Solid electrolyte membrane reactors: Status and trends

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Abstract

A survey of recently published research work on solid electrolyte (SE) membrane reactors is given, with focus on high-temperature oxygen ion conductors, high-temperature proton conductors and low-temperature proton conductors. In these three material classes, the current status and the future trends of membrane reactor development are briefly elucidated. SE membrane reactor principles are realized in gas sensors, fuel cells, electrolyzers and reactors for partial oxidation. In all these fields SE membranes are in contact with porous electrolyte layers at which anodic or cathodic electrochemical reactions take place. In the area of membrane reactors using high-temperature oxygen ion conductors, there is a trend towards lower operating temperatures on order to ensure stable long-term operation of the membrane materials, and to match the optimal temperature window of the applied catalysts. As a younger generation of ion conducting ceramics, high-temperature proton conductors offer new possibilities for the implementation of electrochemical membrane reactors. Finally, current trends in the application of low-temperature proton conductors being based on polymeric materials are discussed. These materials can not only be used for fuel cells but also as membranes in hydrogenation or oxidation reactors.

1. Introduction

Solid electrolyte (SE) membrane reactors are equipped with ion conducting membranes, which ideally are impermeable for non-charged reaction species. These reactors work as electrochemical cells where the oxidation and reduction reactions are coupled and are carried out separately on catalyst/electrodes layers located on different sides of the electrolyte. The development of solid electrolyte membrane reactors have reached a semi-commercial stage in fuel cells, where the maximal generation of electric energy by total oxidation of hydrogen or hydrocarbon feeds is the primary goal of operation. The research on chemical reactor applications is strongly concentrated in the high-temperature range using either oxygen ion conducting or proton conducting inorganic membranes. More recently some interesting examples have been published where

proton conducting polymeric membranes have also been tested for the production of chemicals.

The objective of this paper is to give a brief overview on the current status and the future trends in the development and application of electrochemical reactors equipped with solid electrolyte (SE) materials used as membranes in these reactors. The paper is focused on three important classes of ionically conductive materials:

(i) high-temperature oxygen ion conductors,
(ii) high-temperature proton conductors, and
(iii) low-temperature proton conductors.

Other ionic species, which can be transported in SE materials are e.g. Na^+, K^+, Li^+, Cl^- and F^-. There are some applications using the above ions other than oxygen ions and protons, e.g. the use of Li^+ conducting materials in Li-batteries etc. However, they are not considered further in the present overview.

As a special feature of the present survey, it covers aspects of all the three material classes given above. There

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are some other recent review papers, especially written for high-temperature applications, which we would like to recommend to the readers who are interested in more detailed information on these materials. In the year 2000, Stoukides [1] discussed the current experience and gave an outlook on possible future applications of high-temperature oxygen SE membrane reactors. Very recently, Iwahara et al. [2] published a prospect of hydrogen technology using proton-conducting ceramics. Also very recently, Bolland and co-workers [3] presented high-temperature membranes in power generation processes with CO_2-capture, which is a very important trend in modern power plant engineering. The cited three reviews elucidate SE membranes from the chemical engineers' point of view. For material experts', the excellent reviews of Goodenough [4] and Kreuer [5] are recommended to the readers who would like to be informed about oxide-ion electrolytes or proton-conducting oxides, respectively.

1.1. Classification of membranes

Generally, membranes can be classified into two major groups: porous and dense membranes. The group of gas-dense membranes falls into two categories, namely mixed ion–electron conductors (MIEC) and ion conductors. MIEC are those in which the values of ionic and electronic conductivity are comparable, whereas the latter is referred to solid electrolytes (SE) that exhibit an ionic conductivity at least two orders of magnitude higher than their electronic conductivity. The transport mechanisms of the just mentioned three material classes are illustrated in Fig. 1 using oxygen transport as example.

In porous membranes, oxygen is transferred mainly as O_2 molecules via diffusion, viscous flow and surface diffusion. The dusty-gas-model (DGM) describes the combination of these three transport mechanisms quantitatively [6].

