Fuel Cells – Fundamentals and Applications

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1 Introduction

1.1 The rationale behind fuel cell development [1-8]

The invention of fuel cells as energy conversion systems dates back from the middle of the 19th century. The invention of fuel cells as an electrical energy conversion system is attributed to Sir William Grove, however, the principle was discovered by Christian Friedrich Schönbein [9], a Professor at the University of Basle from 1829 to 1868, who was in close contact with Sir Grove. In any case, fuel cells are one of the oldest electrical energy conversion technologies known to man. Their development, however, lacked a drive during their first century as primary energy sources were abundant, unrestricted, and inexpensive.

At the beginning of the 20th century the conversion of chemical energy into electrical energy became more important due to the increase in the use of electricity. Electrical energy conversion systems were introduced initially as small, distributed power generators but soon further developments yielded megawatt-scale centralized plants. Over the last decade, the tendency to increase the flexibility of electricity generation, and the increase of the world's population have led to an increased interest in the development of more powerful and finely distributed power generation. It is expected that decentralized power plants will reduce both the capital cost for the installer as well as improve the overall efficiency due to the possibility of the co-generation of electricity and heat. The distribution of heat is easier and more efficient in smaller systems, where production of heat and its usage are in closer proximity.

One of the major factors that has influenced the development of fuel cells has been the increasing concern about the environmental consequences of fossil fuel use in production of electricity and for the propulsion of vehicles. The dependence of the industrialized countries on oil became apparent in the oil crises. More importantly, however, is the increasing global awareness of how human activities influence the environment and how a sustainable development can be achieved with a tremendously increasing world population.

Fuel cells may help to reduce our dependence on fossil fuels and diminish poisonous emissions into the atmosphere, since fuel cells have higher electrical efficiencies compared to heat engines (see Section 1.3.2.). Using pure hydrogen, fuel cells only produce water, thus eliminating locally all emissions otherwise caused by electricity production. The share of renewable energy from wind, water and sun will increase further but these sources are not suited to cover the electrical base load due to their irregular availability. The combination of these sources, however, to produce hydrogen in co-operation with fuel cells may well be an option for future power generation.

1.2 Basic principles of Fuel Cells

Fuel cells are galvanic cells, in which the free energy of a chemical reaction is converted into electrical energy (via an electrical current). The Gibbs free energy change of a chemical reaction is related to the cell voltage via [10]:

$$\Delta G = -nF\Delta U_0 \qquad \text{(Eqn. 1)}$$

where n is the number of electrons involved in the reaction, F is the Faraday constant, and ΔU_0 is the voltage of the cell for thermodynamic equilibrium in the absence of a current flow. The anode reaction in fuel cells is either the direct oxidation of hydrogen (detailed discussion in Section 1.4.1.) or the oxidation of methanol (Section 1.4.2.). An indirect oxidation via a reforming step can also occur (see Section 3). The cathode reaction in fuel cells is oxygen reduction, in most cases from air (Section 1.3.3.).

For the case of a hydrogen/oxygen fuel cell – the principle is shown in Figure 1 - the overall reaction is:

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \quad \text{with } \Delta G = -237\ \text{kJ/mol} \qquad \text{(Eqn. 2)}$$

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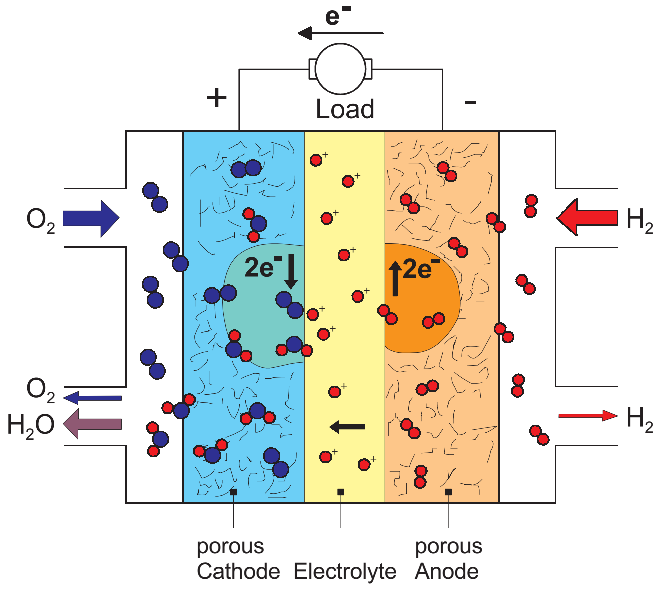

Fig. 1 Schematic drawing of a hydrogen/oxygen fuel cell and its reactions based on the proton exchange membrane fuel cell (PEMFC).

with an equilibrium cell ΔU_0 voltage for standard conditions at 25 °C of:

$$\Delta U_0 = \frac{-\Delta G}{nF} = 1.23\ V \qquad \text{(Eqn.3)}$$

The equilibrium cell voltage is the difference of the equilibrium electrode potentials of cathode and anode which are determined by the electrochemical reaction taking place at the respective electrode:

$$\Delta U_0 = U_{0,c} - U_{0,a} \qquad \text{(Eqn. 4)}$$

The important anodic and cathodic reactions with their equilibrium potentials are described in more detail in the next sections. The basic structure of all fuel cells is similar: the cell consists of two electrodes which are separated by the electrolyte and which are connected in an external circuit. The electrodes are exposed to gas or liquid flows to supply the electrodes with fuel or oxidant (e.g. hydrogen or oxygen). The electrodes have to be gas or liquid permeable and therefore possess a porous structure. The structure and content of the gas diffusion electrodes is quite complex and requires considerable optimization for the practical application. The electrolyte should possess a gas permeability as low as possible. For fuel cells with a proton conducting electrolyte (PEMFC, proton exchange membrane fuel cell), hydrogen is oxidized at the anode (according to the following equation) and protons enter the electrolyte and are transported to the cathode:

$$H_2 \rightarrow 2H^+ + 2e^- \qquad \text{(Eqn. 5)}$$

At the cathode the supplied oxygen reacts according to:

$$O_2 + 4e^- \rightarrow 2O^{2-} \qquad \text{(Eqn. 6)}$$

Electrons flow in the external circuit during these reactions. The oxygen ions recombine with protons to form water:

$$O^{2-} + 2H^+ \rightarrow H_2O \qquad \text{(Eqn. 7)}$$

The reaction product of this reaction is water, which is formed at the cathode in fuel cells with proton conducting membranes. It can be formed at the anode, if an oxygen ion (or carbonate) conducting electrolyte is used instead, as is the case for high temperature fuel cells.

1.3 Operation of a fuel cell

1.3.1 Basics

A fuel cell is an electrochemical cell whereby each electrochemical reaction is characterized by the thermodynamic equilibrium potential described by the Nernst equation. Even under no-current conditions the voltage of a fuel cell can be lower than the thermodynamic value due to mixed potential formation and other parasitic processes. Thus the open circuit voltage can be lower than the Nernstian value. When current flows, a deviation from the open circuit voltage occurs corresponding to the electrical work performed by the cell. The deviation from the equilibrium value is called the overpotential and has been given the symbol η. One of the reasons for the deviation of the potential from the equilibrium value is the finite rate of the reaction at the electrodes. For a redox reaction at one electrode the current density (j) is given by the Butler-Volmer equation:

$$j = j_0\,\{\exp(\alpha_A F\eta/RT) - \exp(-\alpha_C F\eta/RT)\} \qquad \text{(Eqn. 8)}$$

with j_0 the exchange current density, α_A and α_C the transfer coefficients for the anodic and cathodic reaction, respectively, and η the overpotential to drive the reaction. This equation holds when the charge transfer dominates the reaction at small values of j and η.

Other limiting factors such as mass transport hindrance are present in real systems and are described in terms of potential losses. A current density versus overpotential plot for measured half-cell reactions is shown in Figure 2. As can be

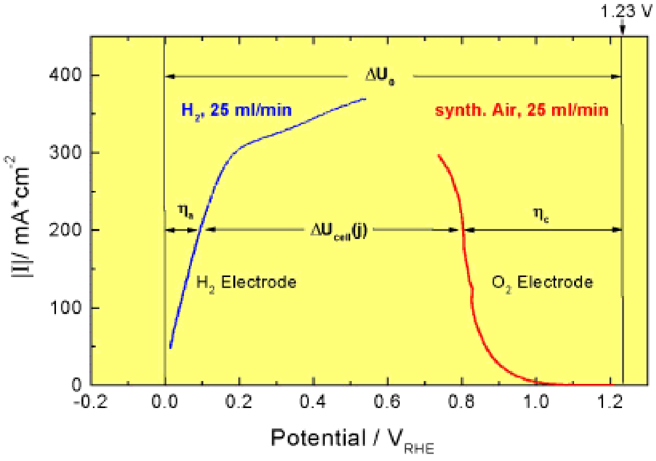

Fig. 2 The dependence of the current density versus potential for anode and cathode reaction. Measured potential dependence regarding hydrogen oxidation and oxygen reduction from air in a membrane electrode assemblie (MEA). Electrolyte: Nafion 117, Pt/C-catalysts.

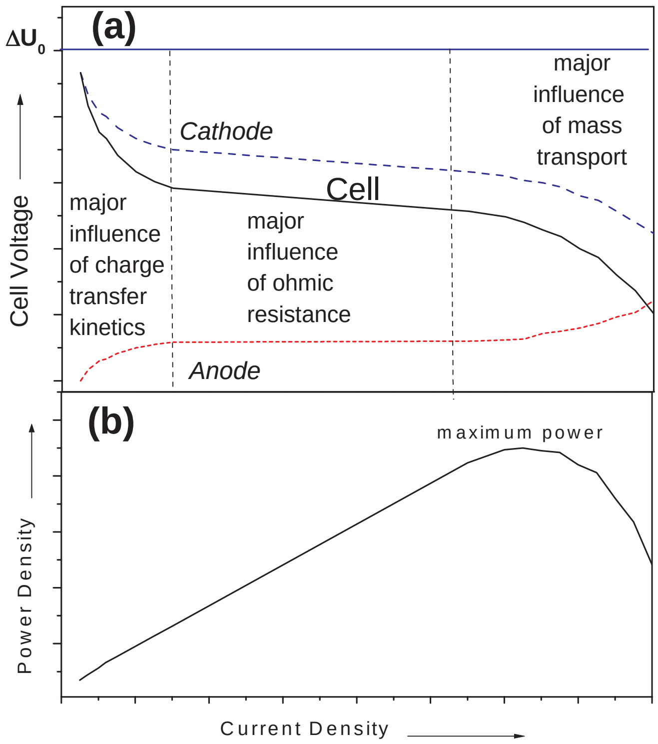

Fig. 3 Schematic of (a) the fuel cell voltage versus current density and (b) the power density versus current density. The anode and cathode overpotentials are shown in (a).

seen from the diagram, with an acid electrolyte the overpotential losses are much higher at the cathode due to slower kinetics of the oxygen reduction reaction compared to the hydrogen oxidation reaction. The anode and cathode overpotentials are:

$$\eta_a = U_a(j) - U_{0,a} \quad \text{with } \eta_a > 0 \text{ (oxidation of fuel)} \qquad \text{(Eqn. 9)}$$

$$\eta_c = U_c(j) - U_{0,c} \quad \text{with } \eta_c < 0 \text{ (reduction of oxygen)} \qquad \text{(Eqn. 10)}$$

In addition to the overpotentials the cell experiences further losses due to the resistance R_e of the electrolyte in-between both electrodes and due to contact resistances, so that the cell voltage can be written as:

$$\Delta U(j) = U_c(j) - U_a(j) = \Delta U_0 - (|\eta_a(j)| + |\eta_c(j)| + R_e j) \qquad \text{(Eqn. 11)}$$

The cell voltage of a fuel cell is the difference between the two half cell potentials as can be seen in Figure 3a. As both half cell reactions suffer from losses, the cell voltage is also not ideal and decreases with increasing current density. From such a graph a power density versus current density plot can be obtained (Figure 3b) and this is a useful representation for comparing different fuel cells.

1.3.2 Efficiencies of fuel cells

In order to compare fuel cells with other systems such as internal combustion engines (ICE) an evaluation of the system efficiency is necessary. An internal combustion engine converts chemical energy into mechanical energy, which can then be transformed into electrical energy by means of a rotating generator.

The combustion of a hydrocarbon (chemical energy) is accompanied by a rise in temperature as these reactions are exothermic and the reaction products are usually gases. The heat increase causes an expansion of the formed gases which in their turn can produce mechanical work by causing the pistons in the ICE to move (or steam is generated to drive a steam cycle). The maximum efficiency of this system is given by the Carnot efficiency, $\varepsilon_r^{thermal}$, as follows:

$$\varepsilon_r^{\text{thermal}} = \frac{W_r}{(-\Delta H)} = 1 - \frac{T_2}{T_1} \qquad \text{(Eqn. 12)}$$

where W_r is the reversible work performed and ΔH is the enthalpy change of the reaction and T_1 and T_2 are the two absolute temperatures for the operation of the heat engine. In general, these efficiencies are not surpassing 50 % for the most efficient engines (e.g. steam turbines).

For a fuel cell the efficiency can be calculated from the Gibbs free energy (ΔG) and the enthalpy change (ΔH) of the electrochemical reaction. Ideally, the free energy of the reaction can be completely converted into electrical energy and the efficiency $\{\varepsilon\}$ is given by:

$$\varepsilon_r^{\text{cell}} = \frac{W_e}{(-\Delta H)} = \frac{nF\Delta U_0}{(-\Delta H)} = \frac{\Delta G}{\Delta H} = 1 - \frac{T\Delta S}{\Delta H} \qquad \text{(Eqn. 13)}$$

where W_e is the electrical work performed, and (ΔS) is the isothermal entropy change of the reaction. $T\Delta S$ corresponds to the reversible heat exchanged with the external environment. The change in entropy of the reaction (ΔS) depends strongly on the reactants and products. In principle, for certain cases fuel cell efficiencies greater than 1 are attainable when the entropy change is positive. This means that the temperature coefficient ($\partial(\Delta U)/\partial T = \Delta S/nF$) of the cell is positive and the supplemental electrical energy is derived from heat of the external thermal reservoir (e.g. the oxidation reaction of carbon monoxide to carbon dioxide is associated with an efficiency of the cell of $\varepsilon_r^{\text{cell}} = 1.24$). In practice, however, electrode overpotentials cause the practical efficiencies to be lower than 1. For negative ΔS, an increase in temperature causes a decrease in thermodynamic efficiency of the fuel cell whilst for an ICE the efficiency increases with higher temperatures.

The lowering of the efficiency by the losses due to electrode overpotentials and by the electrolyte resistance of the cell, is expressed by the electrochemical efficiency which is also used to compare fuel cells amongst each other. Cells of different designs and different components can be compared by using the same reactions and by calculating the electrochemical efficiency given by:

$$\varepsilon_V = \frac{\Delta U_{\text{cell}}}{\Delta U_0} = 1 - \frac{(|\eta_a(j)| + |\eta_c(j)| + R_e j)}{\Delta U_0} \qquad \text{(Eqn. 14)}$$

The electrochemical efficiency gives more information about fuel cells than the thermodynamic efficiency as it is directly related to the performance of the cell. For a complete description of the fuel cell efficiency further factors associated with the practical operation have to be considered. These include the Faradaic efficiency ε_F which is defined as the ratio of the experimental current I_{exp} and the maximal possible current I_{max}. This Faradaic efficiency considers the possibility of parallel reactions which can lead to a lower current yield than theoretically possible, e.g., the formation of formaldehyde or formic acid during the oxidation of methanol reduces the number of exchanged electrons from 6 for the total oxidation to CO_2 to 2 or 4, respectively. It also takes into account the possibility of heterogeneously catalyzed chemical reactions taking place at the electrode surfaces. Furthermore, the total efficiency of the cell requires the consideration of some practical aspects concerned with the specific fuel used. In most cases fuel cells are not operated with 100% fuel utilization in order to avoid a fuel depletion of some areas of the electrodes. Therefore the fuel utilization should be included into the total efficiency. When using mixtures of fuels not all components are electrochemically converted and then an additional heating value efficiency needs to be considered. In the following, the total efficiency is given and the different contributions are shortly described:

$$\varepsilon_{\mathrm{fc}} = \varepsilon_r^{\mathrm{cell}} \cdot \varepsilon_{\mathrm{V}} \cdot \varepsilon_{\mathrm{F}} \cdot U \cdot \varepsilon_{\mathrm{H}} \qquad \text{(Eqn. 15)}$$

with ε_{fc}: fuel cell efficiency,
ε_r^{cell}:thermodynamic efficiency,
ε_V: electrochemical efficiency,
ε_F: faradaic efficiency (Eqn.16)

$$\varepsilon_{\mathrm{F}} = \frac{I_{\mathrm{exp}}}{I_{\mathrm{max}}} = \frac{n_{\mathrm{exp}} * F * v_i}{n_{\mathrm{max}} * F * v_i} = \frac{n_{\mathrm{exp}}}{n_{\mathrm{max}}} \qquad \text{(Eqn.16)}$$

with U the utilization of the fuel
and ε_H: heating value efficiency given by:

$$\varepsilon_{\mathrm{H}} = \frac{\Delta H_r}{\Delta H_c} \qquad \text{(Eqn.17)}$$

with ΔH_r: heating value of all fuel components that are converted electrochemically, (e.g. H_2) and ΔH_C: heating value of all fuels (e.g., including CH_4 or CO).

In spite of all these factors, the electrical efficiencies of fuel cells are superior to that of heat engines. A comparison of electrical system efficiencies (efficiency of the system including fuel cell and periphery) as well as overall efficiency in the case of cogeneration of heat and electricity is given in Figure 4 [11, 12]; it should be noted that PAFCs have even the lowest efficiencies of all fuel cell types.

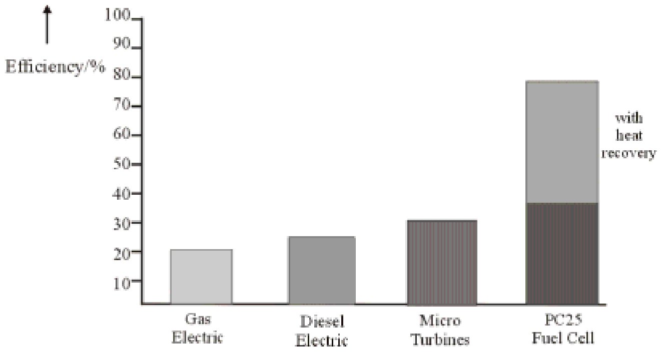

Fig. 4 A comparison of electrical system efficiencies between a PAFC (PC25, commercial system) and other conventional energy conversion systems.

1.3.3 *Co-generation of heat and power*

The simultaneous utilization of electricity and heat from an energy conversion system is called co-generation. This type of energy utilization is more efficient than the sole use of electricity as in most systems considerable heat is produced. The use of this heat to either produce more electricity (in a gas or steam turbine for instance) or to accommodate the plant with heat and warm water increases the overall efficiency as follows:

$$\varepsilon_{\mathrm{overall}} = \frac{Q + E}{Q_0} \qquad \text{(Eqn. 18)}$$

with Q the usable energy obtained in heat, E the electrical energy and Q_0 is the heat content of the fuel. This type of energy conversion is very applicable to fuel cells as they produce heat at temperature levels depending on the system. Especially for stationary applications co-generation has been used to provide homes with both electricity and heat (see Section 5) [13].

1.4 *Important Reactions*

1.4.1 *Hydrogen oxidation*

The oxidation of hydrogen occurs readily on Pt-based catalysts. The kinetics of this reaction is very fast on Pt catalysts and in a fuel cell the oxidation of hydrogen at higher current densities is usually controlled by mass–transfer limitations. The oxidation of hydrogen also involves the adsorption of the gas onto the catalyst surface followed by a dissociation of the molecule and electrochemical reaction to two hydrogen ions as follows:

$$2\,Pt_{(s)} + H_2 \rightarrow Pt\text{-}H_{ads} + Pt\text{-}H_{ads} \qquad \text{(Eqn. 19)}$$

$$Pt\text{-}H_{ads} \rightarrow H^+ + e^- + Pt_{(s)} \qquad \text{(Eqn. 20)}$$

where $Pt_{(s)}$ is a free surface site and $Pt\text{-}H_{ads}$ is an adsorbed H-atom on the Pt active site.

The overall reaction of hydrogen oxidation is:

$$H_2 \rightarrow 2H^+ + 2e^- \qquad U^0 = 0V \qquad \text{(Eqn. 21)}$$

Although this reaction is a fast reaction on Pt catalysts, in a fuel cell some problems may arise as to when impure hydrogen is used. Operating a fuel cell with pure hydrogen gives the best performance but pure hydrogen is expensive and difficult to store. Alternatives to pure hydrogen are natural sources such as natural gas, propane or alcohols. These substances have to be reformed, however, into hydrogen (see

Section 3) and even after gas clean up some contaminants such as carbon monoxide can still exist in the fuel feed. As with the methanol oxidation catalysts, CO poisons the catalyst by blocking the active sites on the surface. So although, in principle, a pure Pt catalyst can be used for hydrogen oxidation, similar studies into alloys as for methanol oxidation catalysts (section 1.3.2.) have been carried out to improve the catalyst activity with contaminated hydrogen [14, 15].

1.4.2 Methanol oxidation

Very few electrode materials have been shown to be capable of adsorbing methanol in acidic media, and of these only Pt-based materials display a high enough stability and activity to be attractive as catalysts. Many studies on the oxidation of organic molecules and specifically on methanol oxidation have been carried out [16-30].

An overview of methanol oxidation and methanol fuel cells has been published in the literature [31] . The overall reaction mechanism for methanol oxidation is:

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \qquad U^0 = 0.046\ \text{V} \qquad \text{(Eqn. 22)}$$

It is assumed that the oxidation of methanol on Pt based catalysts proceeds by the adsorption of the molecule followed by several steps of deprotonation. A scheme for this adsorption/deprotonation process is given in Figure 5 [32].

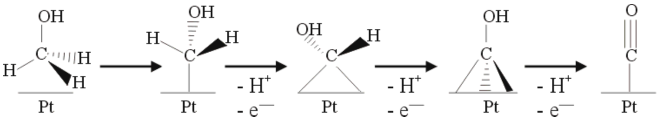

Fig. 5 Scheme of methanol oxidation on Pt showing the consecutive stripping of hydrogen atoms.

The scheme shows that CO is formed during the oxidation of methanol, a result confirmed by IR spectroscopy. This CO species can block the surface of the catalyst and hinder any further reaction. For this reason a number of co-metals are usually added to the Pt catalyst to facilitate CO removal by oxidation to CO_2. This can be achieved by oxidising the CO species using oxygen containing species adsorbed at the surface either from the water in solution or hydroxide ions.

A scheme of the possible reactions for methanol oxidation and their products is shown in Figure 6 [33, 34]. The scheme displays the possible reaction pathways and their products and each reaction step represents the transfer of one electron. Stable compounds are located on the hypothenus; dehydrogenation occurs in the direction from left to right; and oxidation by adsorbed OH occurs in the perpendicular direction. This scheme illustrates that CO is not an obligatory intermediate during the oxidation reaction to CO_2. However, an unambiguous proof of a parallel reaction path has not been published so far.

