hydrogen supply would cost an estimated 240 Billion Euros [ibid] in investments. While this might be the way to go eventually, the time scale to reach this figure will be decades rather than years.

Auxiliary power unit

Instead of replacing the complete drive train an alternative approach would be to just replace inefficient components or reduce operating conditions with low efficiency.

One inefficient component within the car is the electric generator, which adds a second energy conversion process (rotation \rightarrow electricity) to the ICE. The efficiency of belt-driven generators ranges from 50% to 30 % (at maximum RPM) with a possible increase to 80% when replaced by an integrated starter-generator (ISG) [12]. But even the ISG is only the second module in a chain of energy converters starting with the ICE and its low part-load efficiency of less than 25% [13]. While this does not matter so much in the cars today with an electric power consumption of several 100 Watts, future concepts like drive-by-wire or break-by-wire will increase the average electric power consumption to 2-4 kW which, at a base fuel consumption of about 0.7 l/kW/100 km [14], translates into 1,5-3 l/100 km just to generate electricity.

An even worse condition exists when a car or truck engine runs for the sole purpose of generating a few kW for air conditioning, electricity or heating. Truck engines, for example, still consume some 3 l per hour, or 30 kW thermal power input, when idling [15].

The energy needed in such cases may just as well be delivered by a second, auxiliary power generator (APU) dedicated to delivering electric energy. A fuel cell would be ideal for that job, as it would combine a high efficiency with the right form of energy at the output. The overall efficiency of a fuel cell is at least 35 % and therefore nearly twice as high as that of the ICE + generator chain.

In the case of an APU, however, the fuel cell is only a secondary system, so the choice of fuel is usually dictated by the one used by the ICE already - diesel or gasoline. This means that a PEM loses the advantage of the simple system and another type of fuel cell, namely the SOFC, may be the better choice.

First prototypes of such systems already exist: Delphi, a car component manufacturer, has shown working prototypes of such systems during the last years; a cooperation with BMW led to a first working model, a 5 kW system that fit below the trunk of an 7-series BMW and which was presented to the public in 2001 [17]. Delphi improved the system and shrank the size to 44 l and the weight to 70 kg in 2002 (Fig. 11) – 1/4th of the values of the system shown in 2001 [18]. The main issues remaining today are system cost and temperature cycle stability of the stack[ibid].

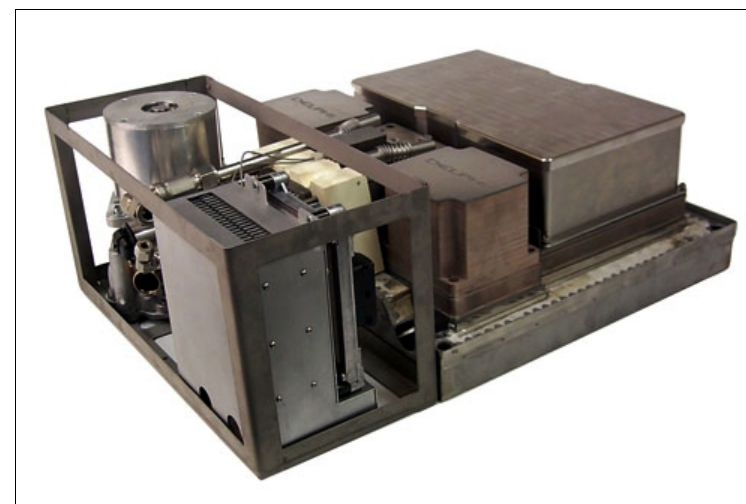


Fig. 11: SOFC APU [16].

While the cost issue might only be solved by high volume production the problems deriving from temperature stability might be overrated as it has been shown that – due to the good thermal isolation –SOFC systems can be switched off for several hours without experiencing a severe temperature drop. The difference between the lowest and the highest temperatures within the system therefore never exceeds 200 - 300 °C while the absolute temperature of the system remains above 600 °C [19]. The number of thermal cycles down to ambient temperatures during the lifetime of an APU will therefore be in the range of several tens of cycles.

Even these few cycles may be further reduced by keeping the system at a minimum working temperature at times of prolonged standstill. The amount of power needed to keep a SOFC

APU at working temperature is in the range of 50-150 W [ibid]. This would reduce the fuel efficiency of the APU by some 5% to 30% or more [20], still more than the 20% of the ICE/generator combination.

2.5.2 Stationary Systems

Fuel cells systems for stationary applications usually include the production of both electricity *and* heat for a better overall efficiency. The fuel for those stationary systems will be natural gas: the amount of CO₂ produced per kWh is low (an important issue today) and the short length of the hydrocarbons speeds reformation and reduces the risk of carbon deposition within the reformer.

A possible system layout for a stationary application is shown in Fig. 12. It shows a complete fuel cell system for stationary production of electricity and heat. Before being supplied to the fuel cell the fuel is compressed, heated, chemically processed in presence of water vapor (for example by reforming), the air is compressed and preheated. After exploitation in the fuel cell stack for energy production, the residual gases are burned in a catalytic burner. The combustion supplies the necessary heat for preheating and reforming. The residual heat is used as process heat.

