Fuel Cell Types and Their Electrochemistry

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Glossary

AFC	Alkaline fuel cell
EC	Electrocatalysis
FC	Fuel cell
GDE	Gas diffusion electrode
GDL	Gas diffusion layer
HOR	Hydrogen oxidation reaction
HT-PEFC	High temperature polymer electrolyte fuel cell
MCFC	Molten carbonate fuel cell
ORR	Oxygen reduction reaction
PAFC	Phosphoric acid fuel cell
PEFC	Polymer electrolyte fuel cell
SOFC	Solid oxide fuel cell

Definition of the Subject

Fuel cells are efficient energy converters, based on electrochemical principles. They convert the chemical energy (heating value) of a fuel directly into electricity, circumventing the various steps of thermal conversion and electricity generation. Fuel cells can be designed and constructed on the basis of a multitude of material combinations for electrolyte and electrodes, opening the choice of different fuels. The electrocatalytic reactions of fuel and oxygen are major challenges to obtain high conversion efficiency. The electrochemical basics of different fuel cell types considered today for technical applications are described in this contribution.

Introduction

Fuel cell technologies have seen a revival in recent years, due to several reasons. Global warming and local air pollution caused by various energy utilization processes have created a multitude of environmental concerns, promoting the development of novel technologies with high conversion efficiencies and low emissions, possibly zero emission, with respect to green house gases and other pollutants [1, 2]. Peak oil is another reason for the renewed interest in fuel cell technologies, in particular for automotive applications [3, 4]. Although this fact is discussed in a highly controversial manner, limitation in crude oil supply is obvious in the long-term perspective. This particular aspect of fossil fuel resources is strongly interlinked to the future perspective of the "oil price" and, hence, its economic competitiveness to other fuels, e.g., fuels from renewable sources. In this context, the installation of new supply infrastructures for alternative fuels, e.g., H_2, is an important additional economical and political factor. Dedicated analysis has clearly shown that energy conversion in fuel cells has to be based on fuels, in particular hydrogen, derived from renewable sources [5]. Further, the geographical distribution of oil reserves causes concerns about the supply security in industrial centers around the world.

Overall, there exist several reasons to ask for novel efficient conversion technologies for

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mobility (electromobility) and combined heat and power systems (CHP) with independence on fossil fuels, in particular crude oil. Another area of interest in fuel cell technology is portable electric and electronic applications, where the argument of potentially higher energy density as compared to today's available battery technologies, hence, longer time of operation, is of prime interest [6].

Electricity generation via fuel cells is an idea, based on fundamental research carried out by Christian Friedrich Schönbein at the University of Basel in the early nineteenth century. Schönbein's basic investigations of the respective reaction of H_2 gas (oxidation) and O_2 gas (reduction) dissolved in the electrolyte at an electrode/electrolyte interface, representing the fundamental fuel cell reactions, led William Robert Grove to the design and construction of the first operating fuel cell. He utilized H_2 as fuel and O_2 as oxidant at platinum metal electrodes in two separated closed compartments, filled with the respective reactant (hydrogen electrode, oxygen electrode), and joined by sulfuric acid as common electrolyte [7].

As will be shown in this chapter, the basic electrochemistry of a fuel cell, an electrochemical gas battery, is determined by the choice of the electrolyte and the two different electrodes immersed therein. In the course of time since this fundamental work of Schönbein and Grove, many combinations of electrolytes and electrode materials have been tested and fuel cell types derived upon there. This development has also been driven in the past by the choice of available fuel and possible application in view, in particular by space and military applications.

This introductory chapter will give an overview on the basic electrochemistry of some fuel cell types, developed today for dedicated technological applications. The respective electrochemistry will depend on the materials composition of the fuel cell, in particular, on the nature of the electrolyte and the temperature of operation. This further determines the choice of fuel, due to the strong influence of temperature on the mechanism of the respective electrocatalytic processes.

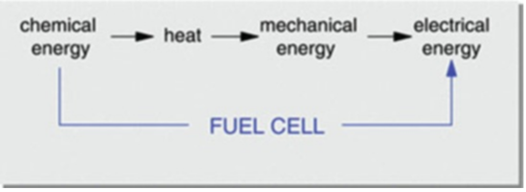
Engineering issues of fuel cell stack and systems design will be dealt with in the following chapters. Hence, issues of, e.g., coflow or counterflow within one cell, stoichiometry and utilization of fuel and oxidant, temperature and current distribution in a fuel cell of technical scale, and, certainly, issues of stacking cells into a bipolar arrangement will not be discussed here.

What Is a Fuel Cell?

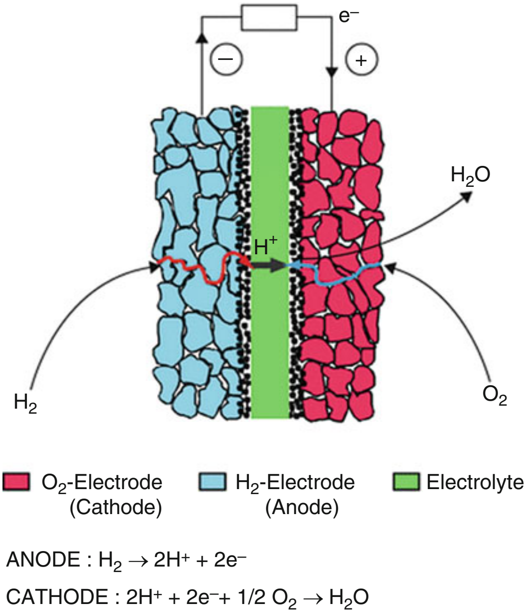
A fuel cell is an electrochemical device, converting the chemical energy (Gibbs free energy) stored in a gaseous or liquid fuel, e.g., hydrogen, methane, methanol, ethanol, others, directly into *work of electrical energy* (*direct current electricity*) at constant temperature (Fig. 1). This type of energy conversion process is different from the classical thermomechanical energy conversion process and is not limited by the Carnot principle (see below).

In short, in a fuel cell, the fuel is oxidized at an electrochemical interface (electrode called anode), accepting electrons and donating these electrons at a second electrochemical interface (electrode called cathode, separated from the anode) to an oxidant, e.g., oxygen, which is reduced by accepting these electrons. Both electrochemical interfaces have to belong to a common electrochemical cell and are joined in the cell by a common medium, an ion-conducting electrolyte. Both electrodes have to be connected electronically by an external circuit, containing the electrical device to be operated, in which the electrons, due to the potential difference created by the two electrode reactions, travel from the anode to the cathode delivering electrical work (Fig. 2). Fuel and oxidant are supplied in gas channels of the cell housing (bipolar plate in stacked cells) on the backside of the porous electrodes (not displayed in Fig. 2) Both gases have to be transported through the porous gas diffusion layers (GDLs) with pores typically in the micrometer range (blue and red bodies in Fig. 2) to the electroactive catalyst layers (ECLs, black dots in Fig. 2) at the interface to the electrolyte. Colloquially, GDL and ECL together are called gas diffusion electrode (GDE).