Much research is being rendered on catalysts for methanol oxidation (see also Section 2) to find a catalyst which can avoid the poisoning effect of the CO species [35-38]. Several promoters have been found to increase the activity of the Pt catalyst. One of the most important and most investigated promoter is Ru. A bimetallic alloy consisting of Pt and Ru supported on carbon has thus far been one of the major research interests in direct methanol fuel cells (see Section 2.3.). Other promoters such as Sn, Os, W, Mo and other metals have also been investigated for methanol oxidation and CO poisoning.

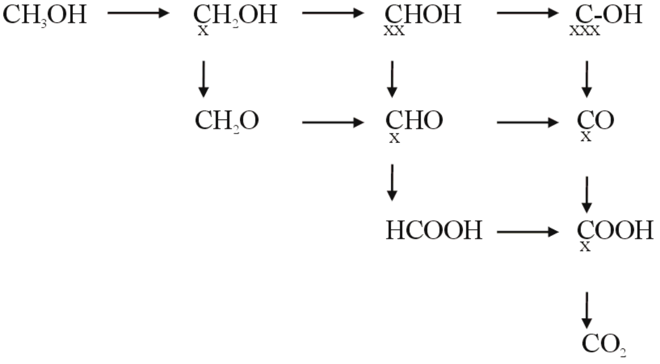

Fig. 6 Reaction scheme for methanol oxidation showing all the possible reaction products and possible reaction paths.

1.4.3 Oxygen reduction [39]

The oxygen reduction reaction (ORR) can proceed by two overall pathways in aqueous electrolytes, a direct 4-electron pathway and an indirect 2-electron pathway. The direct 4-electron pathway is preferable as it does not involve peroxide species in solution and the Faradaic efficiency of the reaction is greater. This pathway, however, consists of a number of steps in which molecular oxygen has to be dissociated at the surface and recombined with hydrogen ions to form water. The adsorption of an oxygen species on the surface of the metal particles is necessary for electron transfer. Detailed mechanisms of these steps for the oxygen reduction reaction on different catalysts can be found elsewhere [40-44].

Other factors can influence the kinetics of a reaction at a particular electrode, an overview on the effects of different elements on the oxygen reduction reaction and oxygen evolution reaction kinetics was given by Kinoshita [45]. It is experimentally difficult to obtain the relevant structural information from the complex electrocatalysts used in fuel cells. The models derived to explain structure-activity relationships are, therefore, often controversial.

A particle-crystallite size effect with respect to the oxygen reduction reaction has been reported by Ross, Bregoli, and Takasu et al. [46-48]. The optimum particle size was found to be around 5nm, smaller particles exhibited lower reactivities. This interpretation was disputed by Watanabe et al. [49] who claim that the inter-crystalline distance on the carbon support is crucial to the ORR and therefore the activity is dependent on the platinum loading.

Another explanation is the structure sensitivity [45, 50] of the oxygen reduction reaction, i.e., the reaction only happens on specific active sites of the catalyst. When the particles are smaller the relative surface increases but it may also involve a decrease of active sites.

Other influencing factors include the geometry, crystal structure, and d-band vacancy of the metal catalyst. Pre-treatment of the catalyst such as heating under hydrogen or in air at high temperatures or the electrochemical activation of the electrodes can also improve the performance for oxygen reduction [48, 51-65].

1.4.4 From fuel to electricity

The basic principles of fuel cells have been shown in this introduction. A power plant is not just a combination of single fuel cell components. For each application different system requirements must be met ranging from the appropriate fuel cell type (with all its own components) to the right fuel. Restrictions in size and weight for certain applications also need careful consideration. This overview is by no means complete but an attempt has been made to cover the different aspects of fuel cell system engineering for possible applications.

This review is based on a paper published recently by Carette et al. [66] which, however, is focused on the discussion of electrocatalysis in fuel cells and microscopic processes. In comparison, this overview stresses the aspects of fuel cell engineering and applications.

The different fuel cell types and their components will be discussed in Section 2. A brief overview on catalysts for the different fuel cells is given and the fuel cell requirements such as operating temperature, electrolytes and specific problems associated with them are also denoted. In Section 3 the importance of fuel processing is elaborated. The reforming of hydrocarbons and alcohols is discussed as well as the storage of hydrogen. Complete systems from fuel cells to power plants are given in Section 4 whereby the periphery, stack design, reforming units and other system components are shown and discussed. Section 5 gives an overview of the applications for all fuel cells classed into three different groups: transportation, stationary and portable applications. A summary of the previous chapters is given in Section 6 with a complete table of all fuel cell types, their applications, temperature range, and other specifications. An extensive literature list will finally be presented in Section 7.

2 Types of fuel cell

Fuel cells are usually classified by the electrolyte employed in the cell. An exception to this classification is the DMFC (Direct Methanol Fuel Cell) which is a fuel cell in which methanol is directly fed to the anode. The electrolyte of this cell is not determining for the class. A second grouping can be done by looking at the operating temperature for each of the fuel cells. There are, thus, low-temperature and high-temperature fuel cells. Low-temperature fuel cells are the Alkaline Fuel Cell (AFC), the Polymer Electrolyte Fuel Cell (PEMFC), the Direct Methanol Fuel Cell (DMFC) and the Phosphoric Acid Fuel Cell (PAFC). The high-temperature fuel cells operate at temperatures approx. 600–1000 °C and two different types have been developed, the Molten Carbonate Fuel Cell (MCFC) and the Solid Oxide Fuel Cell (SOFC). All types are presented in this section in order of increasing operating temperature. An overview of the fuel cell types is given in Table 1 [3, 7, 8, 67, 68].

Table 1: The different Fuel Cells that have been realized and are currently in use and development

	AFC (Alkaline)	**PEMFC** (Polymer Electrolyte Membrane)	**DMFC** (Direct Methanol)	**PAFC** (Phosphoric Acid)	**MCFC** (Molten Carbonate)	**SOFC** (Solid Oxide)
Operating temp. (°C)	<100	60–120	60–120	160–220	600–800	800–1000 low temperature (500–600) possible
Anode reaction	$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$	$H_2 \rightarrow 2H^+ + 2e^-$	$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$	$H_2 \rightarrow 2H^+ + 2e^-$	$H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$	$H_2 + O^{2-} \rightarrow H_2O + 2e^-$
Cathode reaction	$\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^-$	$\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O$	$3/2\ O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$	$\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O$	$\frac{1}{2} O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$	$\frac{1}{2} O_2 + 2e^- \rightarrow O^{2-}$
Applications	Transportation Space Military Energy storage systems			Combined heat and power for decentralised stationary power systems	Combined heat and power for stationary decentralised systems and for transportation (trains, boats, ...)	
Realised Power	Small plants 5–150kW modular	Small plants 5–250 kW modular	Small plants 5 kW	Small – medium sized plants 50kW – 11MW	Small power plants 100-kW- 2 MW	Small power plants 100–250kW
Charge Carrier in the Electrolyte	OH^-	H^+	H^+	H^+	CO_3^{2-}	O^{2-}

2.1 AFC

2.1.1 General

The AFC has the advantage of exhibiting the highest electrical efficiencies of all fuel cells but it works properly only with very pure gases which is considered a major restraint in most applications. The KOH electrolyte which is used in AFC's (usually in concentrations of 30 - 45 wt.-%) has an advantage over acid fuel cells which is that the oxygen reduction kinetics are much faster in alkaline electrolyte than in acid making the AFC a very attractive system for specific applications. The AFC was one of the first fuel cells used in space. The AFC was used in the Apollo missions, the Space Shuttle program and was planned to be used in the European Hermes Project.

The first technological AFC (1950's) was developed by the group of Bacon at the University of Cambridge, provided 5 kW power and used a Ni anode, a lithiated NiO cathode and 30 wt.-% aqueous KOH. Its operating temperature and pressure were 200 °C and 5 MPa respectively. For the Apollo program a PC3A-2 model was used which employed an 85% KOH solution at operating temperatures of 200 - 230 °C. In the Space Shuttles the fuel cells are used both for producing energy, cooling of the Shuttle compartments and producing potable water. Three plant modules are used each with a maximum power output of 12 kW. AFC's are now normally run at operating temperatures below 100 °C as a higher temperature is not needed to improve oxygen reduction kinetics (although higher temperatures are still advantageous for the hydrogen oxidation kinetics).

2.1.2 Electrodes

AFC electrodes used to be Ni based catalysts sometimes activated with Pt. Pt/C gas diffusion electrodes are now generally used for both the anode and cathode (see PEM) although other possibilities are being pursued, e.g., Pt-Co alloys have been suggested [51] and have proved to have a superior activity to Pt for oxygen reduction due to a higher exchange current density. A Pt-Pd anode was tested for stability characteristics in comparison to Raney Ni [69]. It is known that Raney Ni electrodes have a high activity for hydrogen oxidation (see MCFC) but due to the wettability of the inner pores and changes in chemical structure under operation conditions a decay in performance occurs. The Pt/Pd activity was also seen to have a very rapid decay initially but after a short time the decay stopped and the performance remained constant afterwards.

2.1.3 Electrolyte

The space models of AFC's used KOH in a stabilised matrix as a liquid electrolyte is disadvantageous for such applications. It has since been found that a much longer operating life time can be obtained when using circulating KOH [70-72]. A circulating electrolyte provides a good barrier against gas leakage and it can be used as a cooling liquid in the cell or stack. An early demonstration of the AFC with circulating electrolyte was brought about by K. Kordesch in the 1970's [72]. He combined a hydrogen/air AFC with a lead acid battery in a hybrid vehicle. In between operations the complete cell was shut down by draining the KOH electrolyte. This improved the life-expectancy enormously as normally when the cell is under no load (open circuit) the cell voltage is very high. These high voltages can induce carbon oxidation processes which produce carbonates that can destroy the matrix/electrolyte.

The formation of carbonates which can destroy the electrolyte is one of the most controversial issues in AFC's. It is generally accepted that the CO_2 in the air and the CO_2 formed by reaction of the carbon support, interact with the electrolyte in the following reaction:

$$CO_2 + 2OH^- \rightarrow (CO_3)^{2-} + H_2O \qquad \text{(Eqn. 23)}$$

The formation of carbonates is destructive to the electrolyte and the cell performance rapidly decreases. One way of solving this problem was suggested early on by circulating the KOH instead of using a stabilised matrix, in this way the electrolyte can be pumped out of the system in between cycles (see previously). This avoids the build up of carbonates.

CO_2 can be removed cost-effectively from the hydrogen feed and from the air flow by an iron sponge system, which is similar to the shift reaction in a reformer. This process is used in most NH_3 production plants for the same purpose and can be used in AFC applications. Other processes to remove CO_2 are swing adsorption or the water-gas shift reaction, both of which are being used in fuel cell systems [70-73].

2.2 PEMFC

2.2.1 General

PEM fuel cells , also called SPEFC (Solid Polymer Electrolyte Fuel Cells) use a proton exchange membrane as an electrolyte. They are low-temperature fuel cells, generally operating between 85–105 °C and were the first to be used in Space. The Gemini program employed a 1kW fuel cell stack as an auxiliary power source. The historical development of PEM fuel cells has been described recently [74]. It was also used to provide the astronauts with clean drinking water. The membrane used was a polystyrene sulfonate (PSS) polymer which proved not stable enough. This was one of the major reasons for NASA to opt for the AFC system for its further missions (see 2.1.1).

A major breakthrough in the field of PEM fuel cells came with the use of Nafion® membranes by DuPont. These membranes possess a higher acidity and also a higher conductivity and are far more stable than the polystyrene sulfonate membranes. The Nafion® consists of a poly-tetrafluoroethylene (PTFE) based structure which is chemically inert in reducing and oxidizing environments. The characteristic value of proton-conducting polymer membranes is the equivalent weight which is defined as the weight of polymer that will neutralize one equivalent of base, and is inversely proportional to the ion-exchange capacity.

In 1987 Ballard started using a different membrane in their PEM fuel cells which gave about four times higher current densities at the same voltage than Nafion®. The Dow® membrane (Dow Chemicals) together with Nafion® and some other PTFE based polymers are still under scrutinous investigation by several research group. A general overview on polymer electrolytes was published in 1997 [76].

2.2.2 *Membranes* [76]

Nafion® (Figure 7 [77]) is probably the most studied and operated electrolyte for PEM fuel cells but other perfluorocarbon sulfonic acid membranes from Dow, Gore and Asahi Chemical are also used and investigated [78]. Membranes usually have a small temperature range in which they are stable. The upper limit of temperature is dictated by the need of humidification of the membrane, as water is a pre-requisite for conduction (see section 2.2.3.).

Improvements in membrane structure and conductivity are made by producing composite membranes. This can be done in several ways, one of which consists of reinforcing the perfluorosulfonic membrane by PTFE components, which is the successful approach of Gore and Asahi Chemicals (however with different procedures). Another possibility is to impregnate a membrane with a solution or with a solid powder to decrease the permeability of the reactant gases. Another technique is to dissolve the membrane into an appropriate solvent and to mix it with another substance. After recasting (usually by evaporating the solvent) the composite membrane can be used in a fuel cell [79, 80]. Impregnation of PTFE films with Nafion ionomer (18 wt.-% Nafion in EtOH) was carried out to make thinner membranes, thus, reducing the membrane resistance in the system [81]. The conductivity of this membrane was comparable to Nafion 112 (0.1 $\mathrm{Scm^{-1}}$) but its permeability towards gases is higher.

Novel membranes are also prepared by new techniques such as radiation grafting or plasma polymerisation [82-85]. Plasma polymerisation is known to give highly cross-linked, uniform and stable thin films. Radiation grafting of PVDF films gave membranes with a lower oxygen solubility but higher diffusion than through Nafion. These membranes are promising for PEM fuel cells as long as they prove to be mechanically and electrochemically stable.

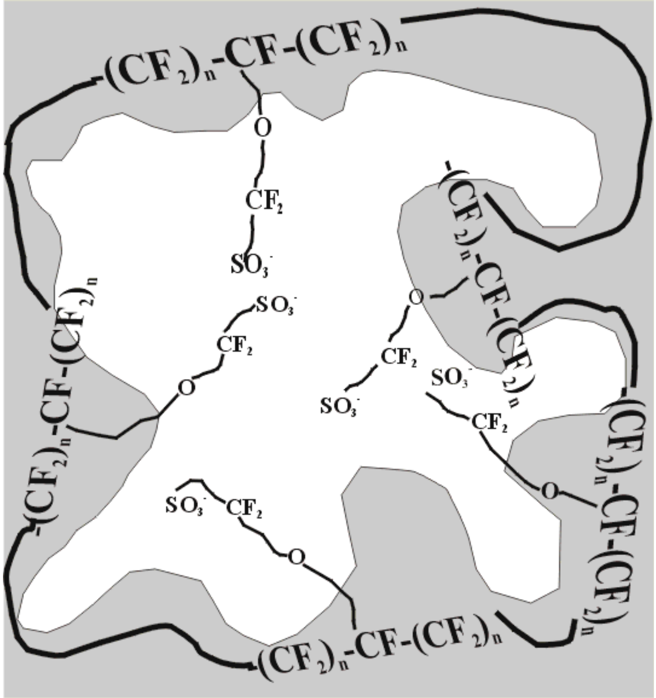

Fig. 7 The structure of Nafion showing the three different regions: the hydrophobic PTFE backbone, the hydrophilic ionic zone, and the intermediate region.

2.2.3 *Water management*

Membranes in PEM fuel cells are generally water filled to keep the conductivity high (Figure 8 [71, 86, 87]), a dried out membrane possesses a lower conductivity as proton transport through a wet membrane is similar to that of an aqueous solution. Water management in the membrane is one of the major issues in PEM technology. Factors influencing the water content in the membrane are water drag through the cell (electro-osmotic) (for every proton a shell of H_2O is also transported through the membrane) and back diffusion from product water from the cathode into the membrane.

One way of improving the water management is to humidify the gases coming into the fuel cell. Another form of water management can be found in the direct hydration of the membrane by mounting porous fibre wicks [88-90]. Twisted threads of porous polyester fibres are placed between the membrane and a cast thin film of Nafion ionomer and is hot pressed at 150 °C. This ensures a direct water supply from either the humidifiers or from product water at the cathode to the membrane by using a pressure difference.

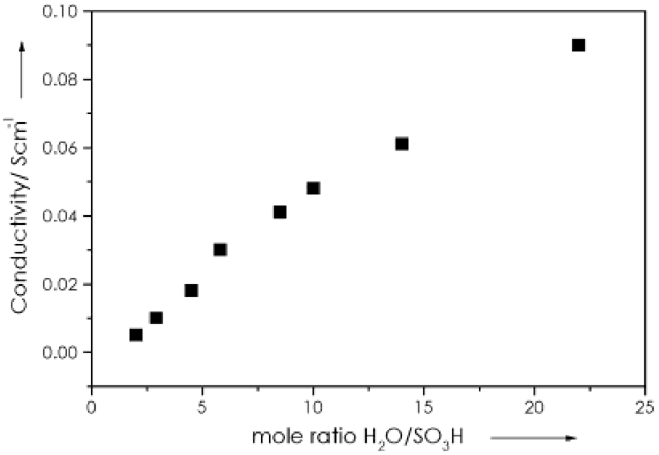

Fig. 8 The influence of the water content on the conductivity of a Nafion membrane.

2.2.4 Electrodes

2.2.4.1 General

Electrodes for PEM fuel cells are generally porous gas diffusion electrodes to ensure the supply of the reactant gases to the active zones where the noble metal catalyst is in contact with the ionic and electronic conductor. The fabrication of gas diffusion electrodes (gde) is an intricate procedure in which all details of the structure and preparation are important. The reason for this is that the function of the electrodes is far more than just catalysing a reaction, which is carried out by the catalyst particles.

The main requirement of a good electrode is a three-phase boundary (Figure 9 [75]) between the gas supply on the one hand, and the catalyst particle and the ionic conductor on the other hand. The particles must be in direct contact with an electronic conductor to ensure the electrons are supplied to or taken away from the reaction site. Electronic conductivity is usually provided by a carbon support onto which the catalyst particles are supported. The three-phase boundary is made by impregnating the catalyst/support powder with some ionomeric binder (usually Nafion solution) before pressing the electrode onto the membrane. This ensures good contact of most catalyst particles with ionomer material that has ionic contact with the membrane.

Gas diffusion occurs through the backing layer and the carbon support to the catalyst particles. When using humidified gases or a methanol/water mixture (see DMFC) the catalyst layer must be sufficiently hydrophobic to prevent the pores from flooding. This hydrophobicity can be provided by introducing PTFE as a binder, in combination with Nafion that is hydrophilic. Usually the catalyst is made into an ink with water and isopropanol and mixed with the binder material (the optimum binder quantity depends on the type of catalyst) after which the ink can be cast straight onto the membrane. The effect of the binder content on the performance of the electrodes was studied both for the PTFE binder as for the Nafion binder [91-93].

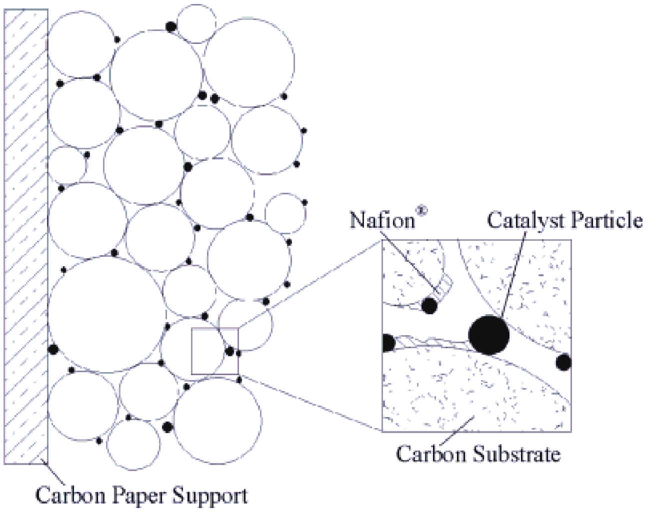

Fig. 9 The three phase boundary formed by the catalyst particles, the ionomer and the gas phase in a porous structure, ensuring both electronic and ionic contact as well as gas transport.

2.2.4.2 Cathode

Although a huge variety of catalysts have been investigated, so far Pt based catalysts are the superior material for the oxygen reduction reaction. Pt dispersed on carbon or other small Pt particles (such as colloids) exhibit a good performance. Due to the low temperature in PEMFC the loadings for the oxygen catalysts are significant to compensate for the slow reaction kinetics [94]. Because pure oxygen is seldom available, fuel cells require air for the cathode gas supply. The lower oxygen partial pressure in air leads to a decrease in activity compared to pure oxygen. Under operating conditions for longer times a "ripening" of the Pt particles has been reported which manifests itself in a decrease of active surface area due to the formation of larger particles [95]. More information on the ORR and its kinetics has been published in a review [39]. Research into less expensive materials and better catalysts for the ORR is being carried out by various groups.

2.2.4.3 Anode

If pure hydrogen is used as fuel the performance of the anode is excellent with pure Pt catalyzing the oxidation of hydrogen. Unfortunately in most practical systems the fuel stream contains certain traces of elements or compounds such as CO, S, and NH_3. All of these substances can to a greater or lesser extent poison the anode catalysts.

CO is one of the major poisons in low temperature fuel cells [96-98]. In PEMFC and PAFC CO poisoning occurs due to adsorption of the species to the active sites of the platinum catalysts so that no, or virtually no, sites are available for reaction with H_2. To reactivate the surface the CO can be oxidised to CO_2.

To avoid CO contamination in the cell a gas clean-up can be built in between the reformer and the fuel cell (see Section 3.5.) which adds complexity to the system. Other methods to remove CO from the fuel cell are the mixing of the fuel feed with small amounts of air or oxygen ("air bleeding", about 1% content in the gas) [96-98]. This stimulates the oxidation of CO over the catalyst. This method requires an extensive control system since the air content has to be closely monitored. The addition of hydrogen peroxide to the fuel stream has also been investigated as a method to minimise the CO contamination [99, 100]. A new method of operating PEM fuel cells with reformed hydrogen with reduced requirements for gas cleaning is the operation applying pulses to the cell. The electrical pulses increase the anode potential to values at which the CO is oxidised to CO_2. In this way the catalyst surface is continuously cleaned and the loss of cell voltage is minimised [101].

CO-tolerant catalysts are still being investigated by numerous research groups in order to reduce the importance of the problem. CO-tolerant anodes usually contain a Pt-Ru alloy as the state-of-the-art catalyst. The mechanism of CO oxidation and CO tolerance of Pt-Ru catalysts with well-defined surfaces has been investigated and clarified by several groups [102-107]. For example, catalysts prepared via a dc-magnetron sputtering technique producing thin layers on standard fuel cell electrode substrates have been investigated [108]. PtRuW and PtRuMo showed an improved CO tolerance over Pt and PtRu catalysts.

2.3 DMFC

2.3.1 General

The direct methanol fuel cell is a special form of low-temperature fuel cells based on PEM technology. It operates at temperatures similar to PEMFC although it is usually operated at slightly higher temperatures in order to improve the power density. In the DMFC, methanol is directly fed into the fuel cell without the intermediate step of reforming the alcohol into hydrogen. Methanol is an attractive fuel option because it can be produced from natural gas or renewable biomass resources. It has the advantage of a high specific energy density (since it is liquid at operating conditions) and it is assumed that the existing infrastructure for fuels may be adapted to methanol. The DMFC can be operated with liquid or gaseous methanol/water mixtures.