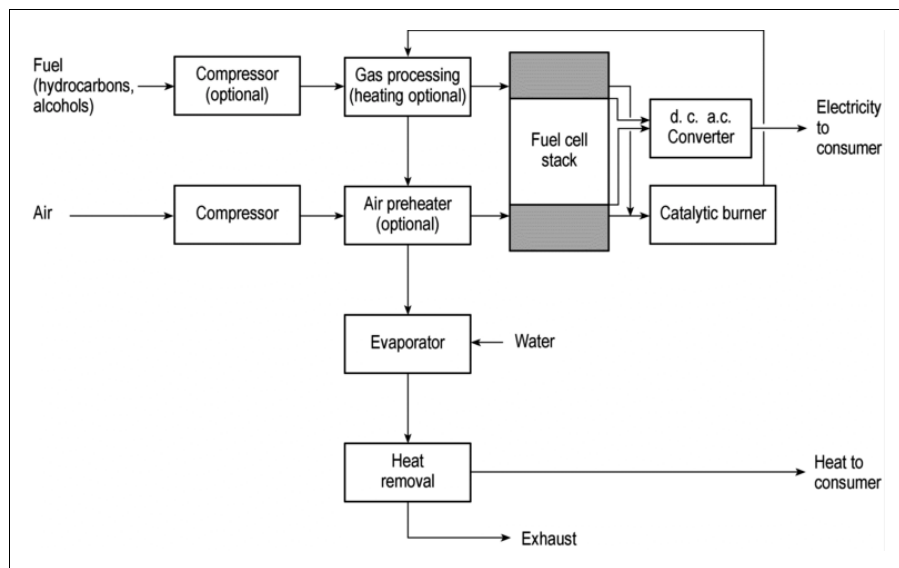


Fig. 12: Fuel cell system for stationary production of electricity and heat. A complete fuel cell system comprises besides the electrochemical device other components such as gas compressors, reformers, catalytic burner, and d.c./a.c. converter.

The gas processing step(s) before entering the stack depend on the type of the cell used: a PEM fuel cell needs the complex arrangement consisting of the reformer, shift reactors and so on which will be discussed in more detail in section 3.1.2. For a SOFC type cell the gas treatment can be reduced to a reformer which converts the natural gas into hydrogen and carbon monoxide. Nevertheless, both types of cells still need a sort of preprocessing of the fuel before it can be used in the cell.

2.5.3 Conclusion

As a summary we can say that while we have both energy sources and fuel cells, we neither have energy sources for our fuel cells nor fuel cells for our energy sources. While changing the base for our energy consumption is a slow process, given the money needed, developing or modifying existing cells which do not carry the burden of backward compatibility issues might well be faster and more affordable.

3. Challenges for the application of fuel cells

The previous sections have shown that fuel cells are feasible for many applications both mobile and stationary. The question then is why fuel cells, being systems with high efficiency, are so scarce. One of the reasons is of course the vicious circle that as long as production is low, prices are high which results in small production runs etc. Once production lots increase the price of fuel cells will be comparable to those of to-days internal combustion engines [21]. But there are other issues as well which will be discussed in the next sections.

3.1 Fuels

The fuel of choice for all fuel cells is *hydrogen*. It can be used in every cell type, has a very high reaction rate and generates only water as reaction product. However, while this may be the way to go in the future when hydrogen will be generated using renewable energies, we have to face the fact that there is no molecular hydrogen available on earth. Most hydrogen used today is obtained by steam reformation of hydrocarbons and a large amount of this hydrogen is used for further processing in the chemical industry (Fig. 13). Any additional amount of hydrogen, for example for energy conversion, would have to be produced especially for that purpose. While this reduces the amount of CO₂ generated at the site where the hydrogen is consumed, the conversion from hydrocarbons to hydrogen itself is not reversible and could result in an overall higher CO₂ output on earth. As a second point, hydrogen has a very low volumetric energy density in comparison to liquid fuels, even when compressed or

liquified [22], which not only means that cars have a lower driving range but also that more freight space is needed to transport the energy to the end user, resulting in higher energy expenditure for the distribution. As long as hydrogen is generated via reforming hydrocarbons and not via renewable energies this effect would increase, not reduce CO₂ emissions worldwide.

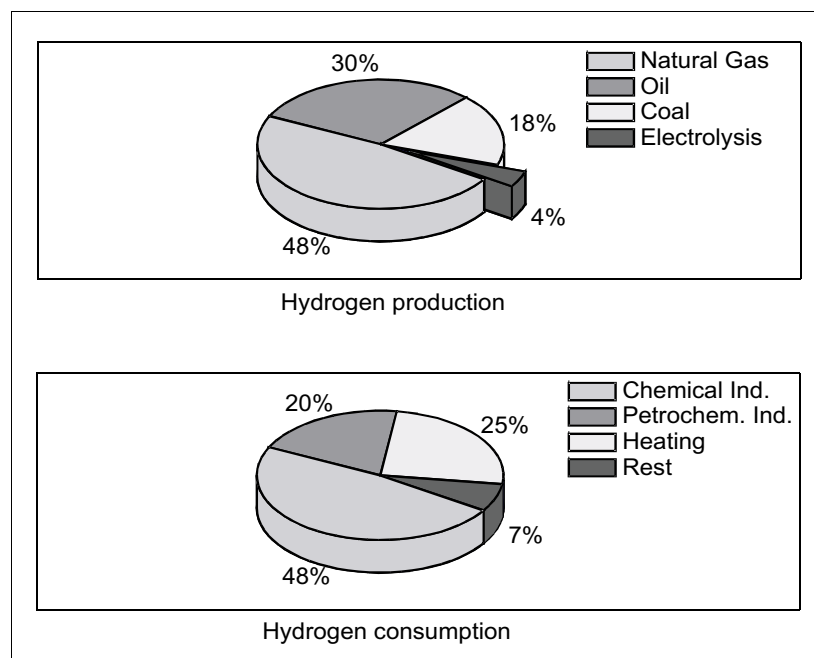


Fig. 13: Hydrogen production and consumption in the world. 96% of the hydrogen stems from reforming hydrocarbons.

So while hydrogen might be the fuel of choice in the future, fuel cell systems designed for today have to use the fuels available today, namely hydrocarbons (natural gas, diesel, gas) and, to a lesser extent, alcohols. That are the fuels fuel cells have to run with, either directly or after reforming them into mixtures more suitable for the cells. Reformates can be tailored to the needs of nearly all types of fuel cells. Using existing fuels, however, limits the types of cells which can be used.

3.1.1 Direct fuels

There are some fuel cells, namely MCFC's and SOFC's, which may use *methane* as fuel. Natural gas, an available energy carrier, consists mainly of methane. But the rest consists of

higher hydrocarbons (ethane, butane etc.), which are large enough to prohibit direct feeding of these cells without endangering their operation, so that the gas has to be pre-reformed before entering the cells.