Alumina, silica and zeolites are typical representatives of materials used for porous membrane preparation. Generally, the permeability in such porous membranes are rather high compared to dense membranes, whereas the permselectivity is moderate. Due to the latter property, an additional air separation process is needed in technical processes in order to separate oxygen and nitrogen, and thereby to be able to feed oxygen-rich gas mixtures. Both, the permeability and the permselectivity can be adjusted by preparing membranes with a suitable pore size distribution and pore structure. As shown in Fig. 1, porous membranes are often designed as asymmetrically structured layers.

Dense membranes rely on the transfer of oxygen in the form the ionic species, O^{2-}, jumping from vacancy to vacancy in the lattice of the solid material, driven by the electrostatic potential difference. Due to this transport mechanism, the permeabilities are lower than in porous materials and this often limits the reactor efficiency. But, as outlined later in this section, the permeability is strongly dependent on the operating temperature, which offers the possibility to enhance the permeability of the SE material. Simultaneously, the permselectivities of SE membranes are excellent. When using air, i.e. a mixture of oxygen and nitrogen, oxygen is transferred exclusively from one side to the other. Consequently, SE membranes allow a direct integration of air separation in the process, i.e. any additional air separation is not necessary. This in turn reduces the operating and investment costs of the oxidation process.

The two categories of dense membranes, i.e. MIEC and SE materials, are distinguished by their conductivities with respect to charged species. MIEC have both, high ionic conductivities as well as high electronic conductivities, whereas SE exhibit high ionic conductivities but very low electronic conductivities. MIEC membrane reactors are simple in design because electrons are transported internally, i.e. inside the membrane material. On the contrary, SE
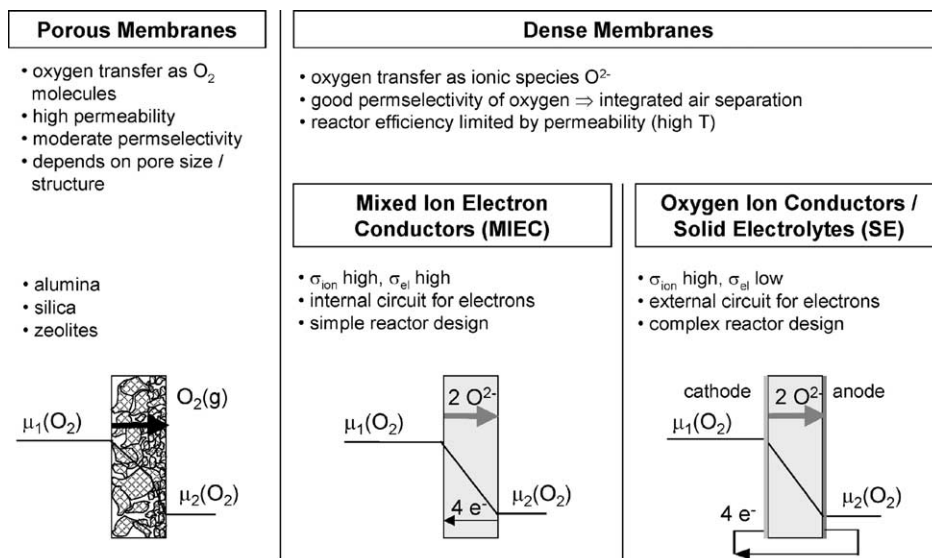

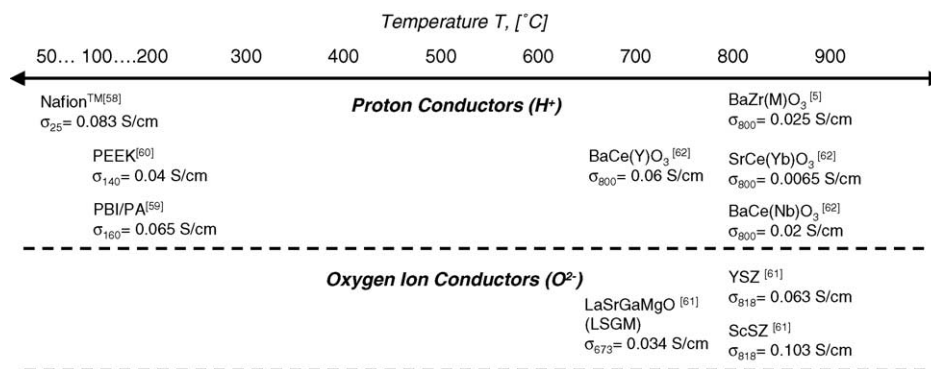Fig. 1. Classification of ceramic membranes for oxygen transport.