The liquid DMFC generally uses a diluted methanol in water mixture (typically 1-2 molar) and only a fraction of the methanol is used at the anode. It is, therefore, important to recycle the effluent and replenish it to keep the concentration in the fuel feed constant. To be able to achieve this, methanol sensors are a very important part of the fuel cell system. Methanol sensors are usually based on an electrochemical system which measures the current from the electro-oxidation of methanol [109-111]. Gaseous feed of the methanol/water mixture is also possible (see Section 4.3.3.).

2.3.2 Catalysts

Catalysts for methanol oxidation need to be improved as the reaction is comparatively sluggish on Pt-based compounds. Compared to hydrogen oxidation the catalytic activity for methanol oxidation is not very effective. It was found early on that additions of other metals to Pt could enhance the activity of the catalyst dramatically. Species such as Re, Ru, Os, Rh, Mo, Pb, Bi, and Sn have been found to have a promoting effect on the catalytic activity for methanol oxidation, e.g [112-119]. For all these species it was found that the determining factor for promotion is the formation of an adsorbed oxygen containing species on the secondary metal at potentials lower than for Pt. The oxygen containing species are needed for the oxidation of intermediate adsorbates. It is still necessary, however, to employ higher loadings for the catalysts than are needed for H_2 oxidation. Pt-Ru alloys are the most widely use anode catalysts for DMFC.

Other factors that influence the catalytic activity of the electrode are the support, [16] the ionomer content in the active layer, [120] the preparation method, and the fuel feed. It was found that the specific activity of supported Pt-Ru/C is much higher than for a Pt-Ru black. The maximum attainable voltage in the cell is, however, much lower for the supported catalyst. The cell employing the unsupported catalyst also features a lower cross-over rate (see Section 2.3.3.) suggesting a higher methanol utilisation. The advantage of using a supported metal catalyst lies in the possibility to reduce the metal loadings drastically. The difference in performance may be due to the difference in morphology between the two types of catalyst. It is therefore necessary to improve the stability of both supported and unsupported metal catalysts [18, 121].

The ionomer content in the catalyst layer can greatly influence the performance of the electrodes as was seen before for the PEM fuel cells (Section 2.2.4.1). Electrodes for methanol oxidation are usually bound together with Nafion to improve the ionic conductivity in the catalyst layer.

A vapour-feed methanol fuel cell minimises the cross-over effect (see further) and can in principle improve the overall performance of the cell using gas diffusion electrodes due to the higher temperature of operation [122, 123] (the highest power densities so far are reached with liquid DMFCs). Using a liquid feed arrangement, which simplifies the design as no humidification system is needed, it is necessary to optimise the hydrophobicity of the backing layer and methanol cross-over and water permeation are more significant due to the importance of electro-osmotic drag through the membrane and the large gradient in chemical potential [124, 125].

Catalysts for oxygen reduction for a DMFC are mostly identical to those for the PEM fuel cell. The operating conditions for both fuel cells are similar although one major problem arises for the DMFC which is the cross-over of methanol from the anode to the cathode. This problem, its effects on the cathode, and possible solutions are discussed in the next section.

2.3.3 DMFC and methanol cross-over

At present, most DMFC research is concentrated on PEM technology. The membranes used in DMFCs were developed for the PEM application (thus optimising the proton conductivity was the priority), however, these membranes are not advantageous regarding methanol blocking. The proton movement in the membrane is associated with the water content of the membrane. Due to the similar properties of methanol as compared to water (e.g., dipole moment) methanol molecules as well as water molecules are transported to the cathode by the electro-osmotic drag as well as diffusion. At the cathode, methanol causes a mixed potential due to the interference of methanol oxidation with the oxygen reduction reaction. As a consequence, a decrease in cell performance results (Figure 10).

Methanol cross-over depends on a number of factors, the most important ones are the membrane permeability/thickness, the concentration of methanol in the fuel feed, the operating temperature, and the performance of the anode itself.

The membrane is a very important factor regarding the methanol cross-over problem. Thinner membranes give lower

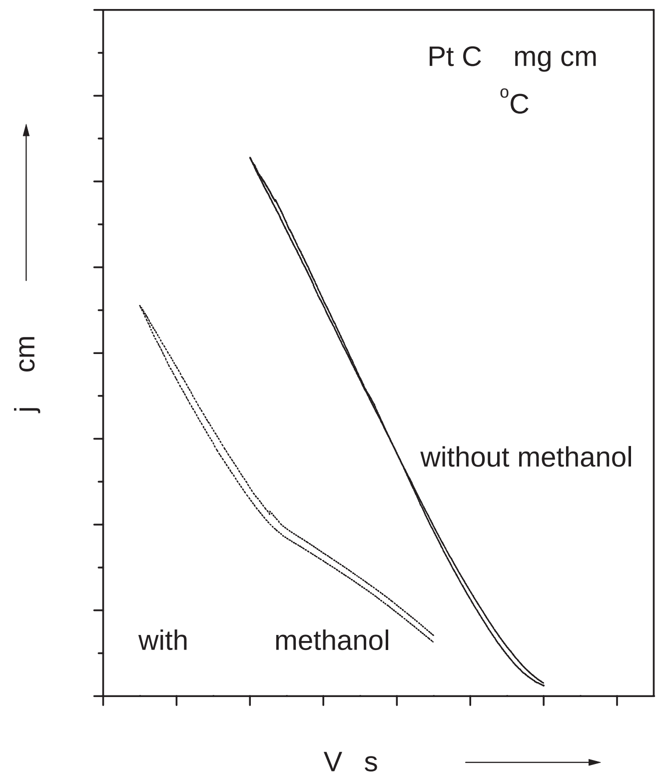

Fig. 10 Current density versus potential for the oxygen reduction from air measured at a MEA with Pt/C catalysts. The effect of methanol crossover on the cathode (Etek commercial catalyst, home-made electrode) of a PEM fuel cell when using a methanol feed at the anode.

resistances in the cell but tend to have a higher permeability for liquid methanol. For methanol fuel cells a thicker membrane, such as Nafion 120, is advantageous [126].

The cross-over effect is dependent on the methanol concentration in the feed. An optimum concentration of methanol was considered to be around 1–2 M methanol in water (around 6% methanol in water). A higher concentration as well as a higher temperature in the cell increases the diffusion of methanol through the membrane [127-129] and, thus, lowers the cell performance. An optimised anode will oxidise more methanol from the feed and the methanol available for cross-over decreases leaving another factor to optimise in the DMFC [130]. A different approach to cope with the methanol cross-over problem is the investigation of methanol-tolerant cathodes. In this concept, the methanol diffusion is not prevented but at the cathode catalysts which are inactive regarding methanol oxidation are used. Thus, the establishment of a mixed potential at the cathode is prevented. Different methanol tolerant cathodes have been investigated [131, 132]: Although a $Mo_2Ru_5S_5$ catalyst (Chevrel phase) exhibits inferior performance than Pt for pure oxygen reduction activity, in the presence of methanol the reactivity of MoRuS based catalysts are superior to Pt. A sulphur treatment of the carbon support also increased the performance of the mixed transition metal sulphides (whereas the same treatment for a Pt/C catalyst inhibits the performance).

Other methanol tolerant catalysts have been found in iron porphyrine-type materials supported on high surface area carbon [133, 134]. These catalysts were tested in fuel cell conditions and it was found that no deterioration of the electrode performance could be seen when utilising methanol in the cell. The catalysts are insensitive to methanol. These catalysts were also combined with a new cell concept whereby the anode and cathode reside in the same compartment. Both electrodes are in contact to the same side of the membrane, thus, eliminating most of the ohmic resistance in the cell. The fuel efficiency in the cell at low current densities was much higher than for a normal bipolar plate design. A methanol-tolerant cathode is a prerequisite to make this concept feasible.

2.4 PAFC

2.4.1 General

The phosphoric acid fuel cell is thus far the most advanced system regarding commercial development. It is mainly used in stationary power plants ranging from dispersed power to on-site generation plants. Power plants based on PAFCs are being installed worldwide with outputs ranging from 5–20 MW supplying towns, cities, and shopping malls or hospitals with electricity, heat, and hot water [135–139].

The advantages of the PAFC are its simple construction, its stability both thermally, chemically, and electrochemically, and the low volatility of the electrolyte at operating temperatures (150-200 °C). These factors probably assisted the earlier deployment into commercial systems compared to the other fuel cell types.

At the beginning of PAFC development diluted phosphoric acid was used in PAFCs to avoid corrosion of some of the cell components. Nowadays with improved materials available for cell construction the concentration of the acid is nearly 100%. The acid is usually stabilised in a matrix which is SiC based. The higher concentration of the acid increases the conductivity of the electrolyte and reduces the corrosion of the carbon supported electrodes.

2.4.2 Electrodes

The electrodes used in PAFCs are generally Pt based catalysts dispersed on a carbon-based support (see PEM electrodes, Section 2.2.4). For the cathode a relatively high loading of Pt is necessary for the promotion of the O_2 reduction reaction. The hydrogen oxidation reaction at the anode occurs readily over a Pt/C catalyst.

In PAFCs it is extremely important to have a hydrophobic backing layer (more than in PEMFCs where the water source is derived from humidifying the gases) as a liquid electrolyte is used. To provide hydrophobicity the backing layer can be immersed in a solution of PTFE. Also the catalyst layer must be prevented from pore-flooding which can be obtained by binding the electrode with PTFE. It is difficult, however, to find the optimum amount of PTFE in the electrode as there is a fine balance between low wettability/good gas diffusion and high wettability/poor gas diffusion [140].

Pt-Co alloys were investigated for oxygen reduction in PAFCs; it was found, however, that Co leaches out from the alloy in two stages. A fast dissolution occurs at the particle surfaces after which a slow dissolution removes the Co from the bulk. Also a "ripening" of the Pt particles occurs which decreases the performance of the catalyst [141]. Pt-WO_3 was found to have an increase in performance over plain Pt/C electrodes by about twice the current density for the same voltage. It was seen, however, that the addition of WO_3 only induces an increase in electrochemically active surface area, which accounts for the increase in performance [142]. A model for PAFC cathodes is described in the literature [143, 144]. Pt-Ru catalysts were found to be better than Pt catalysts for hydrogen oxidation when using reformate hydrogen (see further) as it contains CO which is more easily oxidised with Ru as a secondary metal. Additions of W and Pd also improved the CO-tolerance of the system. It is important to note, however, that at very high overpotentials Ru is not completely stable and an aging of the catalysts is significant.

2.5 MCFC

2.5.1 General

The development of molten carbonate fuel cells started about the mid 20th century [145]. An advantage of the MCFC is the possibility to allow for internal reforming due to the high operating temperatures (600-700 °C) and to use the waste heat in combined cycle power plants (see Section 4.3 and 5.1). The high temperatures improve the oxygen reduction kinetics dramatically eliminating the need for very high loadings of precious-metal catalysts. The molten carbonate (usually a LiK or LiNa carbonate) is stabilised in a matrix ($LiAlO_2$) which can be supported with Al_2O_3 fibres for mechanical strength.

Molten carbonate fuel cell systems can attain electrical efficiencies of up to 50%, or up to 70% when combining the fuel cell with other power generators [146]. MCFCs can operate on a wide range of different fuels and are not prone to CO or CO_2 contamination as is the case for low-temperature cells. For stationary power molten carbonate fuel cells can play an important role in power conversion units (see systems, Section 4.3.5).

2.5.2 Cathodes

Cathodes for MCFCs are usually NiO made by an anodic oxidation of a Ni sinter or by an in-situ oxidation of Ni metal during the cell start-up time [145, 147]. NiO cathodes are active enough for oxygen reduction at high temperatures so that a Pt based metal is not necessary. A problem with the NiO cathode occurs as over time the NiO particles grow as they creep into the molten carbonate melt which reduces the active surface area and can cause short circuiting of the cell. One of the solutions for this problem is the addition of small amounts of magnesium metal to the cathode and the electrolyte for stability. Also the use of a different electrolyte which decreases the dissolution of the NiO cathode is possible (see Section 2.5.4.).

Alternatives for MCFC cathodes have been found in doped lithium oxide materials such as $LiFeO_2$, Li_2MnO_3, and $LiCoO_2$, also in combination with NiO materials to form double-layer electrodes. A tape casting of a NiO/$LiCoO_2$ double layer electrode improved the stability tremendously. The oxygen reduction reaction is improved at these double layer cathodes and the resistance is decreased [148-150].

2.5.3 Anodes

Ni-Al or Ni-Cr metals have been employed as MCFC anodes. These materials are used because Ni metal anodes are not stable enough under the MCFC operating conditions as Ni creeps out (see also cathode) [145, 147]. Cermet (ceramic metal) materials avoid sintering, pore growth, and shrinkage of the Ni metal so that a loss of surface area does not occur. A low-cost process needs to be found, however, as these materials are yet expensive to fabricate.

2.5.4 Electrolyte/matrix

The electrolyte for MCFCs is a molten carbonate which is stabilised by an alumina-based matrix. Initially, Li_2CO_3/K_2CO_3 (Li/K) carbonate materials were used as electrolytes. Degradation of electrode materials is a problem in this electrolyte. A Li/Na melt provides the advantage of a slightly more alkaline system in which the cathode and anode dissolution is lower as it prevents a dendritic growth of the Ni metal. Li/Na electrolytes are expected to have a longer endurance and a lower decay rate than Li/K melts.

The matrix, which stabilises the electrolyte, consists of either an alumina phase or a ceria based material. Usually a gamma-$LiAlO_2$ phase is used whereby a transformation into an α variant during operation is observed. The stability of the α variant was investigated and it was suggested that the α variant may actually be more stable for long term operation than the γ-$LiAlO_2$ phase. Ceria based materials are more stable than alumina based matrices but they are also more expensive. Reinforcements can be built into the matrix in the form of particulates or fibres. These reinforcements act as crack deflectors for the matrix to avoid dissolution in the carbonate melt [146, 148-152]. The formation of the interfaces between electrolyte and electrodes can be obtained by several different techniques which will be described in Section 4.1.2

2.5.5 Cell materials

Material selection is far more important in high-temperature fuel cells due to the degradation, sealing, and thermal expansion properties. There are some high-temperature stainless steel alloys available for use in fuel cells. Ni, Co, and Fe, based alloys or Cr/Al alloys have proven to be more stable than normal stainless steel (SS). A Fe-Cr ferritic SS material was used in fuel cell components as the materials are low cost but it was found that the corrosion resistance was not sufficient. A Fe-Ni-Cr austenitic material was also used and found to be very resistant for the cathodic reduction but not for anodic oxidation. A nickel coating is necessary for the abatement of anodic corrosion. The Cr content in the stainless steel compound influences the corrosion resistance the most. The higher the Cr content, the lower the corrosion rate. Cr containing stainless steels form a $LiCrO_2$ inner layer under operating conditions which is a barrier against Fe^+ diffusion, thus decreasing the corrosion [149, 153]. Cost reduction is still a major factor in the fabrication of fuel cell components. An overview on molten carbonate fuel cell materials has been published.

2.6 SOFC

2.6.1 General

Solid oxide fuel cells employ a solid oxide material as electrolyte and are, thus, more stable than the molten carbonate fuel cells as no leakage problems due to a liquid electrolyte can occur. The SOFC is a straightforward two-phase gas-solid system so it has no problems with water management, flooding of the catalyst layer, or slow oxygen reduction kinetics. On the other hand it is difficult to find suitable materials which have the necessary thermal and stability properties for operating at high temperatures (see also MCFC).

As for the MCFC, internal reforming in SOFCs is possible over the anode catalyst, also partial oxidation reactions, and direct oxidation of the fuel have been found to occur [118, 130, 154-159]. Different concepts for solid oxide fuel cells have been developed over the years. Flat plates have an easier stack possibility while tubular designs have a smaller sealing problem. Monolithic plate and even single-chamber designs have been considered and investigated for SOFC use [32, 160-165]. More about these systems can be found in Section 2.6.2.

Due to the high power density of SOFCs compact designs are feasible. An important advantage of SOFCs is the internal reforming. Due to the high temperature of the exhaust gases a combination with other power generation systems (e.g., gas turbines) is also possible which can provide a high overall electrical efficiency (up to 70% in a combined cycle system).

2.6.2 SOFC cell designs

Different SOFC designs have been developed over the years to implement the fuel cell and reformers into the stack and ultimately the complete system. The tubular design is probably the best known design. It has been developed by Westinghouse (now Siemens-Westinghouse). Tubular designs have a self-sealing structure which improves thermal stability and eliminates the need for good thermal-resistant sealants. The tubular design can be split into two systems, one where the gas flow is along the axis of the tube and the other where the flow is perpendicular to the axis. The first concept (Figure 11 [160]) was pursued by Westinghouse and consisted of an air electrode supported fuel cell. In earlier days the tubes were made from a calcium stabilised zirconia on which the active cell components were sprayed. Nowadays the porous supported tube (PST) is replaced by a doped lanthanum manganite air electrode tube (AES) which increased the power density by about 35%. The LaMn tubes are extruded and sintered and serve as the air electrode. The other cell components are thin-layered on this construction by electrochemical vapour deposition (EVD). Electrochemical vapour deposition of the electrolyte produces a gas-tight film with a uniform thickness but other depositions, such as colloidal electrophoresis, are also under investigation [160].

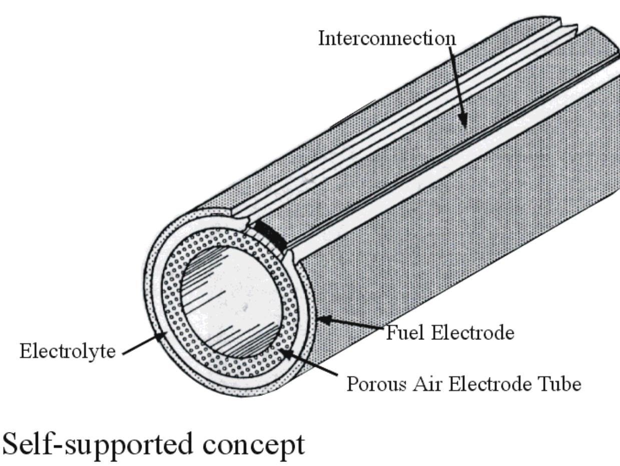

Fig. 11 Tubular concept pursued by Siemens-Westinghouse for SOFCs. Source: Siemens-Westinghouse

A different type of SOFC design is under development by Sulzer-Hexis. The HEXIS (Heat Exchanger Integrated Stack) stack concept is shown in Figure 12. It can be used for small co-generation plants. The interconnect in this case serves as a heat exchanger as well as a current collector and is made by Plansee (Reutte, Austria) (see interconnect materials). Thermal spray coatings on the current collector can improve the stability of the system and performances were tested up to 3000 hours [166].

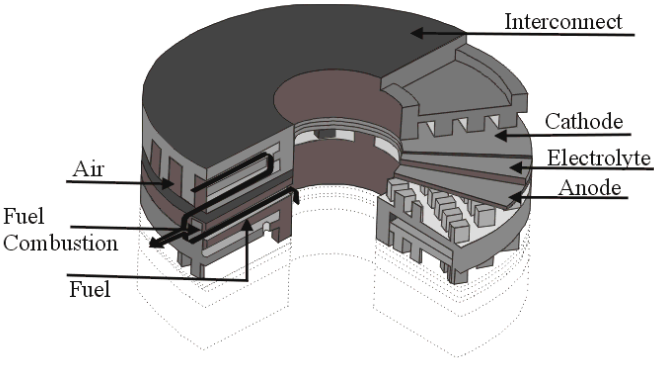

Fig. 12 The HEXIS (Heat EXchange Integrated System) tubular concept for SOFCs. Source: Sulzer Hexis

The planar design (Figure 13 [167, 168]) is more efficient and cheaper than the tubular as the current path is shorter and it is easier to stack than the tubular design. It is, however, still a problem to find good sealants and interconnect materials. Interconnect materials for planar SOFCs have been inves-

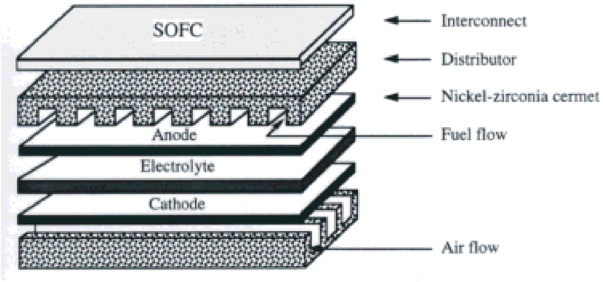

Fig. 13 Schematic of a planar SOFC.

tigated. For lower temperatures it was found that stainless steel had the best performance (also better stabilities were reported when doping the stainless steel, see materials). For higher temperatures an alloyed metal or a La chromite material has to be used [162]. Heat removal in a planar design can be achieved by a direct heat dissipation to air pre-heater coils, small size cells make this heat exchange easier.

The components of SOFC's can be made in different ways. The main differences between the preparation techniques consist of the fact that the whole cell can be made self-supporting (i.e., the electrode/electrolyte assembly supports the structure of the cell and no substrate is used) or supported whereby the electrodes and electrolyte are cast onto a substrate. In the anode-supported planar solid oxide fuel cell (SOFC) concept, with a 20 μm thin electrolyte layer the operation temperature can be reduced significantly, e.g., to 800 °C [169]. This reduces the material requirements considerably.

2.6.3 Cathodes

From the beginning of SOFC development it was found that $LaSrMnO_3$ (LSM) electrodes had a high activity for oxygen reduction at high temperatures and were stable under SOFC operation conditions. These LSM cathodes have been improved over time and it has been seen that an yttria-stabilisation of the cathodes improves the performance [170]. Single-phase LSM cathodes show a low oxide-diffusion coefficient so it is better to use a two-phase cathode which results in a lower overpotential for the oxygen reduction reaction.

Perovskite-type materials have been investigated as cathodes for SOFCs as well. Lanthanide-based perovskites showed a high conductivity and a high catalytic activity for oxygen reduction. Applying a thin porous layer of YSZ particles on the LSM electrode also increased the performance as the polarisation resistance is decreased. Especially for operating at lower temperatures (650–700 °C) it is important to have an efficient cathode [171].

2.6.4 Anodes

Anodes for SOFC are again based on Ni, usually Ni cermet materials are used which are more stable than plain Ni metal. NiO anodes are slightly soluble in the YSZ electrolyte but this stabilises the cubic phase of the electrolyte. A NiO powder mixed with a YSZ powder together with a resin binder produces an anode functional layer onto which the YSZ electrolyte can be deposited and sintered. The cathode can then be sprayed onto this layer and form an anode supported planar SOFC structure [168]. YSZ-Ni anodes can also be produced by vacuum plasma spraying. To fit the thermal expansion mismatch that can occur between the anode and the electrolyte a zirconia stabilised anode is preferable. The performance of plasma-sprayed electrodes is similar to that of the more common screen-printed anodes [172].

2.6.5 Electrolytes

For high-temperature operation most ceramics are conductive enough to give a good overall cell performance. ZrO_2 supported electrolytes have been found to be stable and they give a reasonable conductivity. Special metallic or ceramic materials are investigated to lower the operating temperatures. At these temperatures, however, better cathodes and more conductive electrolytes need to be considered. CeO_2 based electrolytes are more conductive than yttria-stabilised electrolytes and in conjunction with ferritic stainless steel materials they can provide a competitive model for solid oxide fuel cells. [173-176]. However, the advantages of the well-studied ZrO_2 based electrolytes are that thermal expansion of all components of the system have been matched by careful development and there is considerable resistance to change to completely new ceramic systems.