Methanol may be used in specifically designed cells, for example direct methanol fuel cells (DMFC). However methanol is usually obtained from natural gas, losing about 1/3 of the chemical energy in the process [23].

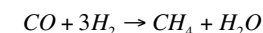
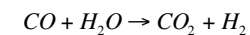
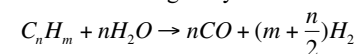
Carbon monoxide is an option for MCFC's and SOFC's (on the other hand, it is a catalyst poison for PEMFC's). As it is not available as fuel in nature but rather generated during the reforming process of hydrocarbons it will be discussed in Section 3.1.2.

Higher hydrocarbons can yet not be used as fuel though there are developments which may lead to diesel-using SOFC's. Today the hydrocarbons have to be converted into a hydrogen-rich gas ('reformat') before it can be fed into a fuel cell.

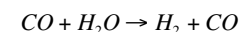
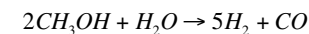
3.1.2 Reformates

The desired composition of the reformed gas strongly depends on the type of fuel cell where it shall be consumed. The carbon containing fuels are converted into a hydrogen rich gas either by reaction with water vapor ('steam reforming') or under-stoichiometric amounts of oxygen ('partial oxidation'). The respective relevant reaction equations are given below.

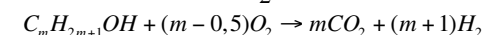
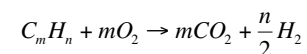
Steam reforming of hydrocarbons:



Steam reforming of methanol:



Partial oxidation:



The advantage of the steam reforming lies in the high hydrogen yields and concentrations which can be obtained, e.g. > 75% H₂ (dry gas) for methane. But as these reactions are strongly endothermic external heating is required. To overcome difficulties encountered with this in start-up and load change situations the use of micro-reaction technology is discussed [24].

In contrast to steam reforming partial oxidation is a slightly exothermic process. The exothermic degree increases with the carbon content of the fuel so that POX reformers for e.g. gasoline or diesel require adequate cooling. As further drawback the use of air as oxidant dilutes the product gas with nitrogen so that only hydrogen concentrations lower than 40% can be obtained.

To avoid an external heat exchange reforming concepts were both reactions run in parallel in the same catalytic bed are emerging. This so called auto thermal reforming (ATR) is a good compromise between the high hydrogen yield as obtained with steam reforming and the lower system complexity and reactant storage volume of a POX. ATR is especially interesting for the reforming of gasoline or diesel fuels in mobile application.

Except for the steam reforming of methanol and some other alcohols which can be processed at relatively low temperatures (250°C) the product gas obtained by the reforming process is rich in CO. It may be directly fed to the high or future intermediate temperature types of fuel cells. But for the use in the PACF and in particular the PEMFC the CO needs to be removed. This is achieved in a multi-step process comprising high and low temperature shift reaction to achieve CO contents of about 1% followed by preferential oxidation or methanation of the remaining CO.

3.2 Efficiency

3.2.1 The utilization of the fuel

The ideal situation for a fuel cell would be to completely use all the fuel to generate electricity and heat. This is achieved in so-called dead-end configurations where the fuel is fed into the anode inlet and consumed without leaving any residue. For most fuel cells or working conditions this however is impossible as can be illustrated by the following two examples:

- Feeding the cell with reformat. The reforming process usually adds some non-reacting gases like N₂ or CO₂ into the gas stream.
- In certain kinds of fuel cells, for example SOFC's, the products are generated on the anode side.

In both cases non-reacting gases accumulate at the anode side which have to be removed from the stack. This is done by providing a continuous flow of gas through the anode. The concentration of fuel gases is high at the inlet and is depleted more and more as the gas flows through the cell towards the gas outlet. Due to fabrication tolerances in the stack, gas manifolds etc. the gas flow within the different cells varies, so the point where all the fuel is depleted varies from cell to cell as well. As complete depletion of fuel within a cell would damage the cell components (much like an accumulator) more fuel than absolutely necessary has to be fed into the stack to prevent this from happening. The utilization of the fuel, U_f , for such a system is given by the partial pressures of the oxidizable gases entering (p_{in}) and leaving (p_{out}) the cell $U_f = 1 - \frac{p_{out}}{p_{in}}$, with typical values of $U_f = 0.8 - 0.85$.

While the fuel utilization directly affects systems generating only electricity, combined heat and power plants can recover some of the energy lost by oxidizing the unconsumed fuel in an afterburner and adding it to the heat output of the plant.

3.2.2 The faradaic efficiency

While most types of fuel cells reach faradaic efficiencies, η_f , of 0.95 to 1.0, the faradaic efficiency of the DMFC is a research topic. The reason for that is the diffusion of the fuel, methanol, through the electrolyte, which causes not only a voltage drop through the cell but also a drop in the faradaic efficiency. The leakage through a typical membrane (Nafion 117) amounts to a current loss of about 100 mA/cm², which even at the maximum power point with typical currents of about 400 mA/cm² reduces the faradaic efficiency to 0.8 [25].

3.2.3 The voltage efficiency

Looking only at thermodynamics the voltage U across both electrodes of a fuel cell should be

$$\Delta U = \frac{\sum \Delta G}{-nF} \quad (3)$$

with ΔG the Gibbs free energy of all reactions in the cell, F the Faradaic constant and n the number of electrons transferred in the chemical reaction (Fig. 14 a). ΔG again depends on temperature and gas concentrations

$$\sum \Delta G = \sum \Delta G^0 + RT \ln \frac{c_{products}}{c_{educts}} \quad (4)$$

However, as larger currents flow through the cell the internal ohmic resistance of the cell reduces the usable voltage at the cell contacts (Fig. 14 b). The internal ohmic resistance of the cell or stack is the sum of all the components involved: the interconnectors between the cells, the anode layer, the electrolyte and the cathode layer. Countermeasures depend on the type of

resistance encountered: in case of the interconnect it is the contact resistance between the interconnector and the adjacent layers, so focus is on improving the contact by reducing possible high-resistant oxide layers on the face of the interconnect. In case of the electrolyte it is mainly diffusion resistance induced by the drift of the ions through the electrolyte so the target is to reduce its thickness. In case of the anode and cathode it is mainly the lateral resistance as only a part of the active area is in contact with the interconnect and the electrons have to flow laterally through the layer in order to get to the contacted areas. Counter measures may comprise the use of a conductive gas diffusion layer (backing) and the appropriate design of the structure of the interconnect to fulfill both the media distribution and the electrical contact requirements.