Temperature T, [°C]

| 50... 100....200 | 300 | 400 | 500 | 600 | 700 | 800 | 900 |

Proton Conductors (H⁺) — *Proton Conductors (H+)*

Nafion[TM][58]
σ_{25} = 0.083 S/cm

BaZr(M)O$_3$ [5]
σ_{800} = 0.025 S/cm

PEEK[60]
σ_{140} = 0.04 S/cm

BaCe(Y)O$_3$ [62]
σ_{800} = 0.06 S/cm

SrCe(Yb)O$_3$ [62]
σ_{800} = 0.0065 S/cm

PBI/PA[59]
σ_{160} = 0.065 S/cm

BaCe(Nb)O$_3$ [62]
σ_{800} = 0.02 S/cm

Oxygen Ion Conductors (O²⁻)

YSZ [61]
σ_{818} = 0.063 S/cm

LaSrGaMgO [61]
(LSGM)
σ_{673} = 0.034 S/cm

ScSZ [61]
σ_{818} = 0.103 S/cm

Fig. 2. Ion conductivities of selected SE materials [58–62].

membrane reactors require an external circuit for electrons. As a consequence, two electrode layers (anode and cathode) have to be installed directly adjacent to the membrane. Therefore, the design of SE reactors – especially the design of the two interfaces between the membrane and the electrodes – is more complicated. But, as a unique feature of SE membrane reactors, the galvanostatic control of the external flux of electrons or, alternatively, the potentiostatic control of electrode potentials offer opportunities to drive the reactions at the two electrodes into the desired direction.

1.2. Ion conductivity of selected materials

Fig. 2 shows a map of selected SE materials and their ionic conductivities as a function of temperature. With respect to proton conductors there are two classes: polymeric materials which can only be operated in the low temperature range up to 200 °C, and certain mixed oxides which show reasonable proton conductivities between about 500–900 °C. Typical representatives of low temperature proton conductors are Nafion, polybenzimidazole (PBI) and polyetheretherketones (PEEK). Currently investigated high temperature proton conductors are Ba–Zr, Sr–Ce and Ba–Ce mixed oxides. Oxygen ion conductors can be only operated in the high temperature range. The most important materials here are classical yttria stabilized zirconia (YSZ), scandia stabilized zirconia (ScSZ), and – nowadays very extensively investigated – perovskite materials such as Sr/Mg-doped lanthan gallat (LSGM). It is interesting to note that the here mentioned materials in the low and high temperature range all have ion conductivities of similar magnitude, i.e. around σ = 0.01–0.1 S/cm.

The total conductivity of ion conducting materials is strongly dependent on the temperature. Fig. 3 illustrates the experimental conductivity values for some selected oxygen ion conductors in the Arrhenius-type diagram. The conductivities were determined by AC impedance spectroscopy using the 2-probe method. The perovskite material LSGM shows the highest oxygen ion conductivities at the temperatures of interest. In the case of ScSZ, the doping content of Scandium has a strong influence on the conductivity property. Moreover, non-linearities in the

conductivity–temperature curve can appear which indicates phase transformation processes.

When applying SE materials in catalytic membrane reactors, it is important that the materials show suitable oxygen transport rates within the catalyst temperature operating window. Example, for butane partial oxidation (POX) at a VPO-catalyst, one has to find a suitable SE membrane which shows good oxygen permeabilities in the range between 400 and 600 °C [7]. Typical oxygen flux densities for YSZ, ScSZ (with 9% Sc) and LSGM are given in Table 1. As discussed in Section 1.1, the fluxes are generally lower than the flux densities of typical porous membranes (supported microporous SiO$_2$, mesoporous Al$_2$O$_3$), at the same temperature.