The fuel cell and its electrochemically active components, i.e., electrodes, electrolyte, etc., as well as its (electrochemically inert) structure



Fuel Cell Types and Their Electrochemistry, Fig. 1 Scheme of direct energy conversion in an electrochemical cell as compared to "conventional" thermal conversion



Fuel Cell Types and Their Electrochemistry, Fig. 2 Simplified fuel cell scheme with an acidic aqueous electrolyte, e.g., the polymer electrolyte fuel cell (PEFC). Fuel: H_2, oxidant: O_2. Only porous gas diffusion electrodes and electrolyte are shown, cell housing is not shown [8]

materials, i.e., current collectors, cell housing, etc., should be as invariant as possible, i.e., they should not be consumed and, ideally, not age (corrode) over the time of operation. Hence, as an electrochemical reactor, they provide the electrochemically active interfaces (or interphases, see below) and the necessary pathways for mass transport for educts and products to and from these active interfaces through porous media (active electrode layers, gas diffusion layers, internally corrugated cell housing (flow fields) in bipolar plates) with open porosity at different scales. At the same time, it is a prerequisite that these materials are as conductive as possible because they are responsible for the collection and transmission of the electric current generated at the two interfaces. Hence, ohmic voltage losses in these materials should be as low as possible.

The electrochemistry of the two electrode reactions is exemplified for the simplest and predominant case by the "cold" electrochemical combustion of H_2 with O_2 (pure O_2 or from ambient air) to H_2O (Fig. 2). The overall reaction is split into two partial reactions, occurring at the two different electrodes of the cell:

$$\begin{array}{l}\textbf{Anodic reaction}: \\ \mathbf{H_2 = 2H + 2e^-} \\ \qquad \text{(hydrogen oxidation reaction, HOR)}\end{array}$$

$$\begin{array}{l}\textbf{Cathodic reaction}: \\ \mathbf{1/2O_2 + 2H^+ + 2e^- = H_2O} \\ \qquad \text{(oxygen reduction reaction, ORR)}\end{array}$$

$$\begin{array}{l}\textbf{Overall reaction}: \\ \mathbf{H_2 + 1/2O_2 = H_2O}\end{array}$$

The reaction product(s) of the individual electrode reactions are constituents of the (aqueous) electrolyte (H^+ in the example of an acidic electrolyte, as displayed in the scheme of Fig. 2), which avoids polarization losses in the electrolyte.

Each of the two electrode reactions creates a characteristic potential difference across the interface solid electrode/electrolyte, which is different for the two reactions according to the different reactants. The overall cell voltage between the two electrodes, which are joined by the same electrolyte, allows the electrons generated at the anode (HOR) and consumed at the cathode (ORR) to create work in the external circuit. Hence, chemical energy released by the individual electrode reactions at the locally separated electrodes is directly transferred into electrical energy. This pathway is different from the combustion step in the "classical" thermomechanical power generation, where the oxidation of fuel and reduction of oxidant occur in the same volume element, thereby generating heat only.

Generally, the available cell voltage of electrochemical cells depends on the thermodynamics of the two electrode reactions in the prevailing electrolyte, hence the difference in the electrode potentials, and is confined, according to the series of electrochemical potentials, to a few volts [9]. According to the individual electrode potentials of the H_2/H^+ reaction (by IUPAC standard zero volt in the series of electrochemical potentials, acidic electrolyte, standard conditions of 1 atm and 25 °C or 298 K) and the O_2/H_2O reaction (1.23 V, respectively), a cell with H_2 and O_2 as reactants should yield an ideal cell voltage of 1.23 V at these standard conditions. In practice, a lower value in the range of 1 V is observed, due to different implications (side reactions, depolarization of electrodes due to crossover of gases through the electrolyte, etc.).

The free energy ΔG (Gibbs energy at constant pressure) of the fuel cell reaction is related to the cell voltage under open circuit conditions (open circuit voltage, OCV) E^0 and standard conditions according to

$$E^0 = -\Delta G/nF$$

n being the number of electrons transferred in the respective reaction (equal to 2 for the reaction $H_2 + ½O_2 = H_2O$) and F the Faraday constant equal to 96,487 C/mol (electric charge per mol of electrons).

Further, ΔG can be expressed as the difference of the free enthalpy ΔH of the reaction (thermal cell voltage E^0_{H} equivalent to 1.48 V for the H_2/O_2 reaction under standard state conditions) and the term $T\Delta S$, (T absolute temperature) expressing entropy losses (or gains) ΔS in the reaction:

$$\mathbf{\Delta G = \Delta H - T\Delta S}$$

Hence, the voltage (thermal) efficiency of a reaction under equilibrium conditions can be written as:

$$\epsilon_{\mathrm{th}} = \frac{\Delta G}{\Delta H} = 1 - \frac{T\Delta S}{\Delta H}$$

The voltage (thermal) efficiency for the electrochemical conversion of the three different fuels H_2, CH_4, and CO reacting with air (oxygen) in dependence of reaction temperature is displayed in Fig. 3. In comparison, also the maximal efficiency $\eta = (T_1 - T_2)/T_1$ for a Carnot process at the respective higher temperature T_1 and the lower temperature T_2 equal to 0 C is included. The different temperature dependence of the three conversion reactions is due to the respective entropy changes, e.g., $\Delta S = 0$ for the reaction $CH_4 + 2O_2 = CO_2 + 2H_2O$ and $\Delta S \neq 0$ for the reactions $2H_2 + O_2 = 2H_2O$ and $2CO + O_2 = 2CO_2$.

Based on thermodynamic arguments only, electrochemical energy conversion offers higher efficiencies within a certain temperature window, depending on the respective reaction.

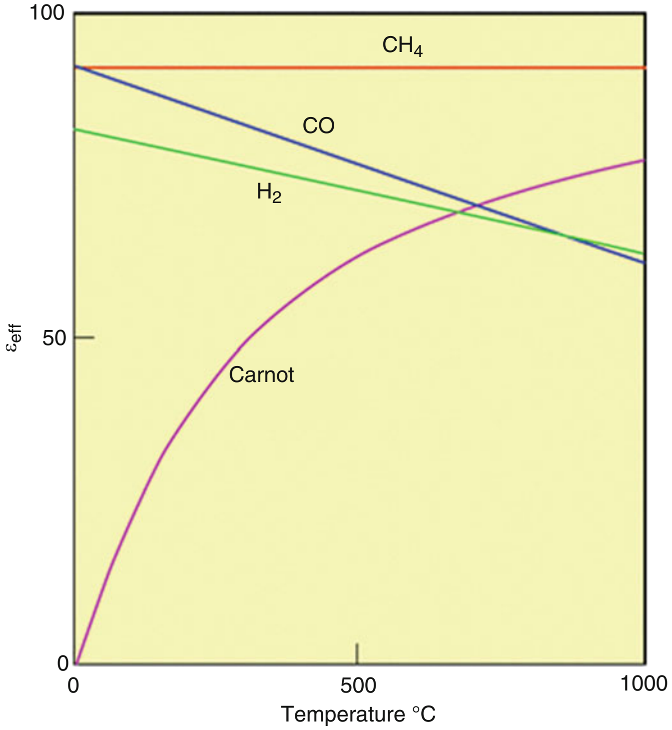
Introducing Nernst's law for the equilibrium case, the situation when no current (and hence power) is delivered by the cell, the equilibrium cell voltage under nonstandard conditions for a H_2/O_2 cell in dependence of the respective reactant/product concentration (partial pressures) can be expressed as:

$$\begin{aligned} E^{\mathrm{eq}} &= -\frac{\Delta G}{n_{\mathrm{t}}F} = E^{\mathrm{eq,\,c}} - E^{\mathrm{eq,\,a}} \\ &= E^0 + \frac{RT}{2F}\ln\left(\frac{[H_2][O_2]^{1/2}}{[H_2O]}\right) \end{aligned}$$

E^{eq} = equilibrium cell potential, $E^{\mathrm{eq,c}}$ = equilibrium potential cathode, $E^{\mathrm{eq,a}}$ equilibrium potential anode, R gas constant, T absolute temperature, E^0 = equilibrium potential under standard state.