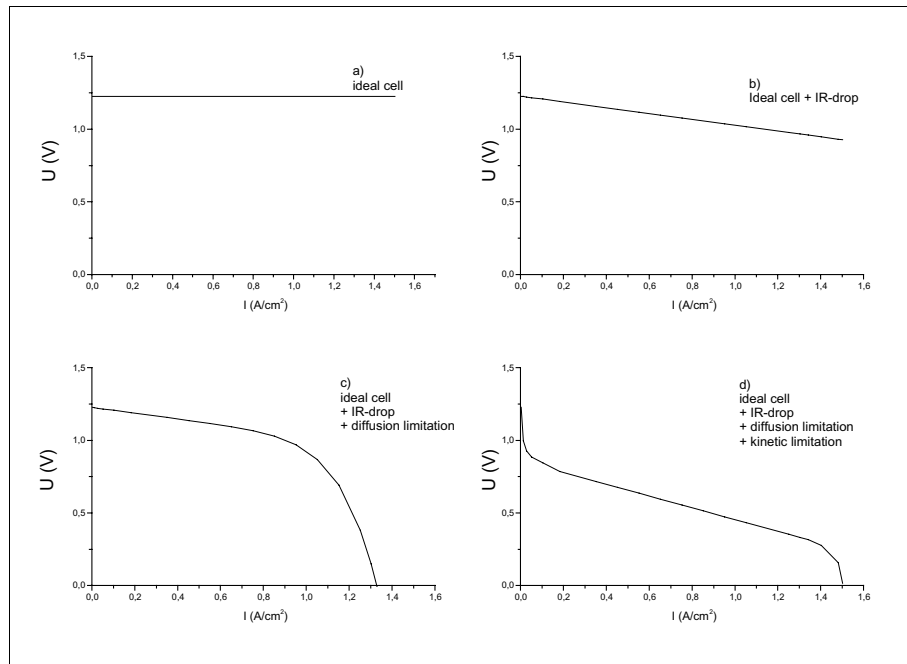


Fig. 14: Contributions to the I/U dependence of a fuel cell.

At still higher currents another effect contributes significantly to the overall voltage drop of the cell: the reactants have to reach the three-phase boundary (TPB) where the actual reaction takes place. The products that are generated have to leave after the reaction as well. Both effects are diffusion controlled which means that the higher the reaction rate (\sim cell current) the lower the educt concentration and the higher the product concentration at the TPB will be. Due to the exponential relationship between the gas concentration and concentration overpotential [4,5] the voltage across the cell will decrease very fast once a certain current limit is

exceeded (Fig. 14 c). It can usually be avoided by designing anode and cathode porosity appropriately.

Finally, there is another contribution to the overall voltage drop of the cell, which becomes important at small currents already and is therefore significant for the overall efficiency of the cell: the kinetic overpotential. As with any electrode the electrochemical reaction is reversible on a microscopic scale at both the anode and the cathode of a fuel cell. Consequently both kinds of reactions – oxidation and reduction – do take place simultaneously (Fig. 15). The number of reactions per time depends on the potential between the electrode and the surrounding: theory shows that both reaction rates should rise or drop exponentially, the sum of which can be detected as the macroscopic current flow of the cell $I = I^0 (e^{-\alpha CU} - e^{(1-\alpha)CU})$.

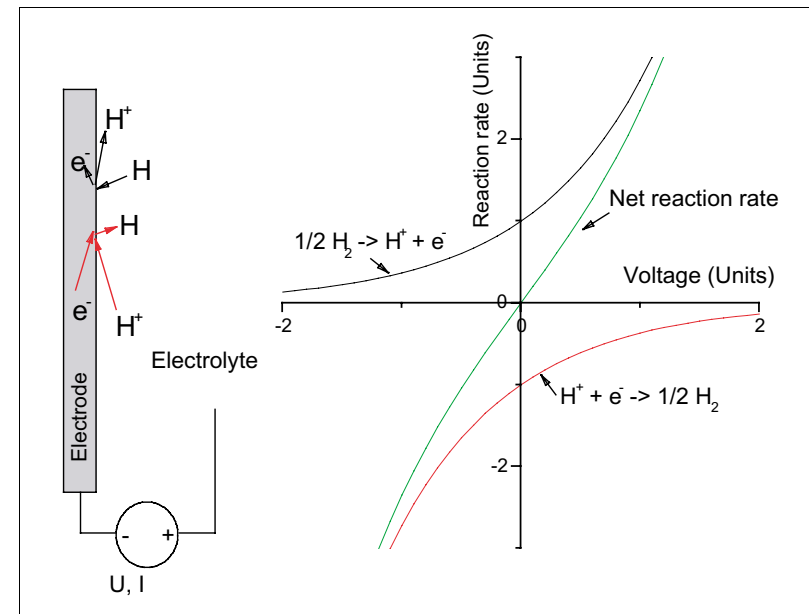


Fig. 15: Reactions taking place at one electrode, in this example hydrogen oxidation respectively proton reduction at the anode. The voltage applied does not control whether the reaction takes place or not but how often the reaction takes place.