1.3. Operating modi of SE reactors

Solid electrolyte membrane reactors can be operated in a variety of modes, which are illustrated in Fig. 4 using the hydrogen–oxygen reaction combined with an oxygen ion conducting membrane as example. In the open circuit mode ($i_{cell} = 0$), the membrane reactor is operated potentiome-

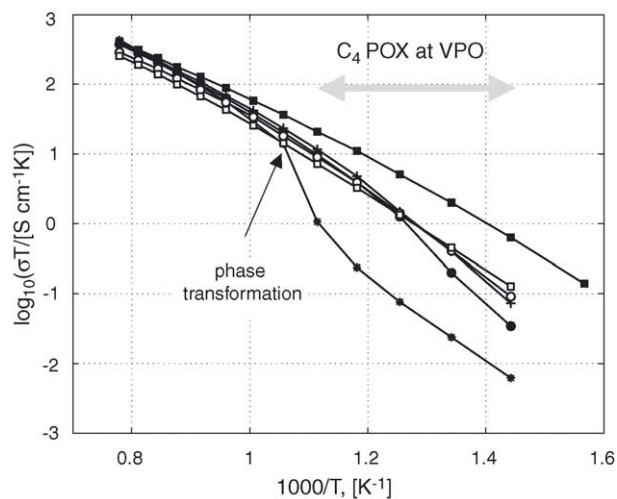Fig. 3. Total conductivity σ of some oxygen ion conductors. Yttria stabilised zirconia 13% (□), scandia stabilised zirconia 7.5% (○), 9% (+), 10% (●), 12% (✳), La$_{0.9}$Sr$_{0.1}$Ga$_{0.85}$Mg$_{0.15}$O$_{3-\delta}$ (■).

Table 1
The total conductivity of solid electrolytes, and the calculated oxygen flux for membrane thickness of 250 μm, and potential difference of 1.0 V

Material	Temperature (°C)	
	420	624
Total conductivity (Sm^{-1})		
YSZ[a]	0.018	0.80
ScSZ[b]	0.011	1.34
LSGM[c]	0.092	2.32
Oxygen flux density (mmol m^{-2} s^{-1})		
YSZ[a]	0.188	8.3
ScSZ[b]	0.114	13.9
LSGM[c]	0.949	24.1

[a] Yttria (13%).
[b] Scandia (9%) stabilised zirconia.
[c] $La_{0.9}Sr_{0.1}Ga_{0.85}Mg_{0.15}O_{3-\delta}$.

trically as a sensor without any net current through the electrolyte. In this mode, the concentration of reactants can be monitored via the open-circuit cell voltage E_{cell}^0, often abbreviated as OCV, based on Nernst's law.

In the fuel cell mode, the cell current is positive ($i_{cell} > 0$) and the cell voltage is below the OCV level due to internal cell resistances. Cathodic reactants are reduced to ionic species at the cathodic electrode, and the ions are transferred through the membrane to the anodic electrode where they react with the anodic reactants. The DC power density, $p = E_{cell} \times i_{cell}$, is positive, i.e. one obtains electric power output from the electrochemical process ($p > 0$). In this mode, the Gibbs free energy of reaction is converted directly into electrical energy, thereby reducing the amount of the reaction heat being released. In the case of partial oxidation reactions e.g. of hydrocarbons, a co-generation of valuable chemicals and energy is feasible in the fuel cell mode.

If the current density exceeds a certain limiting value $i_{lim} > 0$, the cell voltage becomes negative. In this ion pump
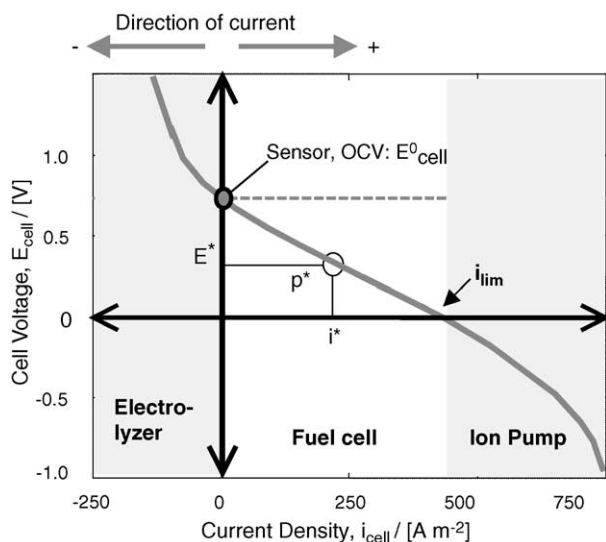
mode, charged species are driven through the solid electrolyte at the expense of external electric energy input to the SE reactor ($p < 0$).