E^{eq} is also called "theoretical" open circuit cell voltage, OCV, in dependence of temperature and reactant, respectively product concentrations. Practical OCVs may observed to be lower, due to losses (mixed potentials due to side reactions or gas crossover, see practical OCV of H_2/O_2 fuel cell) already occurring at zero current flow.

Under current flow, the kinetics of the electrode reactions comes into effect. The Butler-Volmer equation describes the dependency of the current passing through the electrode interface (current density per unit geometric area) on a small voltage excursion (called overvoltage η) from the respective equilibrium potential E^{eq}.



Fuel Cell Types and Their Electrochemistry, Fig. 3 Voltage (thermal) efficiency ε_{th} for the electrochemical reaction of H_2, CO, and CH_4 as fuel with oxygen from air under equilibrium versus temperature (°C). In comparison, Carnot efficiency of a thermal process as function of the respective higher temperature in °C and with 0 °C as lower temperature is displayed

$$i = i_0\left[\exp(\alpha nF\eta/RT) - \exp\left((1-\alpha)nF\eta/RT\right)\right]$$

i = current density at overvoltage η, η = overvoltage (excursion from the equilibrium potential), i_0 = exchange current density (at $\eta = 0$), α = symmetry factor, representing the fraction of overvoltage assisting the reaction, n = number of electrons exchanged, F = Faraday constant, R = gas constant, T = absolute temperature.

The exponential dependency points out that small potential excursions cause a larger change in current, while at larger potential excursions, the current follows a linear behavior. This can be described by the Tafel law, which usually is applied when current densities of technical interest, e.g., several 100 mA per cm^2 geometric surface area in a fuel cell, are passing through the cell.

$$\eta = (RT/\alpha nF)\ln i/i_0$$

For the HOR, exhibiting an exchange current density in the range of $i_0 = 10^{-3}$ A/cm^2 with platinum as electrode material [9], only a small overvoltage arises even by drawing a current density of technical interest, e.g., 1 A/cm^2, due to the fact that the H_2 molecule is easily split into two adsorbed H atoms (Tafel reaction), followed by the transfer of one electron per H atom (Volmer reaction) to the electrode generating two hydrated H^+. Alternatively, one electron is transferred to an adsorbed H_2 molecule, followed by a split into a hydrated H^+ and an adsorbed H atom. In a consecutive step, the second H atom is oxidized (Heyrovsky reaction).

In contrast, the exchange current density of the ORR at a platinum electrode is in the range of $i_0 = 10^{-8}$ A/cm^2. Assuming *direct* reduction of the oxygen molecule, the ORR requires four electrons in total, including the four H^+ generated in the HOR at the counterelectrode (see above). As a consequence, ORR generates a major overvoltage and, hence a major contribution to the overall loss.

In addition to the overvoltage losses due to electrode kinetics, one has to take into account the voltage loss in the ion-conducting electrolyte, due to the finite electrolyte conductivity, and (minimized) losses due to the electric resistance of electrode and cell materials, including contact resistances.

This relationship between cell voltage and current density is schematically displayed in Fig. 4. The various voltage losses are deducted from the equilibrium cell voltage (zero current), yielding the available cell voltage E^* at the respective current density i^*. The difference between E_H^0 and E^* is expressed as (waste) heat. In terms of voltage efficiency, this (heat) loss should be as low as possible; hence, E^* should be as high as possible. On the other side, the current density to be drawn has to be as high as possible to utilize power output values (specific power W/kg or power density W/L) of technical interest.

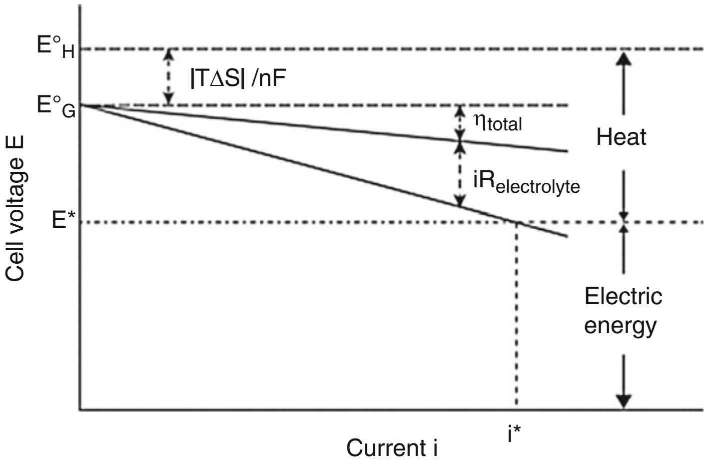
Further, Fig. 4 points to another advantage of (electrochemical) fuel cell technology: Designing a fuel cell to the maximum or rated power for a certain application (power = cell voltage E times current i), one easily realizes that the voltage efficiency ε_{eff} increases at lower power (lower current but higher voltage). This fact is particularly important for applications where maximum power (full load) is only required at certain parts of the duty cycle, while in other parts, only part load is necessary. This case is, e.g., exhibited in automotive applications of fuel cell technology.

Generally, the available cell voltage of electrochemical cells depends on the thermodynamics of the two electrode reactions in the prevailing electrolyte, hence the difference in the electrode potentials, and is confined, according to the Electrochemical Series of Standard Potentials, to a few volts. Cells with an aqueous electrolyte exhibit a limitation given by the stability window of water, namely 1.23 V at standard conditions. As stated above, the H_2/O_2 fuel cell allows practical open circuit voltages of around 1.0 V. At cell voltages above 1.23 V, typically around 1.5 V, decomposition of water into H_2 and O_2 occurs.

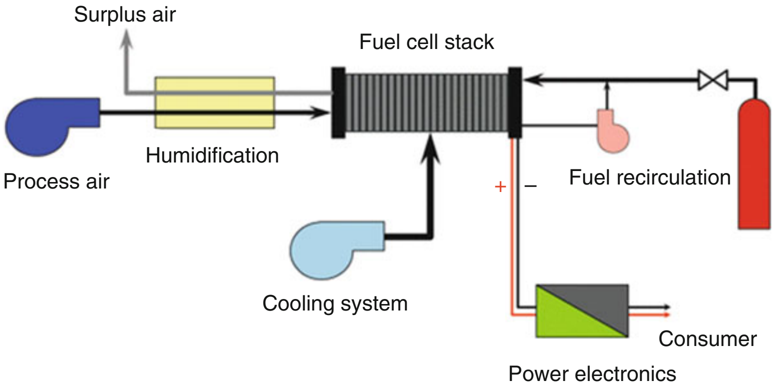
Hence, to accumulate the necessary voltage for technical applications, e.g., 200–400 V, for an electrical power train in a car, cells must be connected in series. Dedicated bipolar arrangements of cells have been designed and put into operation for serial connection, taking into consideration also the necessary parallel mass flow of fuel and oxidant from a manifold into each individual cell and the respective removal of the product. Such an arrangement of cells is called a fuel cell stack, combining the electrical serial connection of individual cells with a parallel connection for mass flow.