The fabrication of the electrolyte/electrodes interfaces will be explained further in the Systems section (Section 4.1.2).

2.6.6 Other cell components

The interconnect material (ICM) is another important issue in SOFC development. It forms the connection between the anode of one cell and the cathode of the next in a stack arrangement (see section 4.2). The ICM has to be electronically conductive but it must also seal the gas chambers for the feed of oxygen and fuel gases at either the anode or the cathode. Different possibilities for the material depending on the stack design are possible. No systematic procedures exist, however, to determine the suitability of a material in a fuel cell or stack as hardly any data on the degradation of interconnect and sealant materials is available [177]. Ni-based alloys, which are mostly used nowadays, have a tendency to evaporate so that silver alloys were investigated instead for operating temperatures under 900 °C. Cheaper options were found in highly conductive metal oxides [178].

Bipolar plates fabricated from ceramics based on $LaCrO_3$ have a heat expansion coefficient similar to ZrO_2 but can only provide a high enough conductivity if a Cr_2O_3 layer is formed on the surface of the material [179]. A new metallic-ceramic alloy made by Plansee (Reutte, Austria) has been found to have a high corrosion resistance and good thermal conductivity combined with a high mechanical strength and a low expansion coefficient. The metal/cermet alloy is based on a CrFe stainless steel metallic component mixed with an yttrium oxide ceramic.

Sealing the SOFC compartments is still a major problem due to the high temperature for which not many sealing materials are available. The most commonly used material for this purpose is glass (SiO_2). Normal glass, however, can evaporate and soften with a higher likelihood of leakages as a result. Pyrex seals can be used to avoid evaporation and glass-ceramic sealants have been proven to have the necessary stability at high temperatures and pressures so that the probability of leakages can be reduced dramatically. [180]. Ceramic foams consisting of Co-doped LSM materials have been found to have a high electronic conductivity and a reasonable compression strength but most of all the material does not creep [181]. A survey of materials for electrolytes and interconnect materials for ceramic fuel cells has been published [174].

3 Fuel processing

3.1 General

The main fuel for fuel cells is hydrogen (a general scheme for the production of hydrogen is shown in Figure 14) but the storage of it is a major and important issue. Hydrogen has been stored in materials such as nanotubes, carbon fibres, metal hydrides, and a number of chemical compounds. Hydrogen storage in alcohols or hydrocarbons, such as methanol or methane gas, can also be an option. Such hydrocarbons/alcohols can be reformed into hydrogen-rich synthesis gases by several methods. The main processes for hydrogen production are: Partial Oxidation (POX), Catalytic Steam Reforming (CSR), and Autothermal Reforming (ATR).

The production of chlorine gas (Cl_2) from sodium chloride (NaCl) can also be used to obtain hydrogen as a by-product of the reaction. The electrolysis of water is one of the few processes which do not rely on fossil fuels to produce hydrogen. It is also one of the cleanest methods and pure hydrogen (and oxygen) is obtained. Hydrogen may be generated from other hydrogen carriers such as ammonia (NH_3), hydrazine (N_2H_4), carbon fibres, and metal hydrides as well.

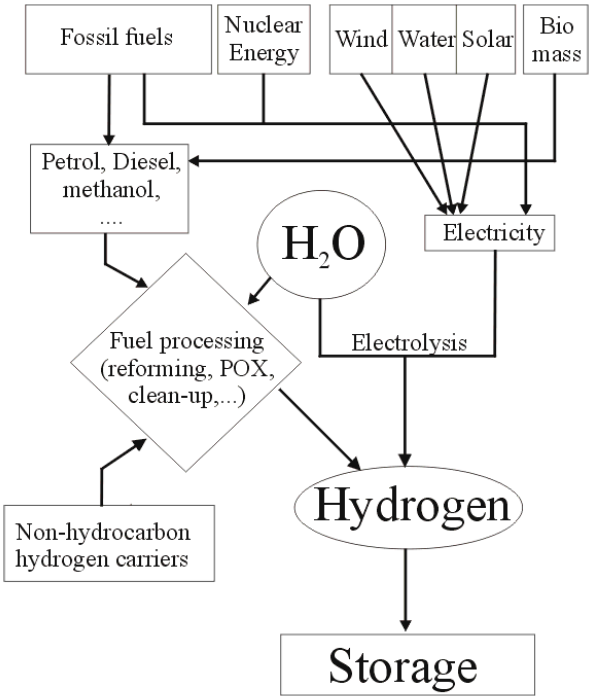

Fig. 14 Hydrogen: possible production paths.

During reforming by CSR and ATR H_2 and CO_2 are formed, but because of the gas-shift reaction CO is also present which poisons the catalysts in most fuel cells with operating temperatures below 250 °C. A gas clean up is therefore necessary. After the reformer system a low-temperature- and high-temperature-shift reactor displaces the reaction towards H_2 formation. A preferential oxidation reactor (PROX) can then be used to selectively oxidise the CO to CO_2 and the concentration of CO can be lowered down to 5 ppm. A selective membrane (usually a Pd-Ag membrane) can also be used which can block the permeation of CO. The acquired CO can then be burnt to CO_2 and eliminated. Methanation is another possibility for gas cleaning (see section 3.5)

3.2 Producing hydrogen from alcohols

3.2.1 General

Alcohols and more specifically methanol, are convenient storage systems for hydrogen (see DMFC). These liquids can easily be transported through the existing infrastructure and have lesser constraints concerning safety than for instance gaseous hydrogen storage. Methanol is made from natural gas and therefore readily available although it is more expensive to produce than hydrogen. A direct-feed system as opposed to the reforming can be more appropriate (feasible in MCFC, SOFC, and DMFC). However, a research effort to design a simple, efficient, compact, and inexpensive reformer is currently in progress which in case of success will diminish considerably the capital costs of small reforming reactors. Methanol reforming is attractive because the required temperatures are relatively low (in the range 250–350 °C depending on the reforming process).

Most reformer concepts for hydrogen generation from methanol favour steam reforming over partial oxidation because the former is more effective for hydrogen production and results in higher system efficiencies. The partial oxidation, however, offers compactness, fast start-up, and rapid responses. Methanol steam reforming can be modelled as either the decomposition of methanol followed by the water gas shift reaction or the reaction of methanol with steam to form CO_2 which can be followed by a reverse shift reaction to establish the equilibrium state. Both reaction mechanisms will be explained in the following sections.

3.2.2. Partial Oxidation [182]

Methanol is first evaporated. Then, it is mixed with a sub-stoichiometric amount of oxygen (air). The initial oxidation reaction of some of the fuel results in heat generation and high temperatures. It leads to the formation of CO, CO_2, and water. The further conversion of fuel with water and oxygen then leads to the formation of a hydrogen-rich gas:

$$CH_3OH + ½O_2 \leftrightarrow CO_2 + 2H_2 \ (\Delta H_0 = -667 kJmol^{-1}) \quad (Eqn. 24)$$

Partial oxidation of methanol is exothermic and occurs over ZnO supported Pd catalysts with a very high selectivity towards hydrogen production (the hydrogen concentration in the reformate gas is about 40%). It was found, though, that at higher temperatures the selectivity for H_2 improved but the catalytic activity overall decreased. Also, methanol reforming over Pd-ZnO catalysts seems to agree with a partial oxidation scheme followed by a steam reforming step which improves the selectivity. Methanol decomposition may also play a role in the methanol reforming reaction over this type of catalyst.

3.2.3 Steam Reforming [183, 184]

As was mentioned before the steam reforming of methanol can be modelled as occurring in two stages by two different pathways, the first one involves the decomposition of methanol into CO and hydrogen:

$$CH_3OH \leftrightarrow CO + 2H_2 \quad (Eqn. 25)$$

followed by a water gas shift reaction:

$$CO + HO \leftrightarrow CO_2 + H_2 \quad (\Delta H_0 = -41.2 kJmol^{-1}) \quad (Eqn. 26)$$

The second mechanism for methanol steam reforming consists of the reaction of water and methanol to CO_2 and hydrogen:

$$CH_3OH + H_2O \leftrightarrow CO_2 + 3H_2 \quad (\Delta H_0 = 49 kJmol^{-1}) \quad (Eqn. 27)$$

which can be followed by a reverse shift reaction to establish the thermodynamic equilibrium:

$$CO_2 + H_2 \leftrightarrow CO + H_2O \quad (Eqn. 28)$$

Methanol steam reforming is endothermic and therefore requires that external heat is supplied. It occurs when methanol and water are mixed and then vaporised and heated to about 300 °C over the appropriate catalysts. The vapour mixture is passed over a catalyst where the reaction occurs. At 300 °C the decomposition of methanol readily occurs as well as steam reforming.

Steam reforming of methanol is usually catalysed by Cu/ZnO type catalysts and can be performed in fixed-bed reactors [185]. The catalytic burner provides the heat for the reaction and the basic burner structure is a ceramic hollow cylinder to which fuel gas, mixed with air, is supplied. Pure methanol from the tank is used for start-up operation, during continuous operation the methanol feed can be diluted with retentate from the anode off-gas (when connected to a fuel cell system).

3.2.4 Autothermal reforming

This type of methanol reforming combines the endothermic steam reforming reaction with the partial oxidation of methanol in an adiabatic system (Equations 24–27). A spherical reactor system was calculated to be the most attractive configuration for an autothermal process. In this configuration an inner oxidation catalyst bed is combined with an outer sphere for steam reforming to promote internal heat exchange and maximise the product selectivity [186].

Autothermal systems are fast starting and compact. A single compact catalyst bed which converts methanol, water, and air into a reformate which mostly contains CO_2 and H_2 has been built. The HotSpot methanol processor uses a combination of POX and SR whereby the relative contributions of the two reactions can be tuned to necessity (see further in Section 3.6) [187].

3.2.5 Membrane reactors

This type of reforming unit combines the process of steam reforming (or cracking depending on the conditions) with a semi-permeable membrane which extracts the product reducing its concentration and thereby the reaction yields are higher. For the methanol reforming reaction the hydrogen partial pressure in the product becomes less of a function of the reaction and depends more on the back-pressure through the membrane. With a membrane reactor pure hydrogen was obtained [188] with a total efficiency of 80%. With better membranes and catalysts the loss of hydrogen could be kept at 5%.

3.3 Producing hydrogen from hydrocarbons

The infrastructure for producing and distributing fossil fuels (natural gas, oil, coal) is well established [189, 190]. Fuel cells operate best on hydrogen which – at least in the near term- will not be widely available. Therefore research and development activities focus on the generation of hydrogen from hydrocarbons. As was the case for methanol, hydrogen can be generated from the hydrocarbons by one of the mentioned processes: catalytic steam reforming (CSR), partial oxidation (POX), or an autothermal reforming (ATR). Natural gas can directly be used without external reforming in the high temperature fuel cells (see further).

3.3.1 Catalytic Steam Reforming [191, 192]

3.3.1.1 General

CSR (Figure 15 [193]) as a process was recognised in the early 19th century and has been developed by several groups and companies. Nowadays CSR is one of the principal processes for the production of H_2 and syngas (synthetic gas = mixture of H_2 and CO). Although partial oxidation and coal gasification also play a vital role in hydrogen production, CSR is cheaper and more energy efficient than the former two methods [194, 195].

3.3.1.2 Reactions

In general, the reaction for steam reforming of a hydrocarbon into a mixture of hydrogen and carbon monoxide (syngas) is as follows:

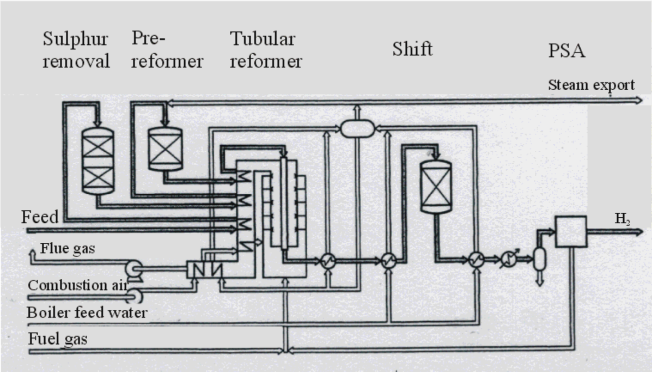

Fig. 15 A schematic showing the reactions and pathways in catalytic steam reforming.

$$C_nH_m + nH_2O \leftrightarrow nCO + (n+m/2)\, H_2 \qquad \text{(Eqn. 29)}$$

This reaction is endothermic ($\Delta H_0 > 0$) which leads to the need of heat transfer. Reactor designs are typically limited by heat transfer rather than the reaction kinetics. Consequently, these reactors are designed to promote heat exchange and tend to be heavy and large. A further process is normally the conversion of CO in the watergas shift reaction (see Equation 26) to CO_2 utilizing the steam.

3.3.1.3 Catalysts

Steam reforming of most hydrocarbons occurs only over appropriate catalysts and at elevated temperatures (> 800°C) where unwanted reforming may occur without a catalyst. Catalysts for SR are usually group VIII metals [196] whereby Ni appears to be the most active of this group.

Hydrocarbons are usually contaminated with small amounts of substances which can poison the reformer catalysts. Sulphur (S) is the most severe poison as it chemisorbs readily on any metal surface. A de-sulphurization step is carried out before the fuel is led into the reformer to avoid this poisoning. Sulphur can also poison the catalysts in the actual fuel cell.

3.3.1.4 Coke formation

Depending on the catalytic selectivity and on the saturation of the used hydrocarbons (meaning the amount of double bonds in the system) the decomposition of the hydrocarbon may be favoured over the reaction with steam. This process, called coke formation, can deactivate the catalyst in different ways. The formed carbon can diffuse through the metal crystal and cause an aging of the catalysts. A slow polymerisation of C_nH_m radicals can also occur which causes a progressive deactivation of the catalyst. An encapsulation of the catalyst particles by carbon precursors limits the catalytic activity by blocking the active sites.

To avoid coke formation an optimum fuel to steam ratio must be maintained throughout the entire system. The affinity for decomposition of hydrocarbons also induces the need for a heat flux whereby the temperature of the catalyst at the tube walls should be lower than the carbon limit temperature. Smaller metal crystallites or promotion of the catalysts with alkaline material also reduce coke formation.

3.3.2 Partial Oxidation [183, 189, 197-199]

Methane and other hydrocarbons can be converted to hydrogen via partial oxidation which may be catalysed or uncatalysed or a combination of both. Partial oxidation (Figure 16 [200]) is a reforming process in which the fuel is partially combusted in an exothermic reaction which provides heat for other reactions in the reforming system (usually in combination with steam reforming). The oxygen fed to the system is sub-stoichiometric so that both CO and CO_2 are formed in the system. A watergas shift reaction can transform the CO from the first reaction further into CO_2 (see gas clean up).
Reactions are:

$$CH_4 + 1/2\, O_2 \leftrightarrow CO + 2H_2 \qquad \text{(Eqn. 30)}$$

$$CH_4 + O_2 \leftrightarrow CO_2 + 2H_2 \qquad \text{(Eqn. 31)}$$

Methane POX occurs over heterogeneous selective catalysts whereby Ni/Al_2O_3 has a high selectivity for CO_2/H_2 at reforming temperatures of 850 °C. $Ni/La/Al_2O_3$ was found to have a lower activity and selectivity. At lower temperatures different catalysts were tested and it was shown that

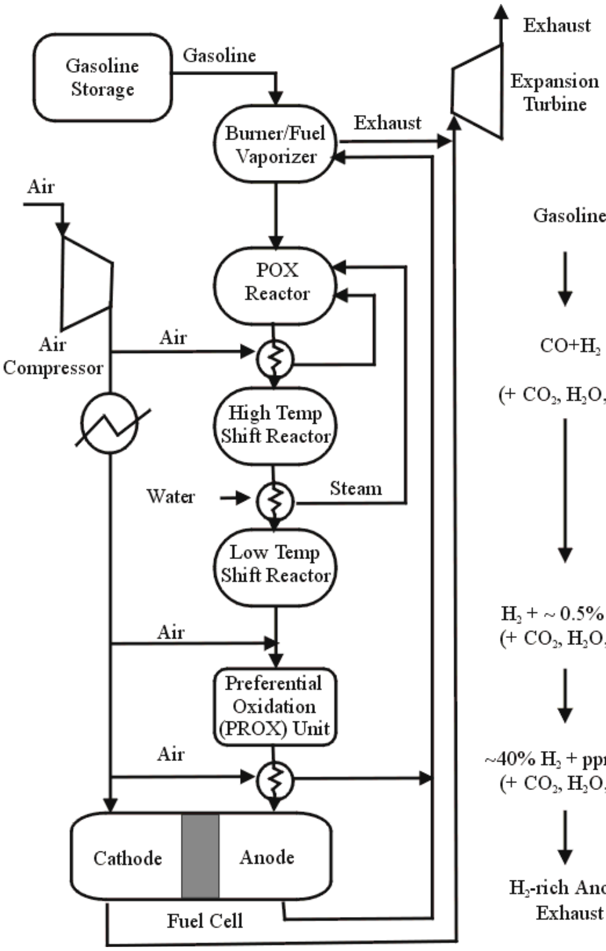

Fig. 16 Partial oxidation for the formation of hydrogen from natural gas.

$Co/La/Al_2O_3$ is active at 750 °C but not at lower temperatures whilst a $Fe/La/Al_2O_3$ catalyst could be used at 600 °C but provided a lower conversion and selectivity [198].

3.3.3 *Autothermal reforming*

The autothermic conversion of methane to H_2 occurs at 850 °C where a partial oxidation process is combined to a catalytic steam reforming process. An improved performance was found for single-bed configurations as opposed to two-bed systems due to the better heat-exchange possibilities in a single-bed reactor [193]. A 60–65% methane conversion could be attained with a selectivity of 80% towards hydrogen production. Systems employing the autothermic conversion of hydrocarbons are being used internally for MCFCs and SOFCs and can be used externally for other fuel cell systems (see Chapter 4).

3.3.4 *Membrane reactors* [193]

As for methanol reforming it is also possible for the reforming of hydrocarbons to combine the reforming step directly to a membrane selectivity to shift the reforming reactions towards formation of the product. Membrane reactors are more economic at lower temperatures, however, they need a minimum temperature of around 650 °C as otherwise the fuel consumption is too high and the feed supply pressure must be increased to very high levels. A very selective membrane is needed to perform the separation of the substances.

3.3.5 *Propane cracking* [201]

The decomposition of hydrocarbons (propane, methane, ...) is an endothermic reaction but provides some advantages to the reactor design. A simple design can be chosen as no shift converter or steam generator are necessary. The reaction for propane cracking is:

$$C_3H_8 \leftrightarrow 3C + 4H_2 \qquad (\Delta H_0 = 103.8\ \mathrm{kJmol^{-1}}) \qquad \text{(Eqn. 32)}$$

This reaction occurs at temperatures above 800 °C so a heat source (e.g., propane burner) is needed for this reaction. The carbon by-product accumulates on the surface of the catalysts thus eventually blocking the whole surface area. The catalyst can be regenerated, however, by passing air over the surface to burn off the carbon. Some small amounts of CO and CO_2 are produced during the cracking process which can be removed by methanation, selective oxidation, or catalytic burning (see Section 3.5.).

3.3.6. *Coal gasification*

This process is endothermic, thus, a high temperature is needed for the reaction to proceed. Solid coal reacts with oxygen and steam to produce a syngas mixture (CO/H_2) according to the following reaction:

$$C + H_2O \rightarrow CO + H_2 \qquad \text{(Eqn. 33)}$$

The reaction process can be very complex, however, as coal is provided in different forms and compositions. The process, therefore, has to be adjusted for each type of coal mined.

3.4 *Hydrogen from other sources*

Ammonia (NH_3) is an easily-liquefied gas produced by the reaction of methane with steam and air. It is easy to find transport facilities as ammonia is widely used in many applications (for instance in fertilisers). Decomposition of NH_3 occurs according to:

$$2NH_3 \rightarrow N_2 + 3H_2 \qquad \text{(Eqn. 34)}$$

This reaction produces hydrogen by cracking at high temperatures. An ammonia fuel cell power plant was developed using an ammonia cracker to power the fuel cells. The biggest advantage using ammonia over hydrocarbons is the lack of carbonaceous species that can decompose alkaline fuel cells or poison the other low-temperature fuel cells [202].

The electrolysis of water is also a major issue in hydrogen production. Hydrogen produced by electrolysis of water is pure and most of all the process can be completely zero-emission if the electricity used to electrolyse the water is taken from a renewable source such as water or wind energy. Hydro-electric power plants could enhance the energy storage by using the electricity to produce hydrogen. Solar energy is also a clean technique for electrolysing water.

3.5 *Gas clean-up*

Reforming hydrocarbons into hydrogen always produces small amounts of CO in the gas stream. This CO is not a problem for high-temperature fuel cells that can use CO as a fuel for the anode reaction. Carbon monoxide must be eliminated before being fed into a low-temperature fuel cell. The gas clean up can be done in several ways. The first step is a water-gas shift conversion of CO into CO_2 hereby producing more hydrogen. The CO content is reduced to the equilibrium value at a specific temperature (in the range of 1% CO; it decreases with decreasing temperature). The next step of CO removal has to be very efficient since it needs to lower the CO content to values in the ppm range so that fuel can be fed into the fuel cell. The three most common techniques are selective oxidation, methanation, and the use of a selective membrane.

An increase of CO tolerance of PEMFCs can be achieved by applying an electrical pulse to the cell which induces an overpotential to the anode [101]. The high potential at the anode clears the surface of CO through oxidation to CO_2. The cleaning of the surface is fast and is repeated on a regular basis. As the re-adsorption of CO is slow the applied pulses can clean the surface faster than the CO re-poisons it. The pulse duration is short and therefore the decrease of operating time can be tolerated [101].

3.5.1 *Shift reaction*

The water gasshift reaction involves the conversion of CO into CO_2 using steam as an oxidant and was discussed before (Eqn. 26). A normal reformer unit usually employs both a high-temperature shift reactor and a low-temperature shift bed. The high-temperature shift reactor uses Fe_3O_4 catalysts and temperatures above 350 °C to produce CO_2 from CO and steam. The low-temperature reactors operate at around 200 °C and employ CuO/ZnO catalysts. After the low-temperature shift reactor the fuel stream still contains a certain amount of CO (0.5-1%) which is still too high for low-temperature fuel cells. Therefore, a second cleaning step has to be carried out.

3.5.2 *Selective oxidation*

Selective removal of CO occurs over some catalysts which oxidise mainly CO and not hydrogen. Catalysts used for this purpose are usually alumina (Al_2O_3) supported structures. Ru and Rh supported on alumina are amongst the most active catalysts. Near to complete CO conversion can be achieved at temperatures as low as 100 °C. Cu particles dispersed on alumina are cheaper, easier to make and, combined with ZnO, they also have a high catalytic activity for CO oxidation. The activity depends on the particle size of Cu with smaller particles being more active. Selective oxidation prevents the loss of hydrogen as opposed to the methanation process which is described in the next section [203, 204].