Finally, the direction of the overall electrochemical reaction will be changed if negative cell currents are applied. In this electrolysis mode, the cell voltage exceeds the OCV level ($E > E_{cell}^0$) and the power density is negative ($p < 0$). Then, the direction of the electronic current and the ionic flux are opposite to the fuel cell mode.

1.4. Gas diffusion electrodes

The reactor scheme in Fig. 4 is a very simplified representation of SE membrane reactors. In reality SE membrane reactors are complicated multi-layered reactors. Electrodes have to be fixed on either side of the ion conducting membrane to be able close the charge circuit. The electrodes have to have intimate contact not only to the membrane but also to the electronic current collectors, which are directly connected to the external electron circuit. The electrodes themselves have to combine the following functions:

- a catalytic function such that the electrochemical reactions can take place;
- electrons released in the anodic reaction or consumed in the cathodic reaction at the reaction sites have to be collected, i.e. the electrode needs an electronic conductivity;
- ions transferred through the membrane have to be conducted towards the reaction sites, i.e. the electrode needs an ionic conductivity;
- non-charged reactants have to be transported towards the reaction sites, primarily via pore diffusion inside the electrode structure.

In order to combine the here described functions, electrodes in SE membrane reactors are designed as gas diffusion electrodes (GDE), or more generally speaking as fluid diffusion electrodes. Fig. 5 shows a schematic of a typical GDE. Optimal electrode design requires a perfectly exec-
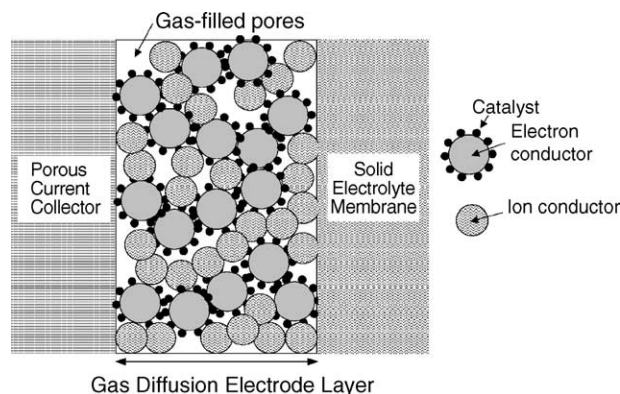

Fig. 4. Operating modi of SE membrane reactors. Electrolyzer: $i_{cell} < 0$, $E_{cell} > E_{cell}^0$, $p < 0$; sensor: $i_{cell} = 0$, $E_{cell} = E_{cell}^0$, $p = 0$; fuel cell: $i_{cell} > 0$, $0 < E_{cell} < E_{cell}^0$, $p > 0$; ion pump: $i_{cell} > 0$, $E_{cell} < 0$, $p < 0$.

Fig. 5. Schematic illustration of gas diffusion electrode (GDE).

Overall cell voltage E_{cell}:

$$E_{cell} = E_{cell}^0 \, (T, c_{feed}) \quad - i_{cell} \, \frac{dM}{\sigma M} \quad - \sum_{i=a,c} \eta_i^c \, (T, (c_{feed} - c_{rxn})) \quad - \sum_{i=a,c} \eta_i^s \, (T, c_{rxn}, i_{cell})$$

Open circuit potentials from thermodynamics	Ohmic resistances a) membr. b) current collectors	Concentration polarisation by a) mass transfer resistances b) educt depletion	Charge transfer resistances at electrodes
	↓ thickness ↑ conductivity ↓ current density	↓ thickness of layers ↓ distance to rxn site ↓ current density	↑ amount of catalysts ↑↓ conc. acc. rxn orders ↓ current density

Fig. 6. Decomposition of cell voltage into main resistances.

uted balance of the different functions. This is often achieved by preparing mixtures of ion conducting particles (made of the membrane material), particles of electron conductor, and catalytic particles. By using well-defined particle size distributions one can adjust the electrode pore structure. This in turn offers the possibility to optimise the transport properties of the GDE with respect to the non-charged reactants.