In contrast to batteries, fuel cells are open systems, which convert the chemical energy available in a fuel stored outside the fuel cell, the electrochemical converter. As a consequence, fuel cells need a fuel tank, also a tank for the oxidant, if the oxidant is pure oxygen and not ambient air, and auxiliaries (for temperature, pressure, etc., control) to be operated (Fig. 5).

Mass flow into (reactants) and out of the cell (products) must be allowed and controlled, as well as cooling to remove the waste heat. At a voltage



Fuel Cell Types and Their Electrochemistry, Fig. 4 Cell voltage E versus current i of a fuel cell, with E_H^0 = thermal cell voltage, E_G^0 = ideal cell voltage based on ΔG, η = sum of overvoltage at anode and cathode, $R_{Electrolyte}$ = electrolyte resistance



Fuel Cell Types and Their Electrochemistry, Fig. 5 Simplified scheme of a fuel cell system (Adapted from L. Gubler, Paul Scherrer Institut)

efficiency of 50%, a cell producing 1 kW electric power also generates 1 kW of heat, which has to be removed efficiently not to cause thermal runaway and, hence, degradation of the cell and its components. In summary, this is called a fuel cell system. Engineering issues of mass and heat transfer, current distribution across the active area of a cell, and voltage distribution along the stack, etc., are governing the design of a fuel cell system.

Fuel cells can be operated continuously, as long as they are supplied with fuel and oxidant. Hence, they are not limited by electrical charge-discharge cycles, as batteries are. This fact can be of utmost importance for certain applications, e.g., with respect to refueling time in mobile applications. For mobile or portable applications, the availability of a fuel infrastructure adds another aspect of consideration.

In terms of achievable specific energy (W/kg) and volumetric energy density (W/L), air-fed fuel cells have the advantage that one reaction partner, namely, oxygen, is derived from air, and consequently does not add to the weight and volume of the device. However, ambient air must be processed (cleaned, humidified, etc.), which has to be taken into account. This advantage is also expressed in the concept of metal air batteries, e.g., the Zn/Air or Al/Air battery, which on the anode (metal) consists as half a battery (closed mass flow) and on the cathode as half a fuel cell (open mass flow).

Next to the multitude of material combinations allowing various fuel cell types to be designed and built, the variety of mobile (transport), stationary, and portable applications provokes a multitude of different cell, stack, and systems designs, guided by the implications of the different fuel cell technologies (see below).

The Role of the Electrolyte

Generally speaking, the ion conduction in the electrolyte contributes to the losses (ohmic losses, see Fig. 3) in the cell voltage. Hence, one of the major tasks in fuel cell development is the reduction of these losses in the ionic circuit part, because the work available in the external electronic circuit should be as high as possible.

The role of the "electrolyte" in a fuel cell is a multiple one:

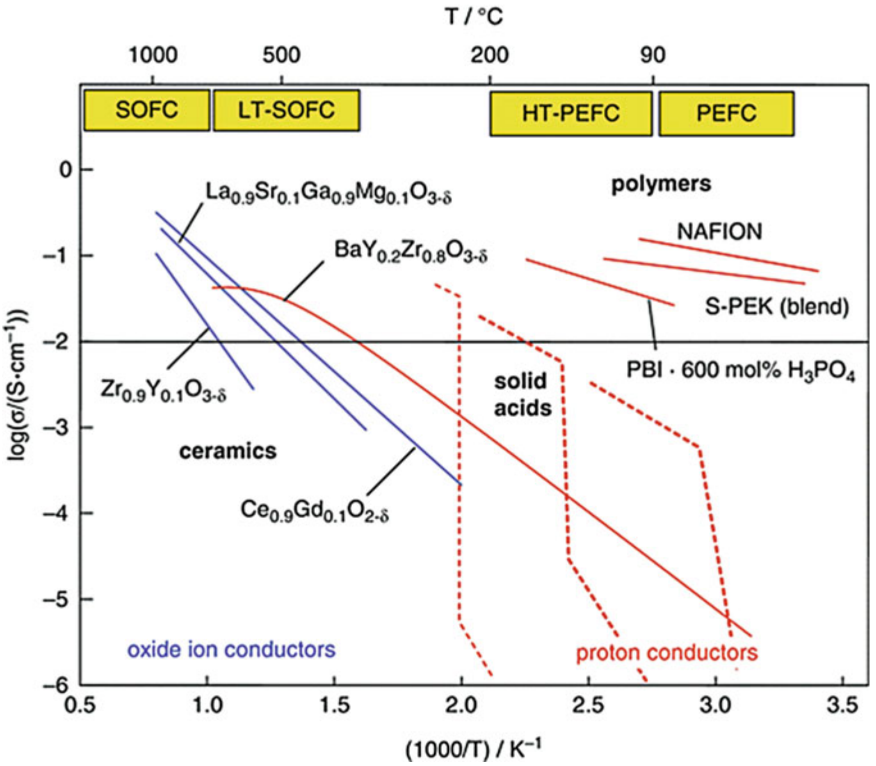
1. Transport the charge in ionic form from one interface to the other within the cell. To minimize losses in the ionic circuit, the ion conduction should be carried by an ion, which is produced at one electrode and consumed at the other to avoid losses caused by concentration gradients [10]. This majority ion should carry as much charge as possible through the electrolyte, hence its transport number (Hittorf number) should be as high as possible, ideally one. For high power applications with an aqueous electrolyte, the concentration of this respective anion or cation must be high and exclusively responsible for conduction. Typically, a specific ionic conductivity in the range of 100 mS/cm is required, which at a current density of 1 A/cm^2 and an electrolyte gap of 100 μm would yield an ohmic voltage loss

in the range of 100 mV. As seen in Fig. 6, the conductivities of various electrolytes are strongly temperature dependent and cover a wide temperature range, depending on the ion-conducting species in its respective environment (material). Again, electrolytes are of interest, which offer the opportunity that the ionic species is participating in the fuel cell reaction.

2. Act as separator to (1) avoid crossover and, as a consequence, “hot” combustion of the fuel and the oxidant at the respective counterelectrode, and (2) to avoid touching of the electrodes by short circuiting the electronic pathway. Thereby, the electrolyte/separator gap should be as narrow as possible to lower the ohmic contribution to the overall voltage loss. In the case of a liquid electrolyte, it can be absorbed into an inert matrix, providing porosity high enough for an ionic conduction path with low tortuosity for the ion and at the same time a high enough bubble pressure to suppress gas crossover. An ideal concept is the one of a solid electrolyte, which fulfills the dual electrolyte and separator function at the same time, providing a transfer number of one for the current-carrying ionic species, as in the case of solid polymer electrolytes (ion exchange membranes), thereby excluding a contribution of electronic conduction.

One has to emphasize that the electrolyte has to sustain the potential window of the respective fuel cell reaction, given by the Gibbs free energy, at least over the device lifetime, specified for a certain application.