3.5.3 *Methanation* [187]

A different approach to CO removal is taken by the methanation process. In this process CO is reacted with hydrogen to form methane and water. The amount of hydrogen needed to carry out this reaction is, however, three times the amount of CO removed. The reaction for this process is:

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \ (\Delta H_0 = -206.2 \text{ kJmol}^{-1}) \qquad \text{(Eqn. 35)}$$

CO_2 present in the gas stream can react with the produced water in a reverse watergas shift reaction (Eq. 28) thereby *producing* the unwanted CO. Methanation can work for removal of CO but severe restrictions are necessary to make this process viable in a gas clean-up system.

3.5.4 *Membranes*

Pd alloy membranes can be very effective in the removal of CO from the fuel stream. The gas is fed through the membrane through which hydrogen permeates selectively. This technique requires a rather large pressure difference and a relatively high temperature which reduces the efficiency of the system (the efficiency depends on the possibility of heat supply by the fuel cell system). The use of membranes was already mentioned before in the reforming section whereby the methanol steam reforming and the reforming of hydrocarbons can be directly combined with a membrane to produce clean hydrogen [188, 193, 205].

A combined system with different catalytic stages can prove to be the best answer to the problem of gas clean-up. The second cleaning step should take the CO level down to around 5–100 ppm which can then be fed to the fuel cell without significant losses.

3.6 *Reformer systems*

Reformer systems that operate on different fuels are being developed world-wide and not all systems and concepts can be discussed here. Some reformers are developed directly in conjunction with complete fuel cell power plants. One of the first industrial scale units was presented by BASF in the 1930's using natural gas. ICI (UK) developed the naphthalene reforming process and one of their first plants was commissioned in the late 1950's. Coal gasification was improved in the middle of the 20th century and the world-wide production of hydrogen via reforming processes is around 10^{12} Nm^3 per year. The Epyx reformer technology uses a combination of partial oxidation and catalytic steam reforming to produce hydrogen from hydrocarbons or alcohols [190].

A compact steam reformer was developed by GASTEC NV (Apeldoorn, The Netherlands) in which the heat for the endothermic reforming unit is supplied by catalytic combustion of methane or anode off-gas. Improved heat transfer was achieved by the application of metallic substrates for the reforming catalysts and arranging the catalysts in stacked plates. Induction heating elements were applied to be able to heat up the metallic substrates rapidly [194].

The HotSpot methanol reformer system was developed by Johnson Matthey Technology Centre (Reading, UK) [187]. This system can convert methanol, water, and air in a single compact catalyst bed to a reformate containing mainly CO_2 and H_2. A combination of steam reforming and partial oxidation is used to produce 750 L of hydrogen per hour in a 245 cm^3 reactor. The relative contribution of either reaction can be tuned to the system requirements at the time. The small amounts of CO produced by the system can be attenuated to under 10 ppm employing a catalytic gas clean-up using several adjacent bed reactors.

3.7 *Hydrogen storage*

Hydrogen can be stored in many forms of which liquid, gaseous, and solid only include a few of them. Hydrogen storage in hydrocarbons and other energy carriers such as ammonia and hydrazine was discussed in the previous section. Other, mostly physical, forms of hydrogen storage will be shown here.

3.7.1 *Pure hydrogen*

It is well known that hydrogen/air mixtures are explosive and most people still have the images of the Hindenburg or the Challenger disaster imprinted in their minds. It should be mentioned, however, that most other gases are far more explosive than hydrogen and that in case of a leak the hydrogen will disperse so quickly that it is near to impossible to ignite it. Nevertheless, safety measures are still one of the major implications when it comes to the commercialisation of hydrogen fuel cells [206-208].

For simplicity, it would be easiest to store gaseous hydrogen directly on-board the vehicle or next to the stationary

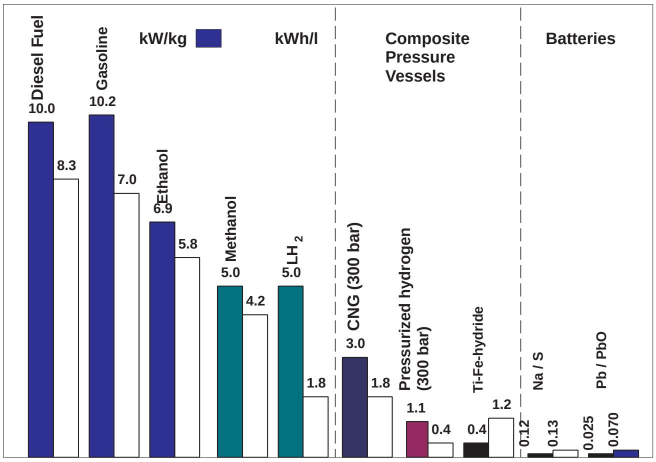

Fig. 17 Specific gravimetric and volumetric energy densities of selected fuels and comparison with batteries

application. In this way problems with reformed hydrogen which contains contaminants that can degrade the fuel cell performance are avoided. Unfortunately, gaseous hydrogen has a low energy density thereby restricting the possible uses. A comparison of the specific energy densities of selected fuels and batteries including the storage materials are presented in Figure 17 [209]. Compressing hydrogen into a tank can be achieved but a restricting factor, especially for transportation applications, is the size and weight of these tanks. Gaseous hydrogen is suited, however, to fuel buses and vehicles in fleet operations since the reduced driving range is of minor importance in these applications.

Liquid hydrogen storage can be achieved by cooling hydrogen gas up to –253 °C. Liquid hydrogen tanks should be extremely well insulated and even then a loss of around 1–2% of the stored hydrogen by evaporation per day should be counted with. Another problem with liquid hydrogen storage is the amount of energy necessary to convert the hydrogen into a liquid.

Although existing refuelling stations could be employed for the refilling of hydrogen tanks, both for liquid and gaseous forms, it is still necessary to completely reorganise these fuelling stations; this could be rather expensive and time-consuming. Localised refilling stations can be employed especially for fleet refill purposes. A project running at Munich's airport (Germany) uses taxis running on hydrogen to take VIP's from the terminal to the plane. The filling station (Figure 18 [207, 208]) is one of Europe's first and also provides hydrogen for a fleet of buses running at the same airport.

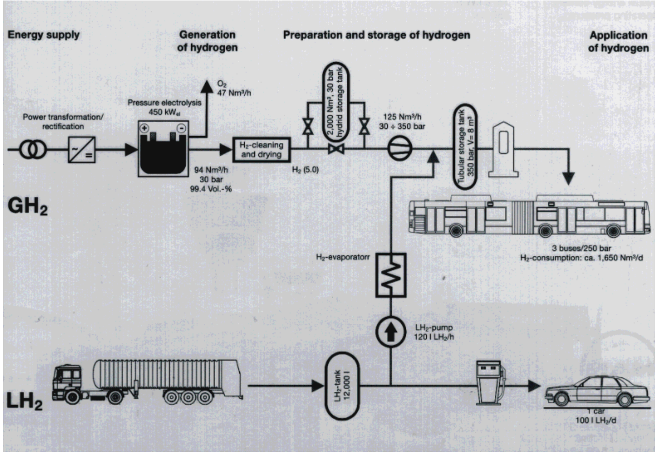

Fig. 18 The Munich airport hydrogen refilling station.

3.7.2 Hydrogen stored in solids

Hydrogen is stored in metals as bound hydrogen or as a gas absorbed into the structure. Metal hydrides are commonly used for hydrogen storage. A metal alloy exposed to hydrogen can form a metal hydride which occurs combined with the production of heat. The conditions under which a metal alloy forms a metal hydride depends on the type of alloy. The release of hydrogen usually involves the heating up of the metal hydride. Metal hydrides are common and can be used for different applications, the storage of hydrogen is only one of them. A database with properties, processing details, and applications of metal hydrides can be found on the internet [210].

Another hot topic in hydrogen storage is the use of graphite nanostructures which can store hydrogen in gaseous form in the crystal structure [211]. The effectiveness of this storage technique is very controversial but, if the results can be reproduced, they have a high potential to play an important role in hydrogen storage.

4 System engineering: from fuel cell to power plant

In order to fulfill the requirements of a specific application with fuel cells, smart system engineering that considers numerous aspects, ranging from safety regulations, user comfort, to the necessary power densities, is necessary. Therefore the fuel cells always need to be integrated into a system in which the components are matched. Single cells do not deliver enough voltage for most applications which is why they are combined serially into stacks. These stacks need a periphery (fuel processing, power conditioning, heat recovery, cooling, etc....) to operate the fuel cell and control the important parameters as well as to ensure a supply of fuel and oxidant (Figure 19 [212, 213]). The stacks can yet again be combined into modules which can then be used in an application.

4.1 Fuel cell engineering

The fuel cell is the heart of a complex system. It generates the power from the combination of a fuel and an oxidant which are electrochemically oxidised and reduced, respectively, and the electrochemical reaction produces electrons which are used as an electric current. A closer look into the cell components, which have thus far not been discussed, and their fabrication is given here.

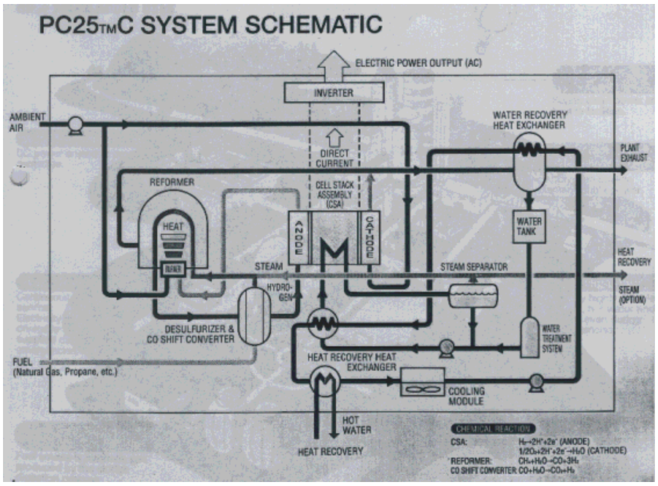

Fig. 19 A schematic of a PAFC (PC25) system showing the fuel cell and its periphery.

4.1.1 Low-temperature systems

Bipolar plates and flow fields for low-temperature fuel cells are important components that have not been discussed in this paper so far. Generally graphite is used to produce the bipolar plates as this material is light, conductive, and has a minimal corrosion in the fuel cell environment. Graphite plates, however, are difficult to machine and costly. An alternative to graphite plates are stainless steel current collectors which are highly impermeable, highly conductive, and have good mechanical properties. Stainless steel (sheet metal) has also a downside which is the weight and the higher corrosion probability [214-216].

Titanium seems to be an excellent material for bipolar plates as it is easily machined, rugged, and has a good electrical conductivity. Pure titanium, however, forms an oxide layer that is electrically insulating which makes it necessary to etch and coat the surface. Exfoliated graphite is generally used in high-temperature gaskets and was, thus, also a subject of investigation as it is commercially available, inexpensive, has a good conductivity, is self-sealing, and corrosion resistant. It is relatively easy to cut the foils in different shapes to form channels when put together, as the material is self-sealing. The interfacial resistance between the flow paths and the electrodes can be reduced enormously when using the Grafoil ™ exfoliated graphite as its compressibility allows an intimate contact with the electrodes [217]. Not only can the materials for bipolar plates be varied, also the structure of the flow fields is very important for the functioning of the fuel cell. Different structures (Fig. 19a-d [218]) for flow fields (e.g., square spot, interdigitated, serpentine, cascade, and metal screens or foams), have been proposed by several groups and a brief overview is given hereafter.

Depending on the nature (gas or liquid) and the concentration (especially oxygen partial pressure in air) of the reactant different flow field designs may be advantageous. A comparative study for some of the above flow fields has been published [218]. The first structure (square spot, Figure 20a) is not optimal for an equal distribution of the gas as the reactant gas can flow through the cell by any path available. This means that if some of the path is blocked by, e.g., liquid water the corresponding part of the electrode will be depleted of reactant and the current distribution over the electrode will not be homogenous. The advantage of this flow field is that the pressure drop is minimal.

The channel or serpentine flow path (Figure 20b) on the other hand is widely used by many groups as they ensure a preferred flow through the system [88, 219]. No channels are sealed so that a blockage of water is less likely to occur. The serpentine flow path makes an even distribution over the whole area of the electrode possible as the reactant gas is obliged to follow the path. Serpentine flow paths, though, are responsible for large pressure drops over the gas path and are difficult to fabricate if the machining is done manually (time-consuming). The structure used mostly in commercial systems seems to be a parallel serpentine flow as this structure avoids the pressure drop but maintains the preferred flow path.

The interdigitated (Figure 20c) channels force the gas through the diffusion layer backing (convectional mass transport instead of diffusion) which can be advantageous for pure gases. Often this is not a preferred structure, especially for air operation, due to the blockage by water droplets and above all it induces a large pressure difference in the cell. For pure gases this may be a suitable structure as the supply of the catalytic active sites is good [220].

The cascade structure (Figure 20d) also uses sealed-off channels that make blockages due to water droplets possible. This structure also suffers from huge pressure differences.

The commercialization of fuel cells requires the development of cost-effective manufacturing procedures. Flow fields made from metal foam or expanded metal components have been studied [221]. The use of inexpensive metal wire, screens, and foils was also investigated for fuel cell purposes [222, 223].

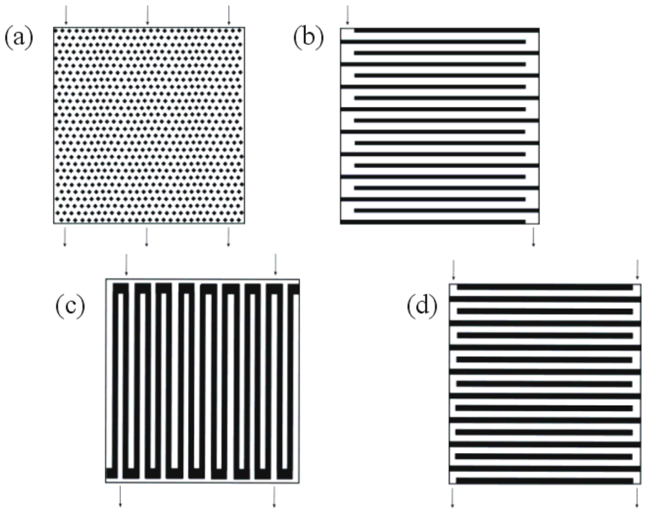

Fig. 20 The different types of flow fields used in fuel cells: a) square spot, b) serpentine, c) interdigitated, d) cascade.

4.1.2 High-temperature systems

For high-temperature fuel cells the different components can be fabricated using various commercial techniques. The following section will give a brief overview. A review on the different techniques was also published by K. Kordesch [71]. As bipolar plate materials were already discussed in the relevant sections for both MCFCs and SOFCs this section will concentrate on the fabrication of electrodes and electrode/electrolyte assemblies.

Tape casting and calandering are techniques used to produce thin, uniform films of a ceramic electrolyte. Casting involves the deposition of a ceramic film onto a temporary support by using a movable doctor blade (therefore also called doctor blade technique). Several layers can be cast on top of each other to produce self-supporting electrolytes. After removal of the support and evaporation, the tapes can be fired. Tape calandering is a basic rolling technique whereby the thickness of the films is controlled by the spacing between the rolls. Tape calandering is used to fabricate components which can be laminated. The cathode and anode can be co-fired with a tape calandered electrolyte to produce a catalyst/electrolyte structure. Co-firing requires the thermal expansion coefficients of the three components to be similar which is one of the drawbacks of this technique. Tape casting and calandering combined with co-firing of the components may be suitable as a low-cost production technique. This manufacturing technique allows the production of thin electrolyte layers for the operation of high-temperature fuel cells at lower temperatures (as low as 500 °C can be attained). [52, 168, 223, 224].

Anodes and cathodes can also be deposited on the electrolyte via a slurry-coating process. This method involves the suspension of the catalyst powder in water, the coating of the substrate with this suspension, followed by drying and sintering. A comparison between slurry-coated anodes and plasma-sprayed anodes (see further) was carried out and it was found that the slurry-coated anodes had a better performance [171].

Another widespread fabrication method is screen printing to produce porous or dense layers with a thickness from a few microns to about 15 microns [71]. Normally a powder containing the necessary components is mixed with an organic binder and plasticizer and is then screen printed onto a substrate. The paste is forced though the openings in the screen by a rubber roller which depresses the screen to contact the substrate. The thickness of the film is determined by the thickness of the screen wires. After screen printing the desired pattern onto the substrate, the film is dried and then fired. Normally shrinkage will occur. A homogenous and crack-free layer can be obtained by carefully controlling all steps of the fabrication process.

Vapour deposition of catalysts is also frequently used to produce electrode/electrolyte assemblies. Chemical, electrostatic, and flame-assisted vapour deposition are the most important forms of this technique. Together with sputtering techniques these methods are essential for the coating of fuel cell components.

Spraying is also used to deposit catalysts onto a substrate. Wet powder spraying or dry spraying can produce a thin cathode layer onto an electrolyte film, whilst vacuum plasma spraying is routinely used to deposit both cathode and anode layers onto the electrolyte [168, 225].

4.1.3 Cell designs

A fuel cell consists of electrodes, an electrolyte, and two plates which serve as current collectors. In a normal cell design these components are put together in a sandwich-like manner to form the complete fuel cell. The current-collector plates also serve as flow fields for the reactant gases to flow through the cell. For the flow of reactants different configurations are available (Figure 21a-c [71]). Co-flow (Figure 21a) involves both the anode and cathode stream to flow in the same direction and along the same axis. A flow along the same axis but in different directions is usually called a counter-flow (Figure 21b) configuration. A cross-flow (Figure 21c) is induced when the anode and cathode gas streams flow perpendicular to each other.

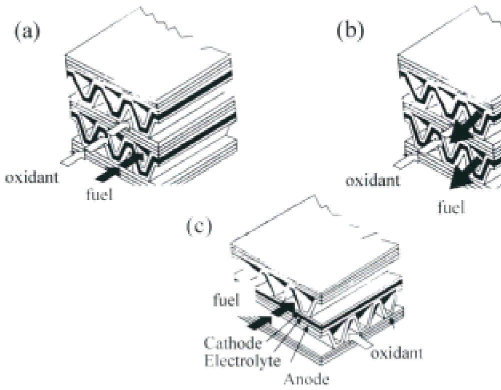

Fig. 21 The configurations possible for the two reactant flows in a fuel cell: a) co-flow, b) counter-flow, c) cross-flow.

4.2 Stack engineering

Single cells do not deliver the necessary voltage for normal applications. Therefore the cells are connected in arrays where the cell voltages are added in series (Figure 22 [226]). The cell current is constant over all cells. Two basic designs can be distinguished (Figure 23 [71]): monopolar (Figure 23a) and bipolar (Figure 23b) constructions:

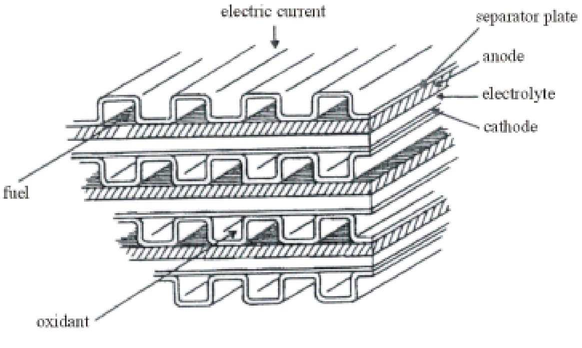

Fig. 22 A fuel cell stack: a flat design showing the bipolar plates with the flow fields that make the combining of two and more cells possible.

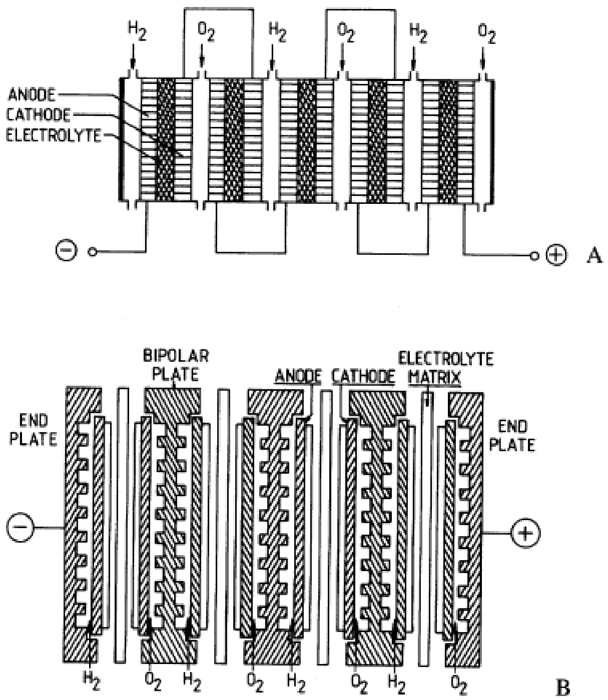

Fig. 23 Different cell constructions: (a) monopolar and (b) bipolar cell

In the monopolar design the gas volume is shared by two cells which are, however, electrically insulated. For serial addition the monopolar electrodes have to be connected to one another at their edges. The edge or frame collection leads to long current paths and therefore good electronic conductivity of the electrode is crucial. When using carbon electrodes supplemental metal screen, expanded metal, or metal felt are necessary. The current distribution can be uneven at high current densities and electrode areas. On the other hand, monopolar cells exhibit the advantage that they can be connected individually in the stack, depending on the voltage-current demands. Single cells may also be disconnected in case of failure without disturbing the overall operation.

In the bipolar arrangement a bipolar plate connects two electrodes with opposite polarities thereby implementing the serial addition in the stack. The current flows perpendicular to the electrode surface and current collection is performed over the whole area of the electrodes. Therefore also electrode materials with low conductivity, such as carbon, can be used without significant resistance losses. A disadvantage of this concept, however, is that a single-cell failure leads to a shutdown of the complete stack. The main advantage is that the bipolar arrangement poses no restriction on the size of the electrodes and cell areas over 400 cm^2 can be used without problems. Due to this aspect, the bipolar design has been used in most technical systems.

Usually single cells are stacked vertically to form a structural module, although some lateral stacking has also been implemented in some cases, especially for small applications. The insulation of all the cells from each other is of course important to avoid a short circuit. It is also important to be able to produce MEA's with good reproducibility. Water management in the stack can be difficult too.

4.2.1 Manifolding of reactants

Manifolding is the way in which fuel and oxidant are supplied to the multi-cell stack. This can be done in different ways (Figure 24 [145]). In the external manifold design (Figure 24a) the distribution of reactants or collection of products is achieved through inlet ports supplying the cells with a flow path parallel to the layering of the stack. External manifolding is mostly used in PAFCs. The internal manifolding (Figure 24b) implies the supply of fuel and oxidant through leads within the stack, i.e., the flow is perpendicular to the stack layering. The bipolar plates and membranes therefore have passages (e.g., bore-holes) in them to accommodate the reactants and products in their flow path throughout the stack. The need for good seals to ensure a leakage free stack is therefore required which is a main priority in fuel cell engineering. A combination of internal and external manifolding is also possible [145].

4.2.2 Fuel processing system

The reforming of hydrocarbons and alcohols was discussed before in the fuel processing section. In this section only external reforming whereby the reforming unit is outside of the fuel cell, was considered. In a different system concept, the reforming is integrated into the stack. Another possibility that can only be used for high-temperature fuel cells is the direct reforming of the fuel at the anode of the cell, which is called internal reforming.