As can be seen in Fig. 14 d, this phenomenon creates a steep voltage drop at small currents, which flattens out as the current increases. This voltage drop depends very strongly on the exchange current I^0 which again depends on the reaction rate of the catalyst under the working conditions of the cell. Those conditions may vary substantially: while a PEMFC with pure hydrogen as fuel and platinum as catalyst shows only small overpotential on the anode, the cathode side exhibits a significant contribution of the electrochemical overpotential to the overall voltage drop (Fig. 16).

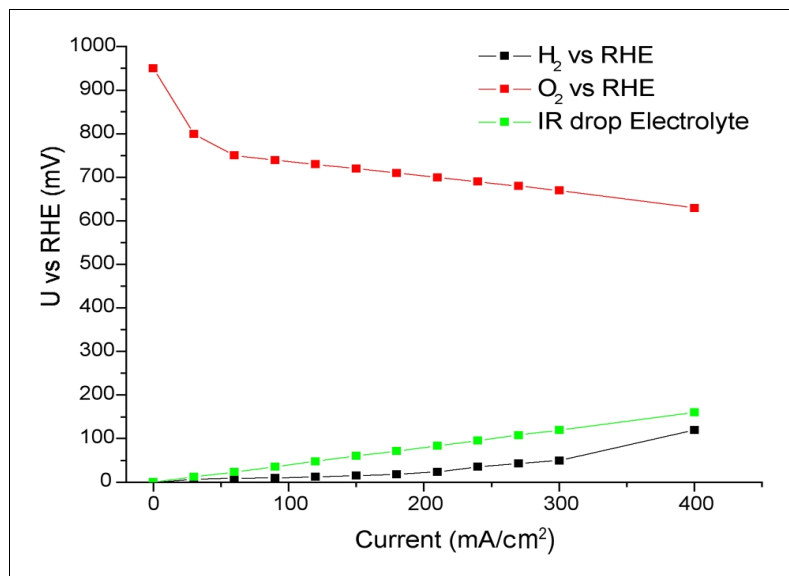


Fig. 16: Over-voltages at a PEM fuel cell [26].

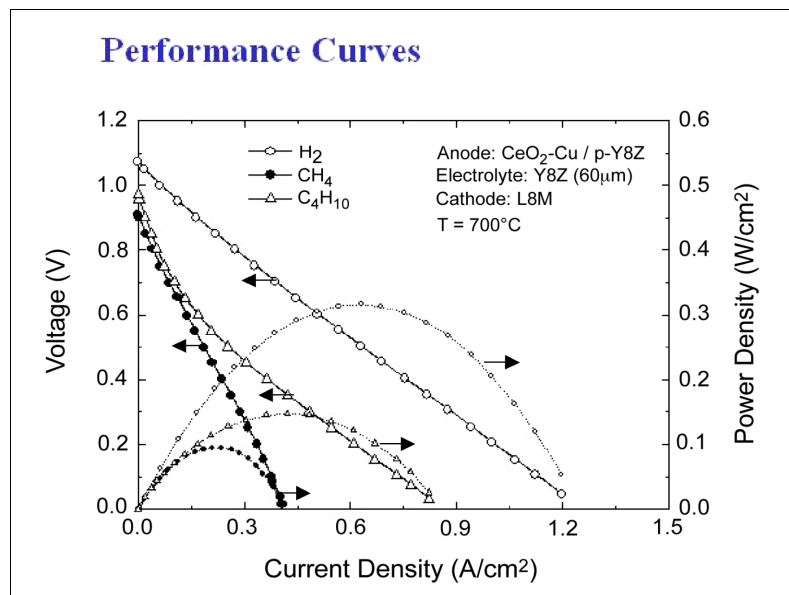


Fig. 17: Performance curve of an SOFC. Both current and power densities are plotted for various fuels [27].

Another example for this can be seen in Fig. 17 which shows current densities and power densities depending on the fuel used. While being fed with hydrogen the cell exhibits only a small overpotential at the beginning of the curve, the cell voltage drop is nearly linear. In the case of Methane and Butane the internal resistance of the cell is much higher. In both cases the cell performance would increase significantly if a catalyst would be known with a much higher activity towards the specific reaction.

The important issue for the near future is to reduce the overvoltage within the fuel cells for readily available fuels. An increased efficiency is not only the key to reducing volume and material expense in construction the fuel cell but also determines the amount of residual heat which needs to be removed. Especially for low temperature fuel cells this important as heat produced at low temperatures is difficult to remove and can often not be utilized.

3.3 Nano-scaled materials for electro-catalytic reactions

An important part of improving the performance and the efficiency of fuels lies in finding enhanced catalysts with a higher activity and better selectivity towards the desired reaction. Research today is aimed on improving the catalyst by providing catalysts with very small active particles and a homogeneous dispersion of them on the used support, usually a sort of carbon black, and by using binary, ternary or higher alloys instead of pure metals.

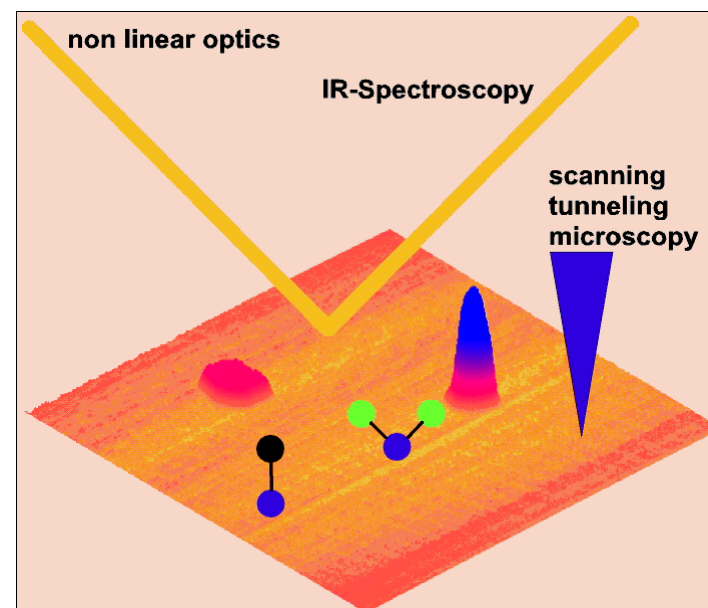


Fig. 18: Methods for the in-situ characterization of electrochemical active surfaces.