In aqueous acidic electrolytes, the ionic conduction is provided by an H^+ ion, respectively, $H(H_2O)_n^+$. As mentioned above, H^+ is created by the anodic oxidation of H_2 as a fuel, and the conducting species is transported to the cathode, where it is consumed in the direct (ideally four



Fuel Cell Types and Their Electrochemistry, Fig. 6 Specific conductivity versus temperature of different electrolytes interesting for fuel cell applications (Adapted from K.D. Kreuer) electrons) cathodic reduction of molecular oxygen. Hereby, water as the reaction product appears at the cathode side of the cell.

In alkaline solution, the ionic conduction is provided by OH^- ions, created by the ORR at the cathode. Principally, OH^- ions are carriers for the O^{2-} ions, produced as intermediate by the cathodic reduction reaction of molecular O_2 and the follow-up reaction with a water molecule. After conduction, OH^- reacts with the H^+ created at the anode and yields water as a product at the anode side.

Solid polymer electrolytes on the basis of a polymer cation exchange membrane in H^+ form or an anion exchange polymer membrane in OH^- form can be considered as quasi-aqueous electrolytes, whereby the water is absorbed in the phase separated ionic nanomorphology of the respective material. This nanomorphology forms ionic pathways through the polymeric membrane connecting the two fuel cell electrodes.

In cells operated at temperatures below 100 °C, liquid water will be the reaction product. For operation temperatures above the boiling point of water, a cell with an aqueous or quasi-aqueous electrolyte can be operated, however, at the expense of pressurizing it to avoid loss of the water and, as a consequence, concentration and conductivity changes in the electrolyte.

An alternative electrolyte for operating temperatures above 100 °C, which also gained technical relevance, is orthophosphoric acid, H_3PO_4. “Water-free” orthophosphoric acid is a self-ionizing amphoteric system, which yields $H_4PO_4^+$ and $H_2PO_4^-$. Protons can be passed along pyrophosphate chains at elevated temperatures of around 200 °C, at which product water appears as vapor and can be rejected easily.

Molten salts can also be utilized as electrolytes. Again, the ion responsible for conductivity should be created in one electrode reaction and consumed in the other. However, due to the (1) corrosive nature, (2) the limited thermal stability, and/or (3) the high melting point of many melts, only a few molten salts have been considered. Up to now, the only fuel cell technology based on a molten salt electrolyte has been using a eutectic mixture of alkali metal carbonates, Li_2CO_3 and K_2CO_3, at temperatures of around 650 °C, absorbed in a matrix of $LiAlO_2$. In this molten carbonate fuel cell (MCFC) the ion conducting the current is O^{2-} in the form of CO_3^{2-}. At the anode, CO_2 is supplied and reacts with O_2 and $4e^-$ to form CO_3^{2-}, which carries the current to the anode, where it is released in the hydrogen oxidation reaction. As a consequence, MCFC, in addition to the mass flow of fuel and oxidant, needs mass flow management of CO_2.

At even higher temperatures in the range of 800–900 °C, ionic conduction can also be observed in solid oxides. Certain doped metal oxides become O^{2-} conductors; hence, they can be utilized as electrolytes in the solid oxide fuel cell (SOFC). The most common oxide used is yttria-stabilized cubic zirconia (ZrO_2), called YSZ, with a doping level of 8% Y_2O_3. This material is a ceramic; the thermal expansion coefficient of its thin layers has to be matched with the other fuel cell components.

As indicated by the terminology of fuel cells, e.g., PEFC, AFC, SOFC, others (see below), the electrolyte is the decisive cell component, which determines operation temperature, the choice the electrodes (electrocatalytic materials), and finally the specifics of the electrochemistry of the reactants. This, on the other hand, has consequences for the layout of the fuel cell design (balance of plant) and possible applications of the respective fuel cell technology, according to the required duty cycle of the application.

Classification of Fuel Cell Types

Today’s fuel cell types under development can be classified in two different ways: either by the temperature range of operation or by the nature of the electrolyte.

The latter classification distinguishes between acidic and alkaline fuel cells. Acidic fuel cells with H^+ conduction require other electrode materials than alkaline with OH^- conduction. Alkaline fuel cells, at least with an aqueous electrolyte, require a CO_2-free fuel, and hence cannot be operated on reformate fuel obtained originally from a C-containing fuel.

The above-described situation displays the fact that there is a temperature gap in the availability of electrolytes between ca. 200 °C and 650 °C. Today, major research efforts are carried out to extend the range of aqueous H^+ and OH^- conduction to temperatures beyond 100 °C, for technological reasons (heat rejection in cars, CO tolerance of platinum-based catalysts). On the other hand, oxide materials are developed with improved O_2^- conductivity al temperatures lower than the operation temperatures of standard SOFCs. Also ceramic proton conductors [11] and proton-conducting salts like CsHSO4 [12] are considered as electrolytes for this temperature regime.

The Role of Electrocatalysis and the Electrode /Electrolyte Interface

Next to the voltage losses due to ionic conduction, voltage losses due to the activation overvoltages of the respective electrode reactions arise, as described by the Butler-Volmer, respectively, the Tafel equation. As stated above, at a certain value of the current density, the overvoltage for the HOR is much smaller than for the ORR, due to the simpler electron transfer kinetics. Overvoltage for an electrochemical reaction shows also a strong temperature dependency, as does activation energy, and decreases with increasing temperature.

For fuel cells with an acidic electrolyte, platinum is the electrocatalyst of choice at temperatures up to 200 °C (e.g., PAFC), due to the stability requirements. High dispersion of the catalyst is required, taking into account its nature as a precious metal, to provide a high surface area to volume ratio. Platinum nanoparticles in the diameter range of a few nanometers, typically 2–5 nm, supported on carbon particles are utilized. Different carbons with different surface areas (up to 800 m^2/g) are used. The amount of platinum in the catalyst powder is specified as wt% per g of carbon and further as mg loading per cm^2 of geometric electrode area.

Platinum is prone to CO adsorption at temperatures of around 100 °C and below. For this reason, care has to be taken with respect to the purity of hydrogen, in particular for hydrogen liberated from a C-containing fuel by a reforming process (steam reforming, partial oxidation, autothermal reforming).

Alkaline electrolytes allow cheaper, non-precious metal catalysts like nickel and its alloys.

High temperature fuel cells, e.g., MCFC or SOFC, require other catalyst materials, which are described in the respective section below.

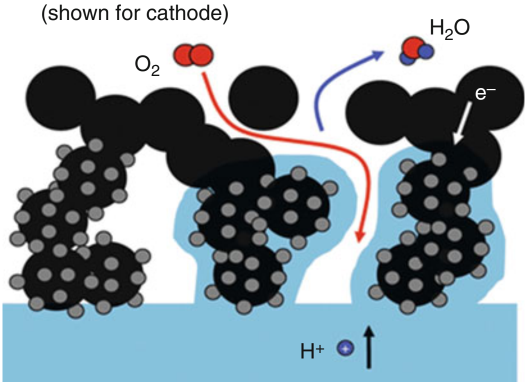
There is a common problem to all material selections for the different fuel cell types, namely, to generate an optimal electrolyte/electrode interface. One has to realize that gaseous molecular reactants are converted into ionic species, solvated/hydrated in their electrolyte medium, by exchanging electrons with the electrode material. This reaction occurs at the so-called triple phase boundary (triple point), where electron conducting, ion conducting, and gas phase (eventually dissolved in the electrolyte) join to each other. To allow a high surface area for current generation, the electrolyte/electrode interface is extended into a three-dimensional *interphase* with a certain thickness. For a polymer electrolyte fuel cell, this *interphase* is drafted in Fig. 7 for the cathode (oxygen) side.