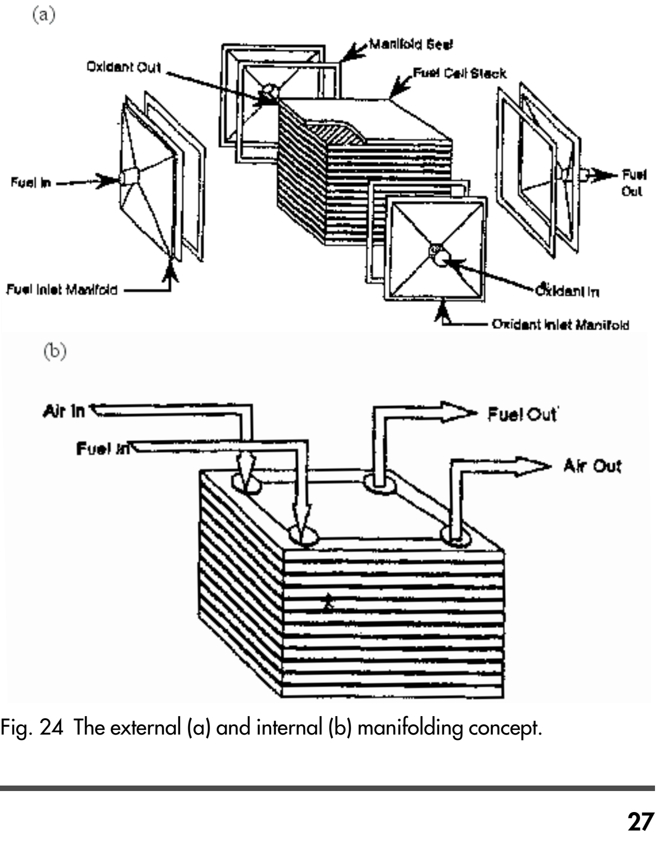

Fig. 24 The external (a) and internal (b) manifolding concept.

The integrated reforming involves the fuel to be fed into the fuel cell stack immediately. The cells can be fed separately whereby each individual cell contains a (micro) reformer unit. Alternatively there could be one reforming unit per block of cells, which can then supply those cells with hydrogen. A combination of both is also possible of course. The extra advantages of integrated reforming is that the waste heat from the fuel cell can be used directly to provide the heat necessary for endothermic reforming processes which simultaneously will cool the stack. External reforming units add to the weight and size of the system and are probably more expensive.

The direct fuel cells (MCFC and SOFC with internal reforming) differ from the above systems in the way that the fuel cell electrodes are used for gas reforming reactions. Either the reforming is performed directly at the electrodes or the reforming is done externally and the electrode catalysts are used for shifting the reaction equilibrium (water-gas shift) in favour of hydrogen which is then converted electrochemically. This internal reforming has even more advantages than the integrated reforming as the heat exchange between the different components can be achieved more effectively.

4.2.3 Periphery

Peripheral systems for stacks include the fuel processing unit, a DC-AC converter, a stack control unit, and many other components. The power conditioner must convert the low-voltage direct current (dc) into a high-voltage alternating current (ac). In most fuel cell systems a battery is implemented to ensure that at peak power the system can handle the demand. Numerous supporting auxiliary subsystems are required to make a fuel cell system operate. However, most auxiliary systems (e.g., heat exchangers, electric drives, pumps, etc.) have not been developed specifically for fuel cell applications and are seldom discussed in the literature. Therefore, they are not described here. Some of these components will be mentioned in the next section, which includes system design for stacks and power plants.

4.3 Fuel Cell Systems

Power plants can be centralised facilities or distributed facilities depending on the specific need of a community or city. Centralised facilities are momentarily dominating the power-generation market in industrialized nations. Smaller scale plants will be used in distributed power generation and on-site generation of electricity and heat thereby providing a better service. It is therefore expected that distributed power will become more important. Fuel cell plants have the advantage, when used for on-site power generation, that the pollutant emissions are much lower, the efficiencies higher, and the operation more silent. Thanks to the modular character of fuel cells power capacity can be added when necessary, thus creating the possibility of large-scale power plants for larger cities and communities where distribution lines are readily available. The distributed power plants can be added to the overall grid to produce on-site extra capacity where needed [227].

Power plants consist of the fuel cell system combined into stacks and modules which are controlled by processing units. The reformer unit is usually implemented into the stack as was seen before. It is not possible here to describe in detail all the available systems and plant engineering designs but a brief description of systems for each fuel cell type will be given in these next few paragraphs.

4.3.1 Alkaline fuel cell systems [73]

The peripheral systems in an AFC support the three main streams (hydrogen, air, and electrolyte) as well as the interface between the stack and the load. The gas systems control and direct the pressure and flow of the gases. The electrolyte is usually circulated through the system using a pump. An interfacial connection between the fuel cell and the load is necessary to isolate the fuel cell from transients in the load. The system controller switches the fuel cell on and off in accordance with load demands.

An early fuel cell car model was built by K. Kordesch in the 1970's. Later an Austin car was converted into an AFC hybrid by Zevco leading to an additional weight of 220 kg. The fuel cell was used for propulsion whereas lead acid batteries provided power during acceleration and hill climbing. The Austin car contained the hydrogen tanks on the roof, refilling the hydrogen tanks took around 2 minutes, and the car could achieve distances up to 300 km on one tank in city traffic [72].

A nitrogen flushing of the tanks was made possible which could be controlled automatically or manually as needed. The system provided about 140 Wh/kg, which converts to about 60% efficiency, and the electrodes used were low-loading Pt/C catalysts dispersed onto porous nickel plates. The same system was used in the London Black Cab project where fuel cell modules (usually 24 cells) were combined into stacks to form up to 10 kW power units. The gas distribution and electrolyte circulation systems were built into the stack. The performance of the fuel cells attained 120 mA/cm^2 at 70 °C at maximum power operation. The London Cab employs a battery to provide the vehicle with power for the first 10 minutes of operation until full output of the fuel cell. The battery also provides heating power and extra power for hill climbing and acceleration cycles [73].

4.3.2 PEM systems [75, 228, 229]

The first PEM stacks were employed in the Gemini space program. The unit provided the spacecraft with 1 kW power. The most famous applications of PEM fuel cells nowadays are the cars and buses from Ballard, Daimler-Chrysler, Toyota, Ford, General Motors, and other motor companies. More about these applications will be given in Section 5.2. Ballard also constructed a power plant operating on by-product hydrogen, which provided 10 kW. A 250 kW commercial prototype was commissioned in 1997 and focussed on weight reduction. Field trials of this prototype are being carried out around the world today.

Plug Power installed a 7 kW residential power system, which provides electricity, heat, and hot water to a home in upstate New York. Residential fuel cells are in essence miniature power plants that provide electrical power efficiently, reliably, and most of all quietly to a home or to a block of homes. One of Plug Power's fuel cells has cleared a milestone of 10,000 hours and the company has announced the completion of 52 fuel cell systems, 37 of which are operated on natural gas and the other 15 operating on synthetic fuels.

A fuel cell stack with internal humidifier has proven to exhibit similar performances as external humidification for PEM fuel cell applications. In an internal humidification configuration water is supplied to the stack through a water flow channel and serves to provide both cooling for the stack and humidifying of the gases. Water and reactant gases flow on opposite sides of the membrane and water can permeate through the membrane. External humidifying only serves as humidification of the gases and can not take part in the cooling of the stack.

It was found that the mass-transfer behaviour of reactants and products of the stack is more complicated compared to a single cell because of the heat exchange, humidity and reactant supply effects. Some of the produced water was lost by evaporation whilst self-humidifying was found to be more efficient at temperatures above 30 °C. Under laboratory conditions humidification can be lowered if cooling power is increased to compensate for the heat released by the electrode reactions. In applications, however, cooling power is limited and humidification is a necessity.

4.3.3 DMFC systems

For the DMFC two alternatives can be used as approaches for the fuel feed: the methanol water mixture can be fed into the cell/stack as a liquid or as a vapour. Gas feeding of the fuel minimises the cross-over problem but it can give more problems with humidification of the cell. Both systems have been investigated and no conclusive arguments have been found as to which of the two systems is better. Methanol cross-over is still the main problem for both configurations so the development of methanol-tolerant cathodes and better membranes remains the biggest issue for these systems. [123, 124].

At LANL (Los Alamos National Laboratories) a DMFC stack was produced which attained a 90% fuel utilization and produced 2.25 kW/kg. The stack temperature was 60 °C, air pressure was the atmospheric pressure at the LANL site. The width of each cell was 1.8 mm and the pressure drop across the cells was minimised. A stoichiometric air flow was achieved and a maximum power density of 1 kW/L (0.3 W/cm^2) was reached. It was found, however, that the concentration of methanol in the fuel flow must be kept as constant as possible for which a methanol sensor was essential.

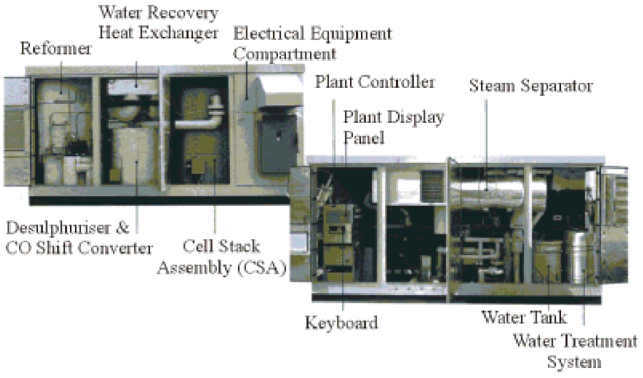

Fig. 25 A PAFC (PC25) plant showing all components.

4.3.4 PAFC systems

The PAFC system is the most commercially advanced fuel cell system. Some of the commercial applications include 1 MW and 4.5 MW plants which operate on natural gas. A major power plant in Japan was commissioned by United Technologies and Toshiba to provide 11 MW power for Ichihara in Tokyo. A 200 kW power plant from Toshiba in co-operation with ONSI was developed and tested. The electrical efficiency was 40%, which is equal to a large-scale thermal power plant. The overall efficiency, however, amounted to a value greater than 80% thanks to the heat-recovery process. The noise and vibration of the whole system was negligible and the exhaust emissions were also very small (NO_x < 5 ppm). The system consisted of a reformer, a desulphuriser and CO shift converter unit, a water recovery heat exchanger, fuel cell stack modules, and an electrical equipment compartment. The plant controller, display panel, steam separator, water tank, and treatment system were also integrated into the final plant management (Figure 25 [212, 213]).

4.3.5 MCFC systems

The stack lifetime for MCFC systems can be critical due to the cell matrix, the leaking of the electrolyte, and the instability of the electrodes [230]. An MCFC plant fuelled by natural gas with about 50% efficiency was tested in Bielefeld, Germany. This plant operated on the hot-module concept [231, 232] (company MTU Friedrichshafen) which is also used in the plant powering the Daimler-Chrysler factory in Alabama. The hot-module concept (Figure 26 [233]) involves the high-integrated fabrication of fuel cell components. It uses a horizontal stack whereby more cells per stack are possible therefore requiring less space and only one seal is necessary. The plant provides 250 kW of electrical power and also provides the university in Bielefeld with heat and hot water.

The 2MW Santa Clara demonstration project is probably the best known MCFC system to date. The power plant was based on the carbonate fuel cell pioneered by Fuel Cell Energy, Inc. (FCE) of Danbury (Connecticut, USA) and was developed by ERC (Energy Research Corporation). The

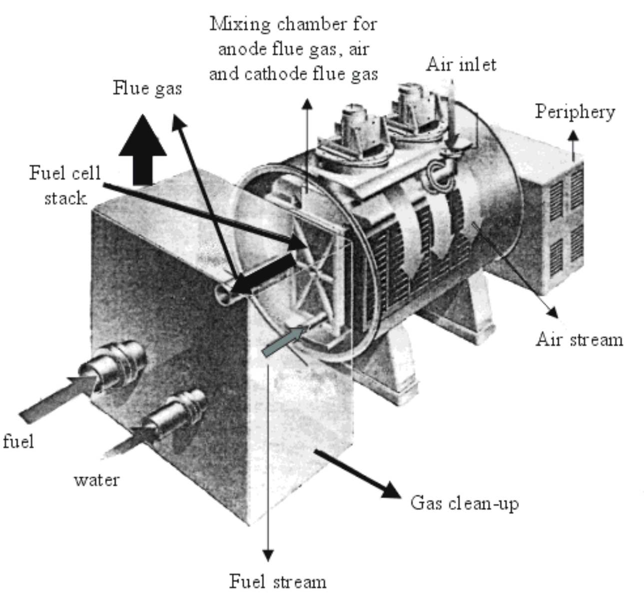

Fig. 26 The MTU hot-module concept.

power plant reached 1.9 MW electrical power and contained 40,000 cells grouped into 16 stacks. The 125 kW per stack in direct current was converted into alternating current by a high-performance power-conditioning unit [234, 235]. Other MCFC demonstration plants include the M-C Power Corporation plant in Miramar (San Diego, USA) which provides 250 kW. M-C Power Corp uses an internal manifolding system but an external reformer and will be targeting the market with 1–15 MW plants. The target market in Japan will be for power systems larger than this, targets of 20–50 MW have been set by Hitachi, Toshiba, Mitsubishi Electric Company (MELCO), IHI, Sanyo, and other companies. In Europe MCFC development is mainly carried out by ECN and ANSALDO [145, 236].

An MCFC system with auto-thermal reforming was developed and has been discussed [237]. At low temperature and pressure the partial oxidation and catalytic steam reforming processes are carried out in the MCFC and syngas is produced (for reactions refer to Section 3). Subsequently the fuel cell can produce power and heat via partial oxidation depending on the amount of oxygen in the system. The hydrogen production increases with an increasing H_2O/CH_4 or O_2/CH_4 ratio. At low current densities the production of CO in the syngas is higher than at high current densities and the higher the oxygen content, the more heat is produced in the system. It is, therefore, possible to tune the system to produce electricity, heat, and syngas for further electricity production which makes the system very flexible to use.

4.3.6 SOFC systems

Syngas and electricity co-production was also achieved in an SOFC system [156, 238]. The plant operates on methane gas and produces energy from the direct oxidation of methane and from the reforming of methane to H_2 and CO_2. The H_2 can then be used in the solid oxide fuel cell or in combination with another fuel cell (for instance a PEM), the H_2 can also be used to provide more energy. The whole system also provides heat, which can be used in a gas turbine. The CO produced can be removed by an internal shift reaction as was discussed before in Section 3.

The direct oxidation of hydrocarbons in high-temperature fuel cells is not uncommon. An SOFC operating on n-butane provided 0.18 W cm^{-2} at 800 °C by using the energy obtained by the direct oxidation of the hydrocarbon. Using a copper-ceria anode and a relatively high temperature ensured that the anode stayed free of coke formation (a major problem when reforming hydrocarbons, see Section 3.3.1.4.) [157, 158].

A 100 kW electrical power production unit was developed in a co-operation of Siemens-Westinghouse [239] and NUON and ELSAM. The system also provided 54 kW of heat at nominal operating conditions (400 V). The efficiency operating with natural gas attained 47% (electrical) + 25% (heat) with relatively low emissions (NO_x, SO_x, CO, and VCH's all under 1 ppm) [240]. The start-up time of the whole system was about 14 hours and the operating temperature was set at 1000 °C. This system passed a one-year operation milestone in December 1999. The system is supplying the current to a local grid as well as hot water to the Westervoort (The Netherlands) heating system. Siemens Westinghouse is also following a new concept combining a pressurised SOFC with a micro-gas turbine (Figure 27). With these combined-cycle plants electrical efficiencies of 58% can be achieved at power plant capacities as low as 250 kW, and 60% for capacities as low as 1 MW using simple small gas turbines. In this highly integrated system, air is pressurized by the turbine's compressor and heated in a recuperator before entering the module. The resulting exhaust is a hot pressurized gas flow that drives the turbine generator. The advantage of this combined - or hybrid - cycle is that both the fuel cell module and the gas turbine generator produce power while using the same fuel and airflow.

Delphi Automotive Systems and Global Thermoelectric Inc. are testing an SOFC running on petrol (gasoline). Both a

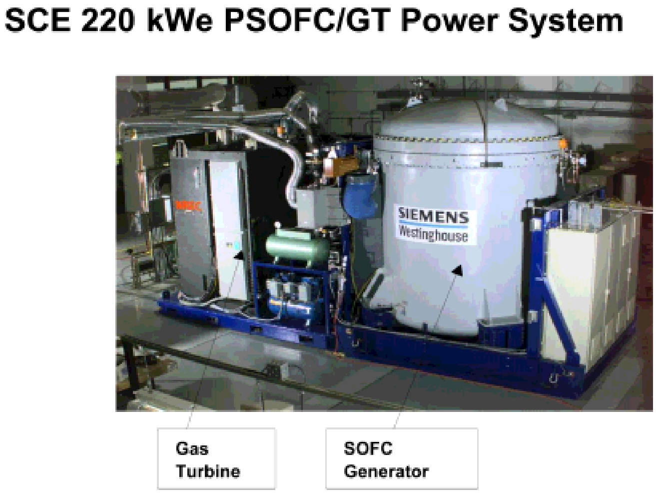

Fig. 27 Combination of a pressurised SOFC with a micro-gas turbine. Concept of Siemens-Westinghouse.

prototype for stationary power and a power system to provide electricity for cars (in conjunction with BMW) were demonstrated on April 26, 2000 [241]. Global Thermoelectric, Inc. have also successfully tested a residential fuel cell system based on a modular design. The modules can be assembled as separate components facilitating commercial production as well as making servicing of the components much more simple [242].

4.3.7 Modelling and studies of systems

Practical applications for fuel cell systems are obviously the best way of testing the viability of a particular system. Trying to understand the processes determining the complex behaviour of a complete system is intricate. Modelling of fuel cell systems and components has been very important for advancing the understanding of these systems. Several researchers are developing models for the different parts of the fuel cell system. A brief overview is given here.

A model for gas diffusion electrodes describing the limiting current densities for oxygen reduction cathodes was published in 1994 [143]. Impedance measurements of catalysts, electrodes, membranes, and other fuel cell components have been studied and published [243]. Simulations of water management in the membrane or the interpretation of power response based on models as well as structural investigations on Pt supported catalysts are also important for the understanding of the processes in fuel cells [244-246].

The performance and modelling of a DMFC fuel cell taking methanol cross-over, pressure, and other effects into account were analysed as well as a model for a DMFC stack predicting the thermal behaviour in the stack [219, 247-249]. Further studies on DMFCs included the analysis of Pt/Ru anode electrochemistry, optimisation of DMFC parameters, a DMFC anode model, and other investigations on the anodic oxidation of methanol [21, 22, 24, 249, 250].

The modelling of high-temperature systems has also been carried out including the effect of different kinds of fuel on the performances of the cells. References in the literature can be found for MCFCs, SOFCs, and reformers [186, 199, 251-260].

A comparison of different fuels for fuel cell vehicles and the implications on vehicle design and infrastructure development was made by J. Ogden et al [200]. Using a vehicle with direct hydrogen storage makes the vehicle design simpler but requires a more complex refuelling infrastructure. Hydrogen vehicles are also more efficient than those with on-board fuel processors. Future improvements in fuel processor technology or development of fuel cells which can operate on reformates without the need for an extensive gas clean-up, could increase the vehicle efficiency. Better storage forms for hydrogen could also add to more cost-effective vehicles. The choice of fuel should be made considering different factors such as environmental benefit, market penetration probability, and data acquired from tests carried out on fuel cell prototypes.

Converting the existing refuelling stations to other fuel dispensing should be achievable and may even be cheaper than building entirely new facilities. Especially for methanol provision the conversion should not be so expensive as existing installations would only need new piping and dispensers which could reduce the cost dramatically as the same lay-out and equipment can be used.

5 Applications

5.1 Stationary power

The most important attributes of fuel cells for stationary power generation are the high efficiencies and the possibility for distributed power generation. Both low-temperature and high-temperature fuel cells could, in principle, be utilised for stationary applications. The low-temperature fuel cells have the advantage that usually a faster start-up time can be achieved. The needed operating time for the stationary application is about 40,000 hours, which may be a challenge for fuel cell systems. The high-temperature systems such as SOFC and MCFC generate high-grade heat which can directly be used in a heat cycle or indirectly used by incorporating the fuel cell system into a combined cycle. SOFCs and MCFCs also have the advantage that they can operate directly on available fuels without the need for external reforming.

For a small distributed power system, e.g., single-home or multiple-home power generation, a PEM, SOFC, or PAFC combined with a heat cycle could be used to provide all the needs for a home. The PAFC start-up time is much lower than this for high-temperature systems, which makes it more attractive for small-power generation. The heat generated by the fuel cell system can be employed for heating and providing the home with hot water. The PAFC produces enough steam to operate a steam reforming system whereas the PEM system due to its lower operation temperature is not able to supply the necessary heat.

Small power plants in the range above 250 kW can be operated by high-temperature fuel cell systems. The high grade heat obtained from these systems can be exchanged at a broad temperature range leaving the possibility of direct heat use or further electricity generation by steam engines. The start-up time of these systems are longer than for low-temperature systems but the advantages of being able to operate the system without external reforming and the higher efficiencies of SOFCs and MCFCs makes these systems more suitable for large-scale power plants.

5.2 Propulsion of vehicles

For vehicular applications fuel cell systems need to be different from stationary power generation. Available space in vehicles is much more critical and fast response times and start-up times are required.

The controversial AFC has proven to be a suitable system for hybrid vehicles as long as a circulating electrolyte is used and pure hydrogen is supplied to the fuel cell. Pure hydrogen distribution centres are not widely spread over the world and, thus, it is to be predicted that AFC vehicles will be limited to specified types (e.g., fleet buses and other centralised vehicles). For space vehicles, AFC technology is established and although the tendency to change to PEM fuel cells is also penetrating the space industry it is likely that AFC systems will be employed for many more years in space. PEM systems still need to be tested concerning the stringent requirements (reliability of operation etc.) for space applications.

Prototype fuel-cell-powered vehicles (an example is shown in Figure 28 [261], NECAR 4, a car from DaimlerChryler with PEM system operated with liquid H_2) have recently been demonstrated in Europe, Japan, and North America by several car manufactures [261]. All of the various demonstration vehicles are based on a basic conceptual design combining the proton exchange membrane (PEM) fuel cell with an electric drive. The PEMFC is regarded as ideally suited for transportation applications due to its high power density, high energy conversion efficiency, compactness, lightweight, and low-operating temperature (below 100 °C). The recent PEM-driven electric vehicles have demonstrated the technical feasibility of the concept. However, among all applications for fuel cells the transportation application involves the most stringent requirements regarding volumetric and gravimetric power density, reliability, and costs.

Since a widespread hydrogen retail infrastructure will not be available in the near future, car manufacturers consider a liquid fuel as the best option for a short-term market introduction of a fuel cell propulsion system. Furthermore, the higher energy density of a liquid fuel guarantees a driving range similar to that of internal combustion engine vehicles. The fuel favoured by many car manufacturers is methanol from which hydrogen can be produced on-board by steam reforming. The reforming of the fuel, however, leads to slower response times, and extensive gas clean-up procedures need to be carried out to supply the fuel cell with high-grade hydrogen.