1.5. Cell voltage analysis

The cell voltage E_{cell} of an electrochemical membrane reactor is a quantity, which is easily accessible in experiments (Fig. 6). The decomposition of the cell voltage into

- the open circuit cell voltage E_{cell}^0 (OCV),
- Ohmic resistances due to the membrane, the electrodes and the current collectors,
- concentration polarization due to mass transfer resistances within the electrode and due to the depletion of reactants from the reactor inlet up to the electrode, and
- charge transfer resistances at the electrodes

yields valuable information on how to improve the reactor performance. As indicated in Fig. 6 there are various cell design parameters, which can be changed in order to reduce the contribution of certain resistances. The most important among them are the thicknesses of the different cell layers, the intrinsic conductivities of the materials used, the amount of the catalyst applied and the current density through the cell.

1.6. Non-Faradaic effects

A review on SE membrane reactors cannot be written without - at least briefly—mentioning the non-electrochemical modification of catalyst activity (NEMCA) effect. Normally the rates of electrochemical reactions taking place

at the electrodes obey Faraday's law, i.e. the current flowing through the membrane and the reaction rate at the considered electrode are proportional to each other. But there are a couple of reactions where deviations from Faraday's law were observed. For example, if ethane and oxygen are fed in the co-feed mode and are reacted at a catalyst, which is placed on top of a YSZ membrane, the catalytic rate under polarization can be higher than calculated from Faraday's law (Fig. 7). This is due to the electrochemical promotion of the catalytic reaction caused by the change of the electrostatic potential of the catalyst, as outlined in a series of papers by Vayenas and co-workers [8,9].
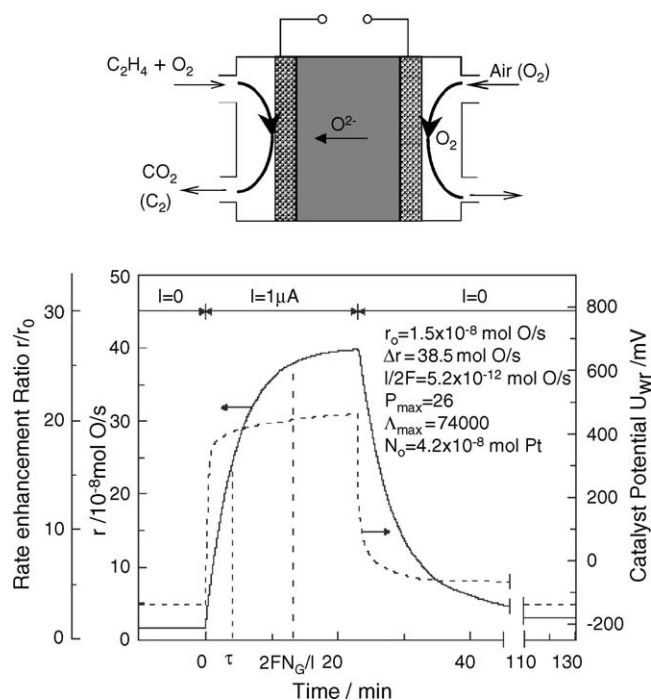
Fig. 7. Non-Faradaic effects in co-feed mode (NEMCA effect) [9]. Reprinted with permission from Elsevier.

2. High-temperature oxygen ion conducting membrane reactors

2.1. Solid oxide fuel cell for electrical energy production

A technology, where the oxygen ion conducting membranes are used semi-commercially is the solid oxide fuel cells (SOFC) for electrical energy production. The electrochemical energy conversion can be carried out highly efficiently in solid oxide fuel cells. Due to the high operating temperatures (>800 °C), wide variety of fuels can be processed, and the sulfur tolerability of the catalyst is high, which are most valuable benefits of SOFC technology compared to the other fuel cells. A significant benefit is also the high achievable electrical net efficiency, which is for small 1 kW units about 50%, for large pressurized SOFC/gas turbine systems, electrical efficiencies up to 70% are expected [10].