Depending on the respective materials for the different fuel cell types, this three-dimensional inter*ph*ase has to be established by very different preparation/manufacturing procedures. In particular, solid electrolyte materials must be processable to be included into the electrode layer.

Fuel Cell Families

The various fuel cell types considered today having some technical relevance are displayed schematically in Fig. 8. They are arranged according to the nature of electrolyte, acidic or alkaline, and to their temperature of operation.

The polymer electrolyte fuel cell, PEFC, and the phosphoric acid fuel cell, PAFC, are acidic fuel cells; the PEFC operates in the temperature range below and around 100 °C (PEFC), respectively, and the PAFC at around 200 °C. Hydrogen is the preferred fuel for both types. A PEFC can also be fed by liquid or gaseous methanol, called direct methanol fuel cell, DMFC. Other fuels based on alcohols, e.g., the direct ethanol fuel cell, DEFC, are subject to research. Fuel cell types utilizing an acidic aqueous electrolyte will not be considered here.



Fuel Cell Types and Their Electrochemistry, Fig. 7 Electrode layer (interphase) with three phase boundary (schematic) of a polymer electrolyte fuel cell (cathode side). Blue: polymer electrolyte, black: carbon particles, gray: platinum nanoparticles (Adapted from L. Gubler, Paul Scherrer Institut)

Most concepts for an alkaline fuel cell in the past have been described with an aqueous alkaline electrolyte. Recently, also anion exchange membranes, alkaline solid polymer electrolytes, have been considered [13].

The molten carbonate fuel cell, MCFC, and the solid oxide fuel cell, SOFC, are high temperature fuel cells, due to their temperatures of operation of around 650 °C, respectively, 800–900 °C. Both can be considered as alkaline fuel cells (chapter ► "Molten Carbonate Fuel Cells").

The local appearance of the reaction product is determined by the current-carrying ion. While for acidic fuel cells the reaction product shows up at the cathode (oxidant side), it is the anode (fuel side) for alkaline fuel cells. In case of C-containing fuels, e.g., methanol, a second reaction product containing the oxidized carbon appears at the fuel side. The appearance and hence the removal of the product/s causes consequences for the mass flow engineering of the stack and fuel cell system.

The following ordering of fuel cell types does not reflect the historical development of the various fuel cell technologies.

Polymer Electrolyte Fuel Cell Types

The idea of using a thin ion-conducting polymer membrane, *solid polymer electrolyte*, as electrolyte and separator can lead to different concepts of cells. Firstly, when ionic charges, anions or cations, are chemically bound to the polymer (ionomer) network, the respective countercharge can move freely within the polymer volume, provided a certain volumetric charge density within the polymer exists, which on uptake of, e.g., water leads to phase separation into a hydrophobic polymer (backbone) and a hydrophilic, charge-containing phase [14]. As a consequence, the polymer morphology allows the continuous transport of this ion from one electrode interphase to the other. This concept is normally called polymer electrolyte fuel cell (PEFC).

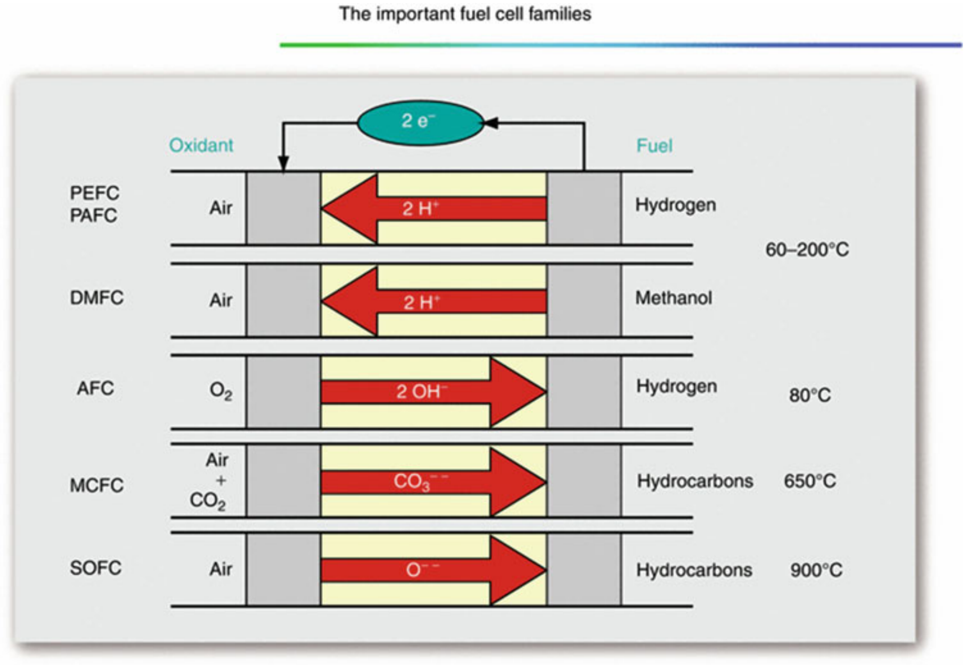
Depending on the fuel, H_2, MeOH (gas or liquid), or others, the solid polymer electrolyte properties have to be tailored, in particular for their properties toward separation of fuel and oxidant.

Further, non-ionomeric polymers can absorb an electrolyte, e.g., phosphoric acid H_3PO_4, which then renders ion conducting. This concept is realized in the so-called HT-PEFC, high temperature PEFC (ca. 100–200 °C), where a polybenzimidazole film imbibed with phosphoric acid becomes proton conducting due to the mechanism described above for non-aqueous phosphoric acid (see this book, chapter ► "Polybenzimidazole Fuel Cell Technology: Theory, Performance, and Applications").

H_2-Fed PEFC

This type of H_2-fed fuel cell, due to its high achievable specific and volumetric power density (in the range of 1 kW/kg and 1 kW/L and above), its cold start behavior, and its fast load following properties, has found interest in the automotive industry and is under development by all major automotive companies.

A thin ion-conducting polymer sheet, typically in the range of 25 μm, is utilized as a solid electrolyte, i.e., electrolyte and separator, in the PEFC (Fig. 1). For thermal stability reasons, only cation exchange membranes in the H^+ form have been considered up to today for technical applications (see also ► "Alkaline Membrane Fuel Cells"). In comparison to cells with liquid electrolyte, this PEFC concept offers the advantage that the "electrolyte" is chemically bound within the polymer matrix and only

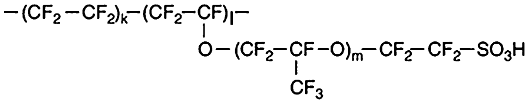


Fuel Cell Types and Their Electrochemistry, Fig. 8 The important fuel cell families of today

water as reactant, in addition to the gases, appears in the peripheral system components. Membranes are perfluorinated or partially fluorinated polymers, with side chains ending in pendant acid groups, e.g., the sulfonic acid group $-SO_3H$ (Fig. 9).