Because of the difficult thermal integration and the size of the reformer and gas-cleaning unit a direct methanol fuel cell (DMFC), where methanol is oxidized directly at the anode, would be more desirable for mobile systems (higher simplicity of the system). Therefore, in addition to the reformer/fuel cell combination, DMFCs using methanol/water vapor or liquid methanol/water mixtures as fuel are being investigated and developed. The development of the DMFC for transportation applications, however, is less advanced as compared to the indirect PEMFC and hampered by problems of reduced power density caused by methanol permeation through the membrane and poisoning of the electrocatalysts. Recent progress regarding power density and compactness of DMFC stacks are encouraging and indicate that this concept may be competitive in vehicles.

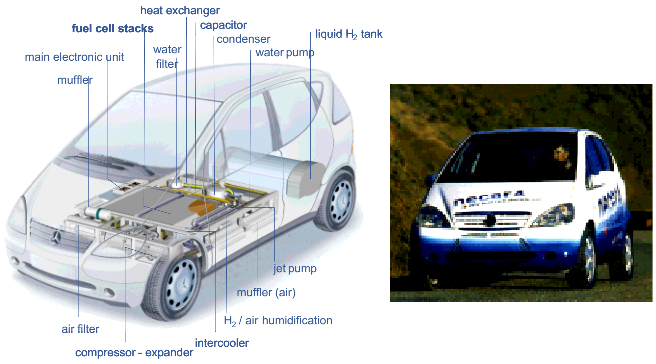

Fig. 28 NECAR 4, components of a fuel cell vehicle with a PEM system operated with liquid H_2

Due to the multitude of realized demonstration vehicles with PEMFC technology it appears a forgone conclusion that only fuel cells based on the PEM technique are suitable for transportation applications. System considerations, however, show beneficial properties of high-temperature fuel cells that could simplify the system considerably. Certainly, PEMFCs have the advantage of the low operating temperature and the high power density. Using alcohols or hydrocarbons as fuel, thermal integration is complicated. The main advantage of SOFCs compared to PEMFCs concerns the unproblematic use of hydrocarbon fuels. SOFCs do not require pure hydrogen as fuel, but can be operated on partially pre-reformed hydrocarbons (e.g., gasoline). They do not exhibit any significant poisoning problem. Several studies have investigated the potential of SOFC for transportation applications and have pointed out this advantage [262, 263]. These beneficial factors have been recognized recently, leading several companies (e.g., Delphi Automotive Systems) to develop SOFCs as Auxiliary Power Units (APU) for gasoline vehicles. BMW is implementing PEM fuel cells in their hydrogen combustion engine vehicles (BMW 7 series) and SOFCs in gasoline vehicles as Auxiliary Power Unit [264]. The APU replaces the traditional battery and provides further electrical energy for air conditioning and car electronics.

5.3 Portable applications [265-271]

For small power applications like laptops, camcorders, and mobile phones the requirements of the fuel cell systems are even more specific than for vehicle applications. Low temperatures are necessary and therefore PEM fuel cells are chosen. Possibilities for fuel cell systems are the combination of PEM with hydrogen storage by hydrides or gas cartridges or the direct methanol fuel cell. Figure 29 shows the Manhattan Scientific portable fuel cell concept (DMFC) with a banded structure membrane. This type of fuel cell will be employed in portable phones and can be adjusted for other portable applications. The requirements for portable applications are mostly focused on size and weight of the system (as well as the temperature). Other fuel cells are, therefore, not suitable for this kind of applications. Portable devices need lower power than other fuel cell applications and, thus, DMFC systems may be well suited for this kind of applications. With further technology improvements and better storage systems PEM fuel cells and DMFC systems will continue to compete in this market.

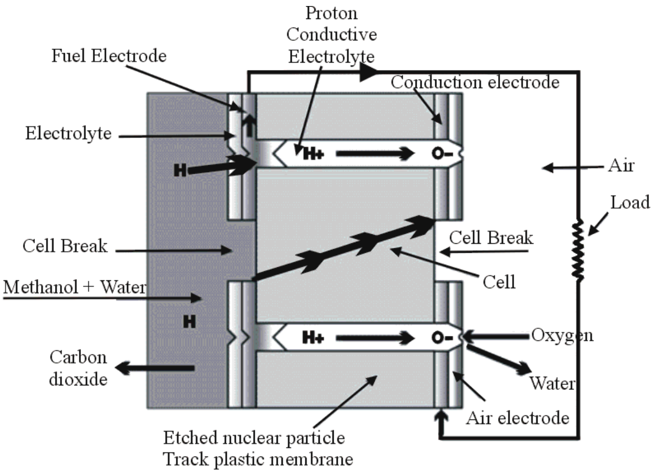

Fig. 29 The Manhattan Scientific Micro Fuel Cell concept demonstrating the banded structure membrane which can be used in mobile applications.

6 Summary and future technologies

Fuel cells will make a valuable contribution to future power generation facilities. They improve the flexibility and increase the options for many applications, such as distributed power, vehicle propulsion, and portable devices. Their main property is the high electrical efficiency compared to other energy conversion devices. Both the low-temperature and the high-temperature fuel cells have their advantages and disadvantages depending on the application. Sometimes, they can both be implemented in similar applications. The modularity of fuel cells makes them quite flexible as the power needed can easily be attained by changing the number of modules.

Twenty years ago, mainly universities and research institutions but only a few companies conducted fuel cell research working on the fundamentals of fuel cells. Nowadays due to the commercial interest innumerable research groups and companies have fuel cell activities ranging from the investigation of catalysts (both improving existing catalyst systems as searching for new catalysts), the development of novel membranes for PEMFCs and DMFCs, to the development of other components for fuel cells. Optimisation of flow field structures, backing layers, and other components of the single cells have intensified.

Fuel cell systems are commercial products in many areas, such as stationary application and some small power devices (power for traffic signs). The imminent commercialisation of fuel cells in areas of high turnover, such as vehicle propulsion, battery replacement, and stationary power generation, has accelerated the research and development dynamics considerably. This positive development is counterbalanced by the negative aspect that the understanding of many processes – complex interactions in the system as well as elementary steps in the membrane conductivity or the reactions – in fuel cells is not sufficiently advanced.

There is no such thing as the ideal fuel cell for all applications. As discussed in Chapter 5 the best suited fuel cell depends on the requirements of the application. Not only the fuel cell itself but the entire system has to be under investigation when customising fuel cells for specific purposes. It may be that a certain type of fuel cell is superior for a certain application but when taking the hydrogen storage and/or the reforming into account this evaluation may change. In this respect, the operation of high-temperature fuel cells with hydrocarbons in an internal reforming configuration offers a simpler system design compared to the low-temperature fuel cells. For portable devices the low-temperature PEM and DMFC systems are the only fuel cell options.

The fuel flexibility and compatibility within the existing fuel infrastructure are requirements that can be met by most fuel cells. The overall efficiencies attained are higher than for conventional systems and it can be seen that fuel cells are entering the market as additions to conventional systems. In a couple of years time they may start to compete when capital costs can be reduced due to technological advances and increases in production volumes.

There are some commercial fuel cell systems on the market so far. The PAFC system marketed by ONSI is the one system in the 200 kW class which can be purchased. Companies such as H-Power Corp, Ballard and Plug Power also advertise their products. Fuel cells for lab demonstrations can be bought from different developers. A full list of all developers and their contact details can be found on the internet. The literature list should also be able to help the search for more information on this topic. The market introduction of fuel cells for other applications is imminent and the message is simple: fuel cells are coming our way.

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7 Literature

[1] F. D. Melle, *Journal of Power Sources* **1998**, *71*, 7.
[2] B. M. Barnett and W. P. Teagan, *Journal of Power Sources* **1992**, 15.
[3] D. Hart, *Journal of Power Sources* **2000**, *86*, 23.
[4] G. D. Callow, *Journal of Power Sources* **1999**, *80*, 16.
[5] A. Bauen and D. Hart, *Journal of Power Sources* **2000**, *86*, 482.
[6] *Platinum Metals Review* **1999**, *43*, 14.
[7] S. G. Chalk, J. F. Miller and F. W. Wagner, *Journal of Power Sources* **2000**, *86*, 40.
[8] A. U. Dufour, *Journal of Power Sources* **1998**, *71*, 19.
[9] U. Bossel, *The birth of the Fuel Cell*; European Fuel Cell Forum: Oberrohrdorf, **2000**.
[10] P. W. Atkins, *Physical Chemistry*; 5th ed.; Oxford University Press: Oxford, **1994**.

[11] L. J. M. J. Blomen and M. N. Mugerwa, *Fuel Cell Systems*; Plenum Press: New York, **1993**.
[12] J. Appleby and F. R. Foulkes, *Fuel Cell Handbook*, **1993**.
[13] F. Albisu, Proceedings of the European Seminar on Combined Production of Heat and Power (cogeneration), Madrid, Spain, **1989**; 10.
[14] B. N. Grgur, N. M. Markovic and P. N. Ross, *Electrochimica Acta* **1998**, *43*, 3631.
[15] B. N. Grgur, N. M. Markovic and P. N. Ross, *Journal of The Electrochemical Society* **1999**, *146*, 1613.
[16] L. J. Burcham and I. E. Wachs, *Catalysis Today* **1999**, *49*, 467.
[17] A. S. Lin, A. D. Kowalak and W. E. O'Grady, *Journal of Power Sources* **1996**, *58*, 67.
[18] L. Liu, C. Pu, R. Viswanathan, Q. Fan, R. Liu and E. S. Smotkin, *Electrochimica Acta* **1998**, *43*, 3657.
[19] R. W. McCabe and D. F. McCready, *J.Phys.Chem.* **1986**, *90*, 1428.
[20] R. P. H. Gasser, *An introduction to chemisorption and catalysis by metals*; 1st ed.; Oxford University Press: Oxford, **1985**.
[21] S. F. Baxter, V. S. Battaglia and R. E. White, *Journal of the Electrochemical Society* **1999**, *146*, 437.
[22] G. T. Burstein, C. J. Barnett, A. R. Kucernak and K. R. Williams, *Catalysis Today* **1997**, *38*, 425.
[23] G. B. Grad, A. F. Guillermet and J. R. Granada, *Zeitschrift fur Metallkunde* **1996**, *87*, 726.
[24] A. Hamnett, *Catalysis Today* **1997**, *38*, 445.
[25] J. Sobkowski, K. Franaszczuk and K. Dobrowolska, *Journal of Electroanalytical Chemistry* **1992**, *330*, 529.
[26] H. Matsui and A. Kunugi, *Journal of Electroanalytical Chemistry* **1990**, *292*, 103.
[27] X. H. Xia, T. Iwasita, F. Ge and W. Vielstich, *Electrochimica Acta* **1996**, *41*, 711.
[28] C. He, H. R. Kunz and J. M. Fenton, *Journal of the Electrochemical Society* **1997**, *144*, 970.
[29] M. Watanabe, S. Saegusa and P. Stonehart, *Journal of Electroanalytical Chemistry* **1989**, *271*, 213.
[30] R. Parsons and T. Vandernoot, *Journal of Electroanalytical Chemistry* **1988**, *257*, 9.
[31] S. Wasmus and A. Küver, *Journal of Electroanalytical Chemistry* **1999**, *461*, 14.
[32] M. P. Hogarth and G. A. Hards, *Platinum Metals Review* **1996**, *40*, 150.
[33] V. S. Bagotzky, Y. B. Vassiliev and O. A. Khazova, *J. Electroanal. Chem.* **1997**, *81*, 229.
[34] A. Hamnett in *Comprehensive Chemical Kinetics*; R. G. C. a. G. Hancock, Ed.; Elsevier:, **1999**; Vol. 37.
[35] M. Watanabe and S. Motoo, *J. Electroanal. Chem.* **1975**, *60*, 267.
[36] Y. Morimoto and E. B. Yeager, *Journal of Electroanalytical Chemistry* **1998**, *444*, 95.
[37] A. B. Anderson, S. Seong and E. Grantscharova, *J. Phys. Chem.* **1996**, *100*, 17535.
[38] A. B. Anderson, E. Grantscharova and S. Seong, *Journal of the Electrochemical Society* **1996**, *143*, 2075.
[39] K. Kinoshita, *Electrochemical Oxygen Technology*; John Wiley & Sons: New York, **1992**.
[40] A. Damjanovic, M. A. Genshaw and J. O. M. Bockris, *Journal of Chemical Physics* **1966**, *45*, 4057.
[41] H. S. Wroblowa, Y. C. Pan and G. Razumney, *Journal of Electroanalytical Chemistry* **1976**, *69*, 195.
[42] A. J. Appleby and M. Savy, *Journal of Electroanalytical Chemistry* **1978**, *92*, 15.
[43] R. W. Zurilla, R. K. Sen and E. Yeager, *Journal of the Electrochemical Society* **1978**, *125*, 1103.
[44] V. S. Bagotsky, M. R. Tarasevich and V. Y. Filinovskii, *Elektrochimiya* **1969**, *5*, 1218.
[45] K. Kinoshita, *Journal of the Electrochemical Society* **1990**, *137*, 845.
[46] M. L. Sattler and P. N. Ross, *Ultramicroscopy* **1986**, *20*, 21.
[47] L. J. Bregoli, *Electrochim. Acta* **1978**, *23*, 489.
[48] Y. Takasu, N. Ohashi, X. G. Zhang, Y. Murakami, H. Minagawa, S. Sato and K. Yahikozawa, *Electrochimica Acta* **1996**, *41*, 2595–2600.
[49] M. Watanabe, H. Sei and P. Stonehart, *J. Electroanal. Chem.* **1989**, *261*, 375.
[50] N. Giordano, E. Passalacqua, L. Pino, A. S. Arico, V. Antonucci, M. Vivaldi and K. Kinoshita, *Electrochimica Acta* **1991**, *36*, 1979.
[51] Y. Kiros, *Journal of the Electrochemical Society* **1996**, *143*, 2152.
[52] Y. F. Yang, Y. H. Zhou and C. S. Cha, *Electrochimica Acta* **1995**, *40*, 2579.
[53] M. Peuckert, T. Yoneda, R. A. Dalla Betta and M. Boudart, *Journal of the Electrochemical Society* **1986**, *133*, 944.
[54] R. S. Weber, M. Peuckert, R. A. Dallabetta and M. Boudart, *Journal of the Electrochemical Society* **1988**, *135*, 2535.
[55] M. Watanabe, S. Saegusa and P. Stonehart, *Chemistry Letters* **1988**, 1487.
[56] D. R. de Sena, E. R. Gonzalez and E. A. Ticianelli, *Electrochimica Acta* **1992**, *37*, 1855.
[57] S. J. Clouser, J. C. Huang and E. Yeager, *Journal of Applied Electrochemistry* **1993**, *23*, 597.
[58] T. Maoka, *Electrochimica Acta* **1988**, *33*, 371.
[59] T. Maoka, *Electrochimica Acta* **1988**, *33*, 379.
[60] P. S. D. Brito and C. A. C. Sequeira, *Journal of Power Sources* **1994**, *52*, 1.
[61] L. D. Burke, J. K. Casey, J. A. Morrissey and J. F. O'Sullivan, *Journal of Applied Electrochemistry* **1994**, *24*, 30.
[62] E. K. W. Lai, P. D. Beattie, F. P. Orfino, E. Simon and S. Holdcroft, *Electrochimica Acta* **1999**, *44*, 2559.
[63] S. Mukerjee and S. Srinivasan, *Journal of Electroanalytical Chemistry* **1993**, *357*, 201.
[64] S. Mukerjee and J. McBreen, *Journal of Electroanalytical Chemistry* **1998**, *448*, 163.
[65] S. Mukerjee, S. Srinivasan, M. P. Soriaga and J. McBreen, *Journal of Physical Chemistry* **1995**, *99*, 4577.
[66] L. Carrette, K. A. Friedrich and U. Stimming, *ChemPhysChem* **2000**, *1*, 162.

[67] L. Carrette, J. Collins, A. Dickinson and U. Stimming, *Bunsenmagazin der Deutschen Bunsengesellschaft für Physikalische Chemie* **2000**, 27.

[68] U. Stimming, W. Wiese and E. Riensche, *Elektrotechnik und Informationstechnik* **1997**, *114*, 564.

[69] Y. Kiros and S. Schwartz, *Journal of Power Sources* **2000**, *87*, 101.

[70] K. Kordesch, V. Hacker, J. Gsellmann, M. Cifrain, G. Faleschini, P. Enzinger, R. Fankhauser, M. Ortner, M. Muhr and R. R. Aronson, *Journal of Power Sources* **2000**, *86*, 162.

[71] K. Kordesch and G. Simader, *Fuel Cells and Their Applications*; 1 ed.; VCH Verlagsgesellschaft mbH: Weinheim, Germany, **1996**.

[72] K. Kordesch, J. Gsellmann, M. Cifrain, S. Voss, V. Hacker, R. R. Aronson, C. Fabjan, T. Hezje and J. Daniel-Ivad, *Journal of Power Sources* **1999**, *80*, 190.

[73] E. De Geeter, M. Mangan, S. Spaepen, W. Stinissen and G. Vennekens, *Journal of Power Sources* **1999**, *80*, 207.

[74] P. V. Wright, *Electrochimica Acta* **1998**, *43*, 1137.

[75] S. Gottesfeld and T. Zawodzinski in *Advances in Electrochemical Science and Engineering*; R. C. Alkire, H. Gerischer, D. M. Kolb and C. W. Tobias, Eds.; Wiley-VCH: Weinheim, New York, 1997; Vol. 5.

[76] G. G. Scherer, *Berichte der Bunsengesellschaft fur Physikalische Chemie* **1990**, *94*, 1008.

[77] H. L. Yeager and A. Steck, *Journal of the Electrochemical Society: Electrochemical Science and Technology* **1981**, *128*, 1880.

[78] M. Wakizoe, O. A. Velev and S. Srinivasan, *Electrochimica Acta* **1995**, *40*, 335.

[79] K. Broka and P. Ekdunge, *Journal of Applied Electrochemistry* **1997**, *27*, 117.

[80] B. Baradiea, C. Poinsignonac, J. Y. Sancheza, Y. Piffardb, G. Vittera, N. Bestaouib, D. Foscalloa, A. Denoyellea, D. Delabouglisea and M. Vaujanya, *Journal of Power Sources* **1998**, *74*, 8.

[81] K. M. Nouel and P. S. Fedkiw, *Electrochimica Acta* **1998**, *43*, 2381.

[82] F. N. Buchi, B. Gupta, O. Haas and G. G. Scherer, *Journal of the Electrochemical Society* **1995**, *142*, 3044.

[83] F. N. Buchi, B. Gupka, O. Haas and G. G. Scherer, *Electrochim. Acta* **1995**, *40*, 345.

[84] K. Yasuda, O. Uchimoto, Z. Ogumi and Z.-I. Takehara, 183rd Meeting of the Electrochemical Society, Symposium on Batteries and Fuel Cells for Stationary and Electric Vehicle Applications, Honolulu, Hawaii, US, 1993; 292.

[85] T. Lehtinen, G. Sundholm, S. Holmberg, F. Sundholm, P. Björnbom and M. Bursell, *Electrochimica Acta* **1998**, *43*, 1881.

[86] M. Cappadonia, J. W. Erning, S. M. Saberi Niaki and U. Stimming, *Solid State Ionics, Diffusion & Reactions* **1995**, *77*, 65.

[87] T. D. Gierke, G. E. Munn and F. C. Wilson, *J. Polym. Sci. Polym. Phys.* , *19*, 1687.

[88] M. S. Wilson, C. Zawodzinski and S. Gottesfeld, Second International Symposium on Proton Conducting Membrane Fuel Cells II, 1998; 424.

[89] M. Watanabe, H. Uchida, Y. Seki and M. Emori, *Journal of the Electrochemical Society* **1996**, *143*, 3847.

[90] M. Watanabe, Y. Satoh and C. Shimura, 183rd Meeting of the Electrochemical Society, Symposium on Batteries and Fuel Cells for Stationary and Electric Vehicle Applications, Honolulu, Hawaii, US, 1993; 302.

[91] O. Teschke, *Journal of the Electrochemical Society* **1983**, *131*, 1095.

[92] Z. Poltarzewski, P. Staiti, V. Alderucci, W. Wieczorek and N. Giordano, *Journal of the Electrochemical Society* **1992**, *139*, 761.

[93] S. J. Lee, S. Mukerjee, J. McBreen, Y. W. Rho, Y. T. Kho and T. H. Lee, *Electrochimica Acta* **1998**, *43*, 3693.

[94] S. Gottesfeld at http://education.lanl.gov/resourcesh2-gottesfeldeducation.html.

[95] M. Wilson, F. Garzon, K. Sickafus and S. Gottesfeld, *J. Electrochem. Soc.* **1993**, *140*, 2872.

[96] S. Gottesfeld and J. Pafford, *Journal of the Electrochemical Society* **1988**, *135*, 2651.

[97] K. Kolbrecka and J. Przyluski, *Electrochimica Acta* **1994**, *39*, 1591.

[98] H.-F. Oetjen, V. M. Schmidt, U. Stimming and F. Trila, *Journal of the Electrochemical Society* **1996**, *143*, 3838.

[99] J. Divisek, H.-F. Oetjen, V. Peinecke, V. M. Schmidt and U. Stimming, *Electrochimica Acta* **1998**, *43*, 3811.

[100] R. J. Bellows, E. Marucchi-Soos and R. P. Reynolds, *Electrochemical and Solid-State Letters* **1998**, *1*, 69.

[101] L. Carrette, K. A. Friedrich, M. Huber and U. Stimming, *Phys. Chem. Chem. Phys.* **2001**, *3*, 320.

[102] W. Chrzanowski and A. Wieckowski, *Langmuir* **1998**, *14*, 1967.

[103] H. A. Gasteiger, N. Markovic, P. N. J. Ross and E. J. Cairns, *J. Phys. Chem.* **1994**, *98*, 617.

[104] H. A. Gasteiger, N. Markovic, P. N. Ross and E. J. Cairns, *J. Phys. Chem.* **1994**, *98*, 617.

[105] H. A. Gasteiger, N. Markovic, P. N. J. Ross and E. J. Cairns, *Electrochim. Acta* **1994**, *39*, 1825.

[106] A.V. Petukhov, W. Akemann, K. A. Friedrich and U. Stimming, *Surf. Sci.* **1998**,*402 - 404, 182.*

[107] K. A. Friedrich, K.-G. Geyzers, U. Linke, U. Stimming and J. Stumper, *J. Electroanal. Chem.* **1996**, *402*, 123.

[108] G. Holleck, D. Pasquariello and S. Clauson, Second International Symposium on Proton Conducting Membrane Fuel Cells II, **1998**; 150.

[109] S. A. C. Barton, B. L. Murach, T. F. Fuller and A. C. West, *Journal of the Electrochemical Society* **1998**, *145*, 3783.

[110] S. R. Narayanan, T. I. Valdez and W. Chun, *Electrochemical and Solid State Letters* **2000**, *3*, 117.

[111] Y. Chen, K. Y. Chen and A. C. C. Tseung, *Journal of Electroanalytical Chemistry* **1999**, *471*, 151.

[112] K. L. Ley, R. Liu, C. Pu, Q. Fan, N. Leyarovska, C. Segre and E. S. Smotkin, *Journal of the Electrochemical Society* **1997**, *144*, 1543.

[113] L. Liu, R. Viswanathan, R. Liu and E. S. Smotkin, *Electrochemical and Solid State Letters* **1998**, *1*, 123.

[114] E. Reddington, A. Sapienza, B. Gurau, R. Viswanathan, S. Sarangapani, E. S. Smotkin and T. E. Mallouk, *Science* **1998**, *280*, 1735.