Where the reduction of size of the active centers aims first at an enlargement of the active surface area the reduction of particle size below a certain degree can cause additional effects which influence the activity of the catalysts. The understanding of these effects by investigating model catalysts is a major issue in current electro-catalysis research. The investigation of these effects is conducted on model catalysts consisting of either numerous nano-particles of the same type on multi-crystalline supports like glassy carbon or single nano-particles deposited onto single-crystalline surfaces [28]. A number of different physical characterization methods is suitable for in-situ measurements in electrochemical systems and can be used to characterize the specimens. Some of the methods applied are shown in Fig. 18.

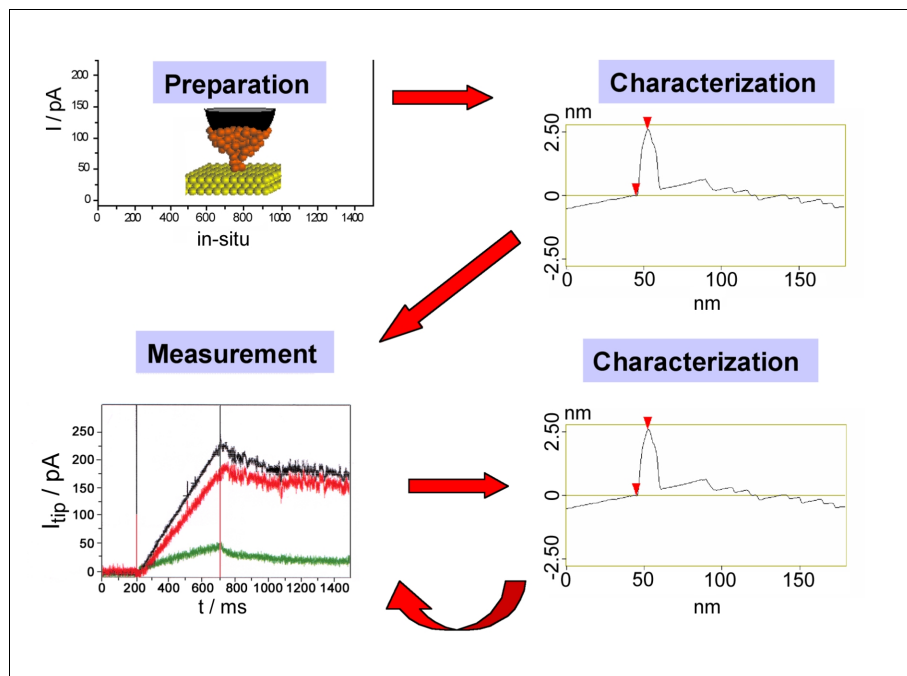


Fig. 19: All in-situ EC-STM measurement sequence.

One of those methods, the electrochemical scanning tunneling microscopy (EC-STM), is especially suited for basic research concerning the reactivity of single nano-particles supported on single-crystalline surfaces: First the tip is coated with the material to be investigated. The tip is mounted in the STM and some of the atoms are transferred onto the single crystal surface by inducing a mechanical contact of tip and substrate. By varying the force and duration of the contact the size of the cluster transferred to the crystal can be controlled. After the deposition the reactivity regarding the hydrogen evolution of the cluster can be investigated by measuring the hydrogen oxidation current at the tip (Fig. 19). The electro-catalytic activity

of the particle is calculated from the current measured during the experiment [28]. This technique allows for an in-situ measurement where a single nano-particle is generated, characterized and the electrochemical measurement performed under complete in-situ conditions.

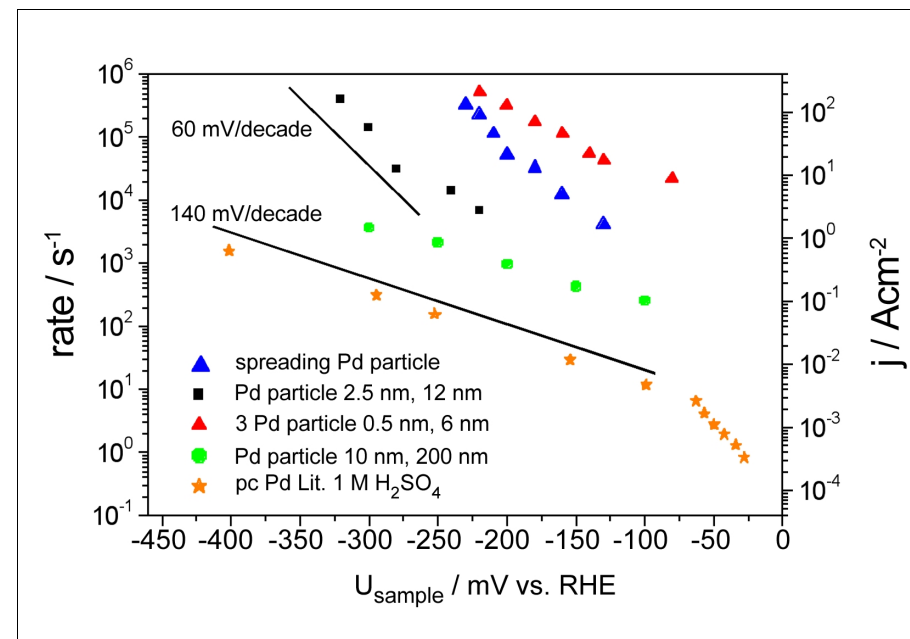


Fig. 20: Reaction rates for proton reduction at a single palladium cluster supported on an Au(III) substrate. A strong dependence on the particle size (height, width) is observed. Reaction rates up to three orders of magnitude larger than for polycrystalline palladium were observed. Small particles exhibit a different Tafel slope [28].