Under operation, the membrane has to contain some water, e.g., 15 water molecules per sulfonic acid group, to provide the necessary specific conductivity. This fact causes consequences for some of the system auxiliaries, as the gases, hydrogen and air, have to be humidified before flowing into the cell to sustain the hydration level in the membrane.

The acidic electrolyte requires a precious metal catalyst; hence platinum supported on carbon particles serves as electrocatalyst, with typical Pt loadings of ca. 0.1 mg/cm^2 at the anode side and ca. 0.4 mg/cm^2 at the cathode side. Platinum nanoparticles, typically a few (3–5) nanometers in diameter, are deposited on various carbon substrates (e.g., 20–40%Pt/C) by wet chemical processes and then further processed in combination with solubilized ionomer material and binder(s) (PTFE) to yield an ink, which then is applied either to the electrolyte membrane surface (CCM, catalyst-coated membrane) or to the GDL to form the GDE.



$$-(\mathrm{CF_2-CF_2})_k-(\mathrm{CF_2-\underset{\displaystyle O-(CF_2-\underset{\displaystyle CF_3}{CF}-O)_m-CF_2-CF_2-SO_3H}{CF}})_l-$$

Fuel Cell Types and Their Electrochemistry, Fig. 9 Generalized structure formula of Nafion® type membranes (DuPont) with $m = 1$, $l = 1$, $k = 5–7$

Extensive characterization of these electrocatalysts for the fuel cell reactions has shown that the electrocatalytic activity of these nanoparticles is by a factor 10 lower than the activity of a polycrystalline platinum surface for the respective reactions, HOR or ORR [15]. This difference is not fully understood yet.

An interesting proprietary approach has been followed recently by the 3 M Company, creating a continuous electrode area covered by nanoscale Pt whiskers. Reactivity of these electrocatalytic layers is in the range of polycrystalline platinum surfaces [16].

Today, pure hydrogen is considered as the ideal fuel. Due to its CO content, hydrogen derived from C-containing fuels (by steam reforming (SR), partial oxidation (POX), or autothermal reforming (ATR) followed by preferential oxidation (PROX)) would need specific measures in terms of electrocatalysis, e.g., PtRu as bifunctional electrocatalyst, to allow oxidation of CO. As an alternative, purification methods of the anode gas stream prior to entering the cell down to only a few parts per million CO (depending on operation temperature) are necessary.

The electrocatalytic layers are contacted by gas diffusion layers, allowing the gases to be passed to the interphase and the product(s), H_2O with H_2 and O_2 as reactants, which consist of carbon cloth or paper (Fig. 2). This arrangement of membrane, electrocatalytic layers, and gas diffusion layers is colloquially called membrane electrode assembly (MEA).

Most of the applications of this fuel cell type are developed for air operation, taking advantage of utilizing one reactant from the ambient environment. However, there exist also some applications in which pure oxygen is employed as oxidant. Due to the higher partial pressure of oxygen and the absence of electrochemically inert nitrogen as the majority component in the cathodic gas stream, humidification issues of the cell can be strongly simplified [17, 18].

Methanol-Fed Fuel Cell (PEFC Type)

The same concept of combination of an acidic solid polymer electrolyte and acid stable precious metal electrocatalysts can also be applied to a methanol-fed fuel cell (direct methanol fuel cell, DMFC). Methanol can be fed in liquid or vapor form, mixed with water. The methanol molecule CH_3OH is electrochemically converted at the anode:

$$\textbf{Anodic reaction}: \mathbf{CH_3OH + H_2O = 6H + 6e^- + CO_2} \quad \text{(methanol oxidation reaction, MOR)}$$

$$\textbf{Cathodic reaction}: \mathbf{O_2 + 4H^+ + 4e^- = 2H_2O} \quad \text{(oxygen reduction reaction, ORR)}$$

$$\textbf{Overall reaction}: \mathbf{CH_3OH + H_2O + O_2 = CO_2 + 3H_2O}$$

As seen above, during MOR, one molecule of water is consumed, which is necessary to oxidize carbon in the CH_3OH molecule to CO_2, while potentially six protons are liberated. The ORR can be formulated the same way as in a hydrogen-fed cell.

The equilibrium potential for the anode reaction is 0.02 V; hence, a theoretical cell voltage close to the H_2/O_2 fuel cell should be observed. In practice, the OCV is lower, for several reasons: Due to the similarity of methanol and water as solvents (e.g., solubility parameter), methanol also penetrates into the water-swollen polymer membrane and passes to the cathode (methanol crossover), causing a mixed potential at a lower value than the oxygen potential. Further, the anode reaction requires a binary or ternary bifunctional catalyst, containing next to platinum one metal component (or two) providing the splitting reaction of the water molecule involved to liberate oxygen for the carbon oxidation at lower potentials as compared to platinum. Examples would be Ru, Sn, Mo, others, or even combinations of two of these together with platinum as the hydrogen-liberating catalyst. Intermediate oxidation species of the methanol molecule, e.g., −COH, may adsorb and poison the platinum catalyst surface, thereby impeding the full oxidation reaction.

These kinetic losses at the anode lead to a high anode overvoltage and, therefore, the cell voltage in the DMFC is lower at a respective value of current density as compared to a H_2-fed cell, as is the achievable power density.

Direct methanol fuel cell concepts with liquid electrolyte have also been considered in the past. One advantage of circulating liquid electrolytes is the option to cool the cell without additional cooling fluid.

High Temperature PEFC

As mentioned above, H_3PO_4 can be absorbed in polybenzimidazole films to yield water-free proton-conducting membranes. The concept is strongly related to the phosphoric acid fuel cell, PAFC. These cells can be operated above 100 °C, typically in the temperature range of 160–180 °C, without humidification, allowing to simplify the balance of plant. Further, due to the higher operation temperature as compared to H_2-fed cells, CO tolerance is drastically increased. Disadvantages are the loss of H_3PO_4 during start-stop cycles, i.e., excursions to temperatures below 100 °C, where liquid product water causes leaching of the ionic component. In addition, achievable power densities are typically lower than with H_2-fed cells, due to the fact that phosphate cations strongly adsorb on platinum even at these temperatures, impeding the ORR (chapter ▶ "Phosphoric Acid Fuel Cells for Stationary Applications"). For more detailed information please see chapter ▶ "Polybenzimidazole Fuel Cell Technology: Theory, Performance, and Applications".

Phosphoric Acid Fuel Cell

Looking back at the development of fuel cell technologies, the PAFC technology has been the earliest one to be commercialized (chapter ▶ "Phosphoric Acid Fuel Cells for Stationary Applications"). Several 200 kW_e power units for co-generation have been delivered to customers over the past 20 years, mainly by the US company UTC Power [19]. Water-free phosphoric acid is absorbed in an inorganic diaphragm and contacted on both sides by platinum-containing gas diffusion electrodes. Advantages and disadvantages are very similar to the ones of the HT-PEFC.