[115] N. A. Hampson, M. J. Willars and B. D. McNicol, *Journal of Power Sources* **1979**, *4*, 191.

[116] A. Hamnett and B. J. Kennedy, *Electrochimica Acta* **1988**, *33*, 1613.

[117] A. S. Arico, Z. Poltarzewski, H. Kim, A. Morana, N. Giordano and V. Antonucci, *Journal of Power Sources* **1995**, *55*, 159.

[118] B. D. McNicol, R. T. Short and A. G. Chapman, *J. Chem. Soc. Faraday I* **1976**, *72*, 2735.

[119] M. Götz and H. Wendt, *Electrochimica Acta* **1998**, *43*, 3637.

[120] S. C. Thomas, X. Ren and S. Gottesfeld, *Journal of the Electrochemical Society* **1999**, *146*, 4354.

[121] A. S. Arico, A. K. Shukla, K. M. El-Khatib, P. Creti and V. Antonucci, *Journal of Applied Electrochemistry* **1999**, *29*, 671.

[122] A. K. Shukla, P. A. Christensen, A. Hamnett and M. P. Hogarth, *Journal of Power Sources* **1995**, *55*, 87.

[123] W. Vielstich, A. Kuver, M. Krausa, A. C. Ferreira, K. Petrov and S. Srinivasan, 183rd Meeting of the Electrochemical Society, Symposium on Batteries and Fuel Cells for Stationary and Electric Vehicle Applications, Honolulu, Hawaii, US, 1993; 269.

[124] A. K. Shukla, P. A. Christensen, A. J. Dickinson and A. Hamnett, *Journal of Power Sources* **1998**, *76*, 54.

[125] A. K. Shukla, M. K. Ravikumar, M. Neergat and K. S. Gandhi, *Journal of Applied Electrochemistry* **1999**, *29*, 129.

[126] X. Ren, T. E. Springer and S. Gottesfeld, *Journal of the Electrochemical Society* **2000**, *147*, 92.

[127] A. Küver and K. Potje-Kamloth, *Electrochimica Acta* **1998**, *43*, 2527.

[128] A. Küver and W. Vielstich, *Journal of Power Sources* **1998**, *74*, 211-218.

[129] M. K. Ravikumar and A. K. Shukla, *Journal of the Electrochemical Society* **1996**, *143*, 2601.

[130] X. Ren, M. S. Wilson and S. Gottesfeld, *Journal of the Electrochemical Society* **1996**, *143*, L12.

[131] N. Alonso-Vante, H. Tributsch and O. Solorza-Feria, *Electrochimica Acta* **1995**, *40*, 567.

[132] O. Solorza-Feria, K. Ellmer, M. Giersig and N. Alonso-Vante, *Electrochimica Acta* **1994**, *39*, 1647.

[133] S. Dong and Q. Qiu, *Journal of Electroanalytical Chemistry* **1991**, *314*, 223.

[134] S. Gupta, D. Tryk, S. K. Zecevic, W. Aldred, D. Guo and R. F. Savinell, *Journal of Applied Electrochemistry* **1998**, *28*, 673.

[135] M. C. Williams, *Fuel Cell* **1996**.

[136] C. E. Trippel, J. L. Preston, Jr., J. Tricciola and R. Spiegel, *Fuel Cell* **1996**.

[137] J. M. Torrey, G. P. Merten, M. J. Binder, W. R. Taylor, F. H. Holcomb and M. S. Bowers, *Fuel Cell* **1996**.

[138] T. Brenscheidt, K. Janowitz, H. J. Salge, H. Wendt and F. Brammer, *International Journal of Hydrogen Energy* **1998**, *23*, 53.

[139] D. H. Archer, J. G. Wimer and M. C. Williams, *IECEC 97, Proceedings of the 32nd Intersociety Energy Conversion Engineering Conference* (Cat. IEEE, New York) **1997**.

[140] D. S. Chan and C. C. Wan, *Journal of Power Sources* **1994**, *50*, 163.

[141] M. Watanabe, K. Tsurumi, T. Mizukami, T. Nakamura and P. Stonehart, *Journal of the Electrochemical Society* **1994**, *141*, 2659.

[142] O. Savadogo and P. Beck, *Journal of the Electrochemical Society* **1996**, *143*, 3842.

[143] L. Qingfeng, X. Gang, H. A. Hjuler, R. W. Berg and N. J. Bjerrum, *Journal of the Electrochemical Society* **1994**, *141*, 3114.

[144] L. Qingfeng, X. Gang, H. A. Hjuler, R. W. Berg and N. J. Bjerrum, *Journal of the Electrochemical Society* **1995**, *142*, 3250.

[145] B. S. Baker and H. C. Maru, 191st Meeting of the Electrochemical Society, Fourth International Symposium on Carbonate Fuel Cell Technology, Montreal, Canada, 1997; 14.

[146] K.-I. Ota, 191st Meeting of the Electrochemical Society, Fourth International Symposium on Carbonate Fuel Cell Technology, Montreal, Canada, **1997**; 238.

[147] M. Kah, H. J. Slage and H. Wendt, 191st Meeting of the Electrochemical Society, Fourth International Symposium on Carbonate Fuel Cell Technology, Montreal, Canada, **1997**; 224.

[148] B. Rohland and U. Jantsch, 191st Meeting of the Electrochemical Society, Fourth International Symposium on Carbonate Fuel Cell Technology, Montreal, Canada, **1997**; 212.

[149] C. Yuh, R. Johnsen, M. Farooque and H. Maru, *Journal of Power Sources* **1995**, *56*, 1–10.

[150] C. Y. Yuh, C. M. Huang and M. Farooque, 191st Meeting of the Electrochemical Society, Fourth International Symposium on Carbonate Fuel Cell Technology, Montreal, Canada, **1997**; 66.

[151] Y. Fujita, T. Nischimura, H. Urushibata and A. Sasaki, 191st Meeting of the Electrochemical Society, Fourth International Symposium on Carbonate Fuel Cell Technology, Montreal, Canada, 1997; 191.

[152] R. Nowak, Fuel Cell Seminar, Palm Springs California, **1998**.

[153] A. C. Schoeler, T. D. Kaun, I. Bloom, M. Lanagan and M. Krumpelt, *Journal of the Electrochemical Society* **2000**, *147*, 916.

[154] S. Hamakawa, R. Shiozaki, T. Hayakawa, K. Suzuki, K. Murata, K. Takehira, M. Koizumi, J. Nakamura and T. Uchijima, *Journal of the Electrochemical Society* **2000**, *147*, 839.

[155] D. Reid, at http://www.dcht.com, DCH Technology Company, **2000**.

[156] M. Ihara, C. Yokoyama, A. Abudula, R. Kato, H. Komiyama and K. Yamada, *Journal of the Electrochemical Society* **1999**, *146*, 2481.

[157] S. Park, J. M. Vohs and R. J. Gorte, *Nature* **2000**, *404*, 265.

[158] S. Park, R. Craciun, J. M. Vohs and R. J. Gorte, *Journal of the Electrochemical Society* **1999**, *146*, 3603.

[159] U. Birnbaum, E. Riensche and U. Stimming, Proceedings of the 5th International Symposium on Solid Oxide Fuel Cells (SOFC-V), **1997**; 112.

[160] S. C. Singhal Proceedings of the 5th International Symposium on Solid Oxide Fuel Cells (SOFC-V), **1997**; 37.

[161] Y. Sasaki, Y. Esaki, M. Hattori, H. Miyamoto, T. Satake, F. Najo, T. Matsudaira and K. Takenobu, *Proceedings of the 5th International Symposium on Solid Oxide Fuel Cells (SOFC-V)*,**1997**; 61.

[162] T.-P. Chen, J. D. Wright and K. Krist, *Proceedings of the 5th International Symposium on Solid Oxide Fuel Cells (SOFC-V)*, **1997**; 69.

[163] H. Ringel, J. Schüle and D. Grunwald, *Proceedings of the 5th International Symposium on Solid Oxide Fuel Cells (SOFC-V)*, **1997**; 124.

[164] S. Kawasaki, K. Okumura, Y. Esaki, M. Hattori, Y. Sakaki, J. Fujita and S. Takeuchi, *Proceedings of the 5th International Symposium on Solid Oxide Fuel Cells (SOFC-V)*, **1997**; 171.

[165] T. Hibino, H. Tsunekawa, S. Tanimoto and M. Sano, *Journal of the Electrochemical Society* **2000**, *147*, 1338.

[166] R. Diethelm, J. Brun, T. Gamper, M. Keller, R. Kruschwitz and D. Lenel, *Proceedings of the 5th International Symposium on Solid Oxide Fuel Cells (SOFC-V)*, **1997**; 79.

[167] R. E. Smith, M. Prica and K. Kendall, **1997**, 645.

[168] H. P. Buchkremer, U. Diekmann, L. G. J. d. Haart, H. Kabs, U. Stimming and D. Stöver, *Proceedings of the 5th International Symposium on Solid Oxide Fuel Cells (SOFC-V)*, **1997**; 160.

[169] L. G. J. de Haart, K. Mayer, U. Slimming and I. C. Vinke, *Journal of Power Sources* **1998**, *71*, 1.

[170] Y. Shibuya and H. Nagamoto, *Proceedings of the 5th International Symposium on Solid Oxide Fuel Cells (SOFC-V)*, **1997**; 510.

[171] M. Juhl, S. Primdahl, C. Manon and M. Mogensen, *J. Power Sources* **1996**, *61*, 173.

[172] M. Lang, R. Henne, G. Schiller and N. Wagner, *Proceedings of the 5th International Symposium on Solid Oxide Fuel Cells (SOFC-V)*, **1997**; 461.

[173] R. Doshi, V. L. Richards and M. Krumpelt, *Proceedings of the 5th International Symposium on Solid Oxide Fuel Cells (SOFC-V)*, **1997**; 379.

[174] B. C. H. Steele, in *Ceramic oxygen ion conductors and their technological applications*; B. C. H. Steele, Ed.; The Institute of Materials:, **1996**; Vol. British Ceramic Proceedings.

[175] R. Doshi, V. L. Richards, J. D. Carter, X. Wang and M. Krumpelt, *Journal of The Electrochemical Society* **1999**, *146*, 1273.

[176] J. P. P. Huijsmans, F. P. F. van Berkel and G. M. Christie, *J. Power Sources* **1998**, 107.

[177] H. Nabielek, *Proceedings of the 5th International Symposium on Solid Oxide Fuel Cells (SOFC-V)*, **1997**; 26.

[178] W. Baukal and W. Kuhn, *Journal of Power Sources* **1967/77**, *1*, 91.

[179] H. P. Buchkremer, KFA SOFC-Industrieseminar, KFA-Jülich, **1995**; 166.

[180] A. Momma, Y. Kaga, K. Fujii, K. Hohjyo, M. Kanazawa and T. Okuo, *Proceedings of the 5th International Symposium on Solid Oxide Fuel Cells (SOFC-V)*, **1997**; 311.

[181] J. Will and L. J. Gauckler, *Proceedings of the 5th International Symposium on Solid Oxide Fuel Cells (SOFC-V)*, **1997**; 757.

[182] M. L. Cubiero and J. L. G. Fierro, *Journal of Catalysis* **1998**, *179*, 150.

[183] K. Kochloefl, L.H. Lunsford, J.B. Hansen, and J.H. Sinfelt in *Handbook of Heterogeneous Catalysis*, Volume 4 *Energy-Related Reactions* **(**Eds. G. Ertl, H. Knözinger, J. Weitkamp), Wiley-VCH, Weinheim **1997.**

[184] B. Emonts, J. B. Hansen, S. L. Jörgensen, B. Höhlein and R. Peters, *Journal of Power Sources* **1998**, *71*, 288.

[185] H. G. Dusterwald, B. Hohlein, H. Kraut, J. Meusinger, R. Peters and U. Stimming, *Chemical Engineering and Technology* **1997**, *20*, 617.

[186] L. Ma, C. Jiang, A. A. Adesina, D. L. Trimm and M. S. Wainwright, *The Chemical Engineering Journal* **1996**, *62*, 103.

[187] N. Edwards, S. R. Ellis, J. C. Frost, S. E. Golunski, A. N. J. v. Keulen, N. G. Lindewald and J. G. Reinkingh, *Journal of Power Sources* **1998**, *71*, 123.

[188] R. Buxbaum; REB Research & Consulting: information leaflet, **2000**.

[189] A. L. Dicks, *Journal of Power Sources* **1996**, *61*, 113.

[190] J. C. Cross *Portable Fuel Cells, Proceedings*, Lucerne, Switzerland, **1999**; 205.

[191] J. R. Rostrup-Nielsen *Catalytic Steam Reforming*; Springer-Verlag: Berlin, **1984**.

[192] J. Meusinger, E. Riensche and U. Stimming, *Journal of Power Sources* **1998**, *71*, 1.

[193] K. Aasberg-Petersen, C. S. Nielsen and S. L. g. Jörgensen, *Catalysis Today* **1998**, *46*, 193.

[194] M. v. Driel and M. Meijer, Fuel Cell Seminar, Palm Springs California, **1998**.

[195] E. A. Gilles, *Chemical Engineering Progress* **1980**, *76*, 88.

[196] K. Kendall, *Nature* **2000**, *404*, 233.

[197] V. Recupero, L. Pino, R. D. Leonardo, M. Lagana and G. Maggio, *Journal of Power Sources* **1998**, *71*, 208.

[198] Ä. Slagtern, H. M. swaan, U. Olsbye, I. M. Dahl and C. Mirodatos, *Catalysis Today* **1998**, *46*, 107.

[199] O. Deutschmann and L. D. Schmidt, *AIChE Journal* **1998**, *44*, 2465.

[200] J. M. Ogden, M. M. Steinbugler and T. G. Kreutz, *Journal of Power Sources* **1999**, *79*, 143.

[201] K. Ledjeff-Hey, T. Kalk, F. Mahlendorf, O. Niemzig and J. Roes, Portable Fuel Cells, Proceedings, Lucerne, Switzerland, **1999**; 193.

[202] L. Yang and D. P. Bloomfield, Fuel Cell Seminar, Palm Springs California, **1998**.

[203] K. Sekizawa, S.-i. Yano, K. Eguchi and H. Arai, *Applied Catalysis A: General* **1998**, *169*, 291.
[204] S. H. Oh and R. M. Sinkevitch, *Journal of Catalysis* **1993**, *142*, 254.
[205] A. Heinzel, R. Nolte, K. Ledjeff-Hey and M. Zedda, *Electrochimica Acta* **1998**, *43*, 3817.
[206] B. Nierhauve, *"Alternative Kraftstoffe,"* Aral Aktiengesellschaft, **1997**.
[207] A. B. Lovins and B. D. Williams, 10th Annual U.S. Hydrogen Meeting, National Hydrogen Association, Vienna, Virginia, **1999**.
[208] MAN *"Hydrogen project Munich airport,"* brochure, **2000**.
[209] Ch. Borroni-Bird, *J. Power Sources* **1996**, *61*, 33.
[210] Sandia National Laboratories at http://www.ca.sandia.gov/CRF/03_hydrogen/03_HRT.html
[211] National Renewable Energy Laboratory (NREL) at http://www.nrel.gov/nrel_research.html.
[212] TOSHIBA Corp. Brochure: Environmentally friendly cogeneration package - 200 kW Fuel Cell Power Plant.
[213] ONSI Corp, Brochure **2000**.
[214] C. Zawodzinski, M. S. Wilson and S. Gottesfeld, Fuel Cell Seminar, Palm Springs California, 1998.
[215] R. Hornung and G. Kappelt, *Journal of Power Sources* **1998**, *72*, 20.
[216] D. P. Davies, P. L. Adcock, M. Turpin and S. J. Rowen, *Journal of Power Sources* **2000**, *86*, 237.
[217] P. L. Hentall, J. B. Lakeman, G. O. Mepsted, P. L. Adcock and J. M. Moore, *Journal of Power Sources* **1999**, *80*, 235.
[218] L.R.E. Matejcek, *PhD thesis (German)*, Universität Duisburg, 1999.
[219] K. Scott, W. Taama and J. Cruickshank, *Journal of Power Sources* **1997**, *65*, 159.
[220] T. V. Nguyen, *Journal of the Electrochemical Society* **1996**, *143*, L103.
[221] O. J. Murphy, A. Cisar and E. Clarke, *Electrochimica Acta* **1998**, *43*, 3829.
[222] C. Zawodzinski, M. Wilson and S. Gottesfeld, Second International Symposium on Proton Conducting Membrane Fuel Cells II, 1998; 446.
[223] Y.-S. Han, Y.-H. Han, W.-S. Song, J.-M. Yun, S.-H. Lee and I.-Y. Seo, *Proceedings of the 5th International Symposium on Solid Oxide Fuel Cells (SOFC-V)*, **1997**; 575.
[224] S. A. Wallin, S. Wijeysekera, Y.-H. Chiao and M. J. Semer, Electrode materials and processes for energy conversion and storage IV, Montreal, Quebec (Canada), **1997**; 157.
[225] G. Schiller, R. Henne and M. Lang, *Proceedings of the 5th International Symposium on Solid Oxide Fuel Cells (SOFC-V)*, **1997**; 635.
[226] K. Joon, *Journal of Power Sources* **1998**, *71*, 12.
[227] M. C. Williams, 191st Meeting of the Electrochemical Society, Fourth International Symposium on Carbonate Fuel Cell Technology, Montreal, Canada, **1997**; 1.
[228] D. Chu and R. Jiang, *Journal of Power Sources* **1999**, *80*, 226.
[229] D. Picot, R. Metkemeijer, J. J. Bezian and L. Rouveyre, *Journal of Power Sources* **1998**, *75*, 251.
[230] A. Dicks and A. Siddle, *Journal of Power Sources* **2000**, *86*, 316.
[231] P. Hoffmann, *the Hydrogen and Fuel Cell Letter* **2000**, *XV*, 1.
[232] Hoffmann, *Hydrogen and Fuel Cell Letter* **1998**, *XIII*.
[233] H. Wendt and M. Götz, *Chemie in unserer Zeit* **1997**, *31*, 301.
[234] D. R. Glenn, *J. Power Sources* **1996**, *61*, 79.
[235] P. H. Eichenberger, *J. Power Sources* **1998**, *71*, 95.
[236] P. J. Kortbeek, P. C. v. d. Laag, L. A. H. Machielse, G. P. M. d. Koning, R. G. Fellows and A. L. Dicks, 191st Meeting of the Electrochemical Society, Fourth International Symposium on Carbonate Fuel Cell Technology, Montreal, Canada, **1997**; p 203-211.
[237] S. Cavallaro and S. Freni, *Journal of Power Sources* **1998**, *76*, 190.
[238] H.-E. Vollmar, C.-U. Maier, C. Nölscher, T. Merklein and M. Poppinger, *Journal of Power Sources* **2000**, *86*, 90.
[239] H. J. Beie, L. Blum, W. Drenckhahn, H. Greiner, B. Rudolf and H. Schichl, *Proceedings of the 5th International Symposium on Solid Oxide Fuel Cells (SOFC-V)*, **1997**; 51.
[240] J. Sukkel, *"Experience with a 100 kW SOFC-plant and future plans,"* report by Nuon, The Netherlands, **1998**.
[241] Deutscher Wasserstoff Verband article in: *Wasserstof-Spiegel*, **2000**.
[242] Global Thermoelectric at http://www.globalte.com/fuelcells.htm.
[243] V. A. Paganin, C. L. F. Oliviera, E. A. Ticianelli, T. E. Springer and E. R. Gonzalez, *Electrochimica Acta* **1998**, *43*, 3761.
[244] T. Okada, G. Xie and M. Meeg, *Electrochimica Acta* **1998**, *43*, 2141.
[245] D. R. de Sena, E. A. Ticianelli and E. R. Gonzalez, *Electrochimica Acta* **1998**, *43*, 3755.
[246] K. R. Williams and G. T. Burstein, *Catalysis Today* **1997**, *38*, 401.
[247] P. Argyropoulos, K. Scott and W. M. Taama, *Journal of Power Sources* **1999**, *79*, 169.
[248] P. Argyropoulos, K. Scott and W. M. Taama, *Journal of Power Sources* **1999**, *79*, 184.
[249] A. S. Arico, P. Creti, H. Kim, R. Mantegna, N. Giordano and V. Antonucci, *J. Electrochem.Soc.* **1996**, *143*, 3950.
[250] A. S. Arico, P. Creti, P. L. Antonucci, J. Cho, H. Kim and V. Antonucci, *Electrochimica Acta* **1998**, *43*, 3719.
[251] J. Ding, P. S. Patel, M. Farooque and M. Maru, 191st Meeting of the Electrochemical Society, Fourth International Symposium on Carbonate Fuel Cell Technology, Montreal, Canada, **1997**; 127.
[252] T. Matsuyama, A. Matsunaga and T. Ogawa, 191st Meeting of the Electrochemical Society, Fourth International Symposium on Carbonate Fuel Cell Technology, Montreal, Canada, **1997**; 167.
[253] T. Kivisaari, 191st Meeting of the Electrochemical Society, Fourth International Symposium on Carbonate Fuel Cell Technology, Montreal, Canada, **1997**; 179.
[254] P. Silberg and E. Handschin, Fifth International Symposium on Solid Oxide Fuel Cells, Aachen, Germany, **1997**; 1368.

[255] S. Sunde and P. V. Hendriksen, Fifth International Symposium on Solid Oxide Fuel Cells, Aachen, Germany, **1997**; 1329.

[256] P. V. Hendriksen, Fifth International Symposium on Solid Oxide Fuel Cells, Aachen, Germany, **1997**; 1319.

[257] W. He, *Fuel Processing Technology* **1997**, *53*, 99.

[258] J. C. Amphlett, R. F. Mann, B. A. Peppley, P. R. Roberge, A. Rodrigues and J. P. Salvador, *Journal of Power Sources* **1998**, *71*, 179.

[259] E. S. Matveeva, V. A. Shepelin and E. V. Kasatkin, *Soviet Electrochemistry* **1981**, *17*, 506.

[260] B. A. Peppley, J. C. Amphlett, L. M. Kearns and R. F. Mann, *Applied catalysis A: General* **1999**, *179*, 31.

[261] DaimlerChryler at *http://www.chrysler.com*
Toyota at *http://www.toyota.com*
General Motors at *http://www.gm.com/environment/products/technologies.html* .

[262] K. Kendall, I. Killbride, M. Palin and R. Copcutt, *European FC News* **1997**, *3*, 2.

[263] U. Bossel Commercializing Fuel Cell Vehicles, Chicago, 1996.

[264] Delphi at *http://www.delphiauto.com/* .

[265] Portable Fuel Cells, Lucerne, Switzerland, **1999**.

[266] C. K. Dyer in *Scientific American*, **1999**.

[267] T. I. Valdez, S. R. Narayanan, H. Frank and W. Chun, *IEEE* **1997**, 239.

[268] S. Abens, *International Power Generation* **1981**, *4*, 10.

[269] T. Ogata, M. Ishizawa, K. Kimata and Y. Kuwata, *NTT Research and Development, Information Newsletter* **1997**, *46*, 327.

[270] K. Scott, *IEE Colloquium on Compact Power Sources* **1996**, *107*.

[271] A. Watanabe, H. Mukai, N. Nishizawa, T. Itoh and Y. Nomura, *Sanyo Technical Review* **1994**, *26, 18*.