Of special interest are measurements of metallic nano-particles supported on a single crystal of different metal. The difference of the lattice constant strains the layer of the nano-particle in close contact to the substrate so that a strong influence of the size of the particle can be observed (Fig. 20). This may help to understand the effects relevant in the alloy formation on the electrochemical activity.

However, first experiments trying to find a correlation between the density of low correlated surface atoms and the reactivity did not reveal any apparent correlation (Fig. 21). We found that the catalytic activity of gold supported palladium nano-particles regarding the hydrogen evolution depends on the height of the particles which can be explained on the basis of strain exerted by the substrate (Au) on the Pd nano-particle and thus its electronic structure, as predicted by the d-band model of Hammer and Norskov [29,30,31]. Such a strain leads to modified adsorption and activation energies, e. g. of hydrogen, and the rate of hydrogen evolution.

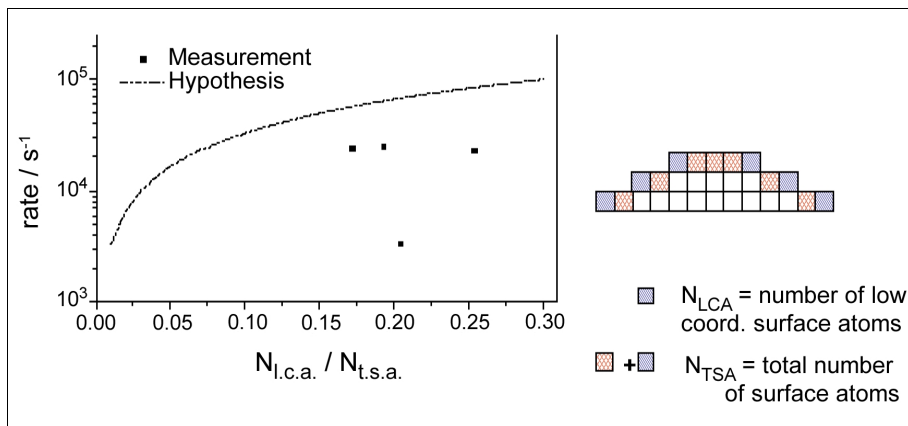


Fig. 21: Reaction rate as function of the density of low coordinated surface atoms: Experiment and simulation (for assumptions see text).

To further understand the effect of the particle size the investigation of systems containing multiple nano-particles of a certain size is important. The major factor to influence the size of the particles is the loading of noble metal on the support. High loadings lead to larger particles and in the end to the formation of larger clusters of multi-crystalline particles or agglomerates. The best way to characterize these particles is transmission electron microscopy (TEM) to achieve an overview of the number and size of the particles. High-resolution transmission electron spectroscopy allows to distinguish between different orientations of the crystallites forming the nano-particle and so detect the formation of poly-crystalline or agglomerate particles (Fig. 22).

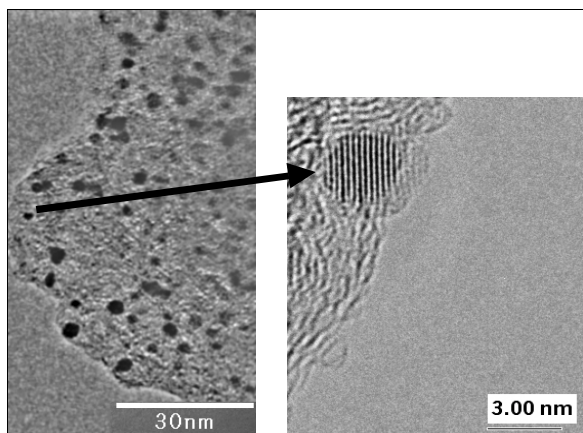


Fig. 22: TEM (left) and HRTEM (right) picture of nano-particles in a carbon supported platinum catalyst specimen.

An important effect of an increased particle size is the reduction of the density of atoms with a low coordination number on the surface – experimentally confirmed recently by Frenkel et al. [32] using extended x-ray absorption fine-structure (EXAFS) (Fig.23).

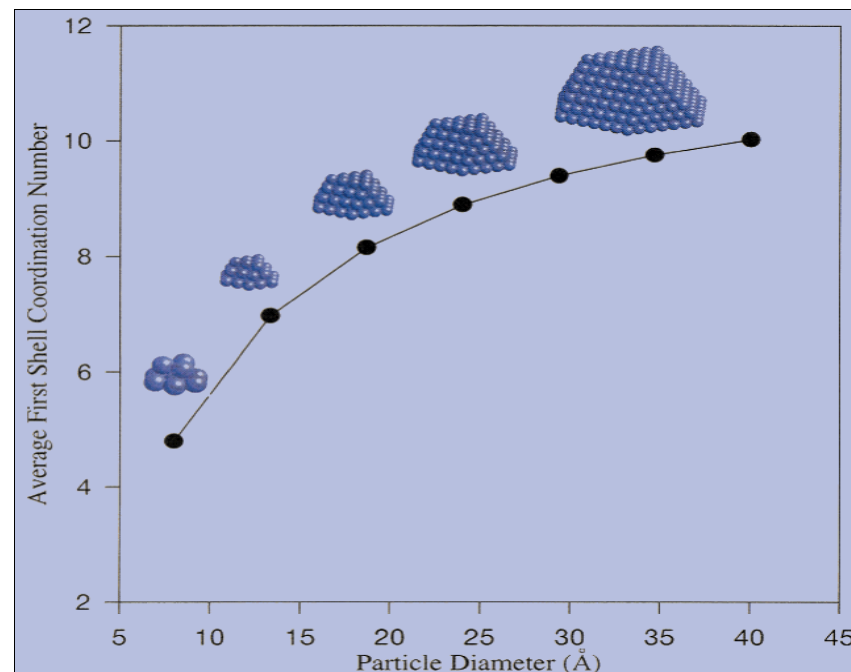


Fig. 23: Coordination number as function of the particle size [32].