The planar SOFC technology is applied by the company Sulzer-Hexis (see Fig. 8, [56]). This technology provides sophisticated heat management with integrated in-direct reforming. In the near future, this company is planning the launch of a new generation of their technology, where especially the water management is further improved or preferably replaced by partial oxidation [11]. Further developers of SOFC technology among others are Siemens–Westinghaus with their 250 kW multi-tubular units, Rolls-Royce with a segmented series arrangement of individual cells [12], Allied-Signal Aerospace Company with the monolith concept [13]. So far the development has concentrated mostly on stationary units, but a new, attracting field for this technology is SOFC based auxiliary power units (APU) for mobile applications [57].

Regardless of the present success of pilot-tests with pre-commercial SOFC units, the problems of the SOFC technologies are well known and still unsolved. Due to the present high operating temperature, the long-term stability is poor, and material degradation is a severe problem. The thermal expansion coefficients of the fuel cell components – electrolyte, electrode layers and interconnections – have to match well with each other, while otherwise the thermal stress will cause delamination at the unit interfaces or cracking of the electrolyte. At the prevailing temperature further demands
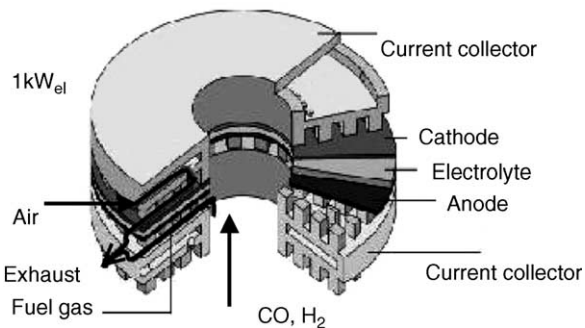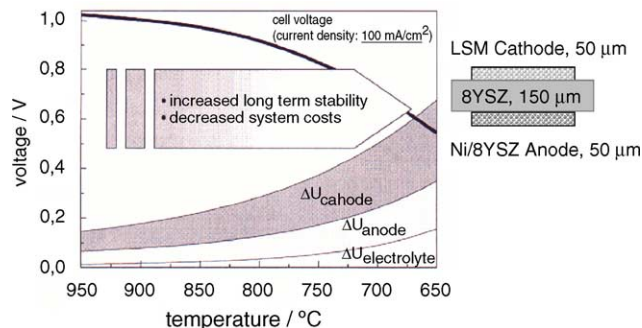

Fig. 9. Cell voltage of an electrolyte-supported single cell at constant current density of 100 mA/cm^2 as a function of operating temperature [10]. Reprinted with permission from Elsevier.

are high chemical compatibility and stability as discussed in detail in the recent review by Weber and Ivers-Tiffée [10]. Increased long term stability and decrease in system cost would be possible, if the development of low or intermediate temperature SOFC-technologies (600–800 °C) are successful in the near future. With the present standard materials, a strontium-doped lanthan–manganate (LSM) cathode, an yttria stabilized zirconia (8YSZ) electrolyte, and a nickel-YSZ cermet anode the internal cell resistances increase unacceptably causing insufficient performance below temperatures of 850 °C as illustrated in Fig. 9 by Weber and Ivers-Tiffée [10]. Alternative electrolyte materials owing high oxide ion conductivity in intermediate temperatures are e.g. Sr/Mg-doped lanthanum gallat (LSGM) and gadolinium doped CeO_2 (GCO). However, the latter material becomes a mixed ion electron conductor under reducing atmosphere at higher temperatures, which results in a decreased system efficiency. The operating range for the GCO electrolyte can be estimated by the electrolytic domain illustration in Fig. 10, where the electronic and ionic conduction are presented as a

Fig. 8. Planar structure of Sulzer-Hexis SOFC [56]. Reprinted with permission from Wiley.