Alkaline Fuel Cell

Alkaline electrolytes played an important role in the beginning of fuel cell development, due to its less stringent requirements for electrocatalysts. An aqueous solution of NaOH or KOH at higher concentration is absorbed in a matrix, formerly asbestos, today a composite material of an oxide and a polymer binder. The electrochemistry of the respective HOR and ORR can be written the following way:

$$\begin{gathered}\textbf{Anodic reaction}:\\ \mathbf{H_2 + 2OH^- = 2H_2O + 2e^-}\\ \text{(hydrogen oxidation reaction, HOR)}\end{gathered}$$

$$\begin{gathered}\textbf{Cathodic reaction}:\\ \mathbf{1/2O_2 + 2H_2O + 2e^- = 2OH^-}\\ \text{(oxygen reduction reaction, ORR)}\end{gathered}$$

$$\begin{gathered}\textbf{Overall reaction}:\\ \mathbf{H_2 + 1/2O_2 = H_2O}\end{gathered}$$

As described above, an alkaline cell generally has to be operated on H_2 and O_2, due to the CO_2 problem. As advantage, a non-precious metal, such as Raney nickel, can serve as electrode material. ORR in alkaline solution shows a lower overpotential loss than in acidic solution; hence, higher specific power densities (mW/cm^2) can be generated in cells.

Recently, some progress in the preparation of anion exchange membranes was reported, leading to the application of the PEFC concept to alkaline fuel cells. However, performance in terms of power output and stability/lifetime is far below the acidic technology [13].

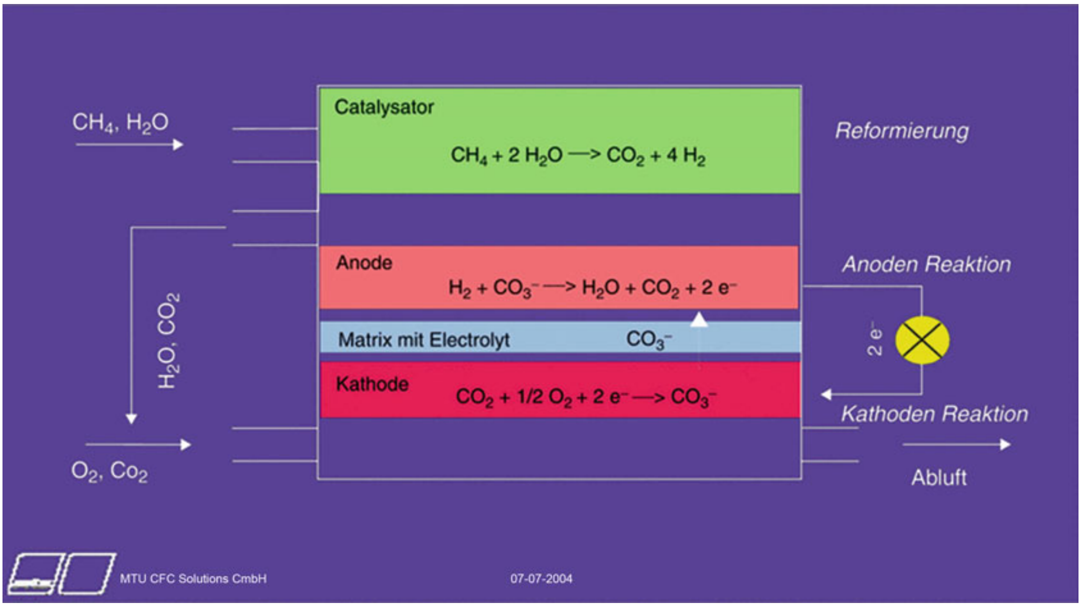
Molten Carbonate Fuel Cell

As a high temperature fuel cell, which operates in the temperature range around 650 °C, the MCFC can use the waste heat of the fuel cell reactions for internal reforming of C-containing fuels (Fig. 10). No further processing of the reformed fuel is necessary. Reformed hydrogen is oxidized at the anode, consisting of a porous nickel electrode, under consumption of the CO_3^{2-} cation, which carries the current through the electrolyte, to H_2O and CO_2. The anode reaction product CO_2 has to be recycled to the cathode compartment, where it is consumed during the ORR at a porous Ni-Oxide cathode to CO_3^{2-} and taken up by the electrolyte melt again, therefore balancing the CO_3^{2-} concentration in the Li_2CO_3/K_2CO_3 eutectic electrolyte, which is absorbed in a $LiAlO_2$ matrix.

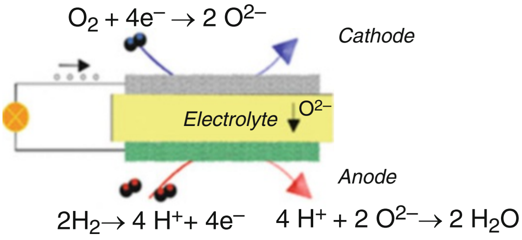
MCFC systems in the power range of 250 kW have been delivered for on-site testing, using a variety of fuels, like biogas, reformed natural gas, and others [20].

Solid Oxide Fuel Cell

The electrolyte in a solid oxide fuel cell is a thin ceramic body, which is an O_2-conducting oxide material. O^{2-} conduction is established by doping a stoichiometric material like ZrO_2 by Y_2O_3, thereby generating O^{2-} vacancies in the lattice. Around 8% of Y_2O_3 are required to stabilize the cubic form of ZrO_2 at temperature of operation. A reasonable specific conductivity for this 8YSZ material is obtained in the range of and above 800 °C (Fig. 11).



Fuel Cell Types and Their Electrochemistry, Fig. 10 Scheme of the molten carbonate fuel cell, MCFC (Adapted from MTU CFC Solutions)



Fuel Cell Types and Their Electrochemistry, Fig. 11 Scheme of the planar solid oxide fuel cell, SOFC, and its electrochemistry (Adapted from L. Gauckler, ETH Zürich)

Electrode materials consist of a Ni/8YSZ cermet (mixture of ceramic and metal) as anode and $La_xSr_yMnO_3$ (perovskite) as cathode.

Ohmic losses in the electrolyte can be lowered by designing cells with thin electrolyte layers, typically 10 μm thick, supported on one of the electrode structures, instead of utilizing a thicker, free-standing electrolyte layer.

For many years, also a tubular concept had been developed by Siemens Westinghouse, addressing the challenges in matching the thermal expansion coefficients of the different materials, namely for the electrolyte and the electrodes. However, the further development of this concept had been abandoned. SOFC technology development mainly addresses stationary co-generation of power and heat, at a power scale of 100 kWe and more (e.g., Topsoe Fuel Cell, Denmark), as well as small scale (1 kW_e) co-generation for private homes (e.g., Hexis Switzerland).

Interestingly, low power application micro-SOFCs are developed as battery alternatives, utilizing materials which allow operation temperatures in the range of 550 °C (One-Bat-Project, ETZ Zürich [21]).

Future Directions

After two decades of intensive fuel cell research and development, some of the described technologies have come close to the market. This is particularly the case for the PEFC technology developed worldwide by automotive industry. Preliminary market introduction is planned, according to various sources, by the year 2015. However, still issues of cost and reliability remain and provide ample space for further research. Unfortunately, other technologies, e.g., the SOFC and MCFC technology, have recently seen some setbacks, due to the fact that some longstanding prominent advocates of fuel cell development have decided not to continue their effort (e.g., SOFC by Siemens, MCFC by Tognum (formerly MCFC solutions), others).

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