4. Conclusions

Due to their high conversion efficiencies and their low emissions of pollutants fuel cells are a promising technology for future energy conversion systems. A major obstacle for the wider introduction is the lack of a suitable infrastructure for distribution and storage of the preferred fuel, hydrogen. Means for the on-site production of hydrogen from more readily available sources are therefore developed with some success.

Although today's fuel cells have achieved a quite high level of efficiency and stability future improvements are required for their commercialization. A key role herein play improved catalysts, especially for the PEMFC operated with reformed gas. These improvements will be achieved more easily if a better understanding of the relevant processes can be provided. Here the investigation of the correlation of the structure of the used nano-particles with the reactivity is essential.

References

- [1] Umweltbundesamt (ed.)
- [2] Historical CO₂ records from the Law Dome DE08, DE08-2, and DSS ice cores. Cores taken from the Law Dome, Antarctica (66°44' S, 112°50'). Data downloaded on the 19.01.2004 from <http://cdiac.esd.ornl.gov/trends/co2/lawdome.html>.
- [3] Measurements of the CO₂-concentrations in the in atmosphere at Mt. Mauna Loa (Latitude:19.539, Longitude:155.578, Hawaii). Data downloaded on the 16.01.2004 from <http://cdiac.esd.ornl.gov/ftp/trends/co2/lawdome.combined.dat>.
- [4] K. Kordesch, G. Simader: "Fuel Cells", VCH, Verlagsgesellschaft, Weinheim **1996**.
- [5] K. Ledjeff (ed.): "Brennstoffzellen", C. F. Müller, Heidelberg **1995**.
- [6] Published by Siemens.
- [7] Press release photography from Ballard Power Systems.
- [8] Ballard XCells Hy80, without electric motor and hydrogen tank. Ballard sales brochure.
- [9] NECAR 4 data: G. Friedlmeier, J. Friedrich and F. Panik: "Test Experiences with the DaimlerChrysler Fuel Cell Electric Vehicle NECAR 4", *Fuel Cells*, **2001**, p. 92-96.
- [10] R. Wurster; DWV; Presentation at Hessischer Mobilitätskongress **2003**
- [11] DaimlerChrysler Press photography.
- [12] SiemensVDO automotive press release.
- [13] A. Armstrong: "Well to Wheels Efficiency Standards and Climate Change", *New Zealand Road to Cleaner Air workshop*, Wellington, June **2001**, published in the proceedings on CD.
- [14] Continental press release March 11th 2003.
- [15] United States Environmental Protection Agency: "Study of Exhaust Emissions from Idling Heavy-Duty Diesel Trucks and Commercially Available Idle-Reducing Devices", EPA420-R-02-025, October **2002**

- [16] Delphi Systems press photography.
- [17] Press release BMW, ex. at <http://www.bmwworld.com/models/750hlc.htm>.
- [18] J. Zizelman: "Development Update on Delphi's Solid Oxide Fuel Cell System", Presentation at the 4th SECA meeting **2003**.
- [19] P. Holtappels, U. Stimming and P. Lamp: "Concept for Simple Small SOFC System for Automotive Application", *Proceedings of the VIIth international symposium on Solid Oxide Fuel Cells*, **2001**, ISBN 1-56677-322-9.
- [20] Based on the average 12,700 km/year (1999) driving per vehicle, 1l/100 km fuel consumption by the SOFC-APU, 100 W heating power and 50 sundays + 30 holidays supplementary heating per year.
- [21] L. S. Dixon, I. Porche, J. Kulick: "Driving Emissions to Zero: Are the Benefits of California's Zero Emission Vehicle Program Worth the Costs?" *RAND study*, **2002**, ISBN: 0833032127
- [22] James J. Eberhard: "Energy Efficiency and Renewable Energy", US Department of Energy 2002 DEER Workshop, **2002**
- [23] U.S. Department of Energy, Office of Domestic and International Energy Policy: "Assessment of Costs and Benefits of Flexible and Alternative Fuel Use in the U.S. Transportation Sector: Technical Report Three: Methanol Production and Transportation Costs", Washington, DC, November **1989**.
- [24] 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).
- [25] S. Wasmus, A. Küver: "Methanol Oxidation and Direct Methanol Fuel Cells: a Selective Review", *Journal of electroanalytical chemistry* Vol 461, **1999**, p. 14-31.
- [26] H₂, O₂ Data: S. Escribano and P. Aldebert: "Electrodes for Hydrogen/Oxygen Polymer Electrolyte Membrane Fuel Cells", *Solid State Ionics* 77, **1995**, p. 318-323

[27] R. J. Gorte, S. Park, J. M. Vohs, and C. Wang: "Anodes for Direct Oxidation of Dry Hydrocarbons in a Solid Oxide Fuel Cell", *Advanced Materials* 12, **2000**, p. 1465-1469.

[28] J. Maier, K. A. Friedrich, and U. Stimming: "Novel Method for the Investigation of Single Nano Particles", *Faraday Discussion* Vol. 121, **2002**, p. 365-372.

[29] M Mavrikakis, B Hammer, JK Norskov: "Effect of Strain on the Reactivity of Metal Surfaces". *Phys. Rev. Lett.* 81 (**1998**) 2819.

[30] A Ruban, B Hammer, P Stoltze, HL Skriver, JK Norskov: "Surface Electronic Structure and Reactivity of Transition and Noble Metals". *J. Mol. Catal. A* 115 (**1997**) 421.

[31] B Hammer, JK Norskov: "Theoretical Surface Science and Catalysis - Calculations and Concepts". *Adv. Catalysis* 45 (**2000**).

[32] A. I. Frenkel, C. W. Hills, and R. G. Nuzzo: "A View from the Inside: Complexity in the Atomic Scale Ordering of Supported Metal Nanoparticles", *J. Phys. Chem. B*, **2001**, 105(51) p. 12689 – 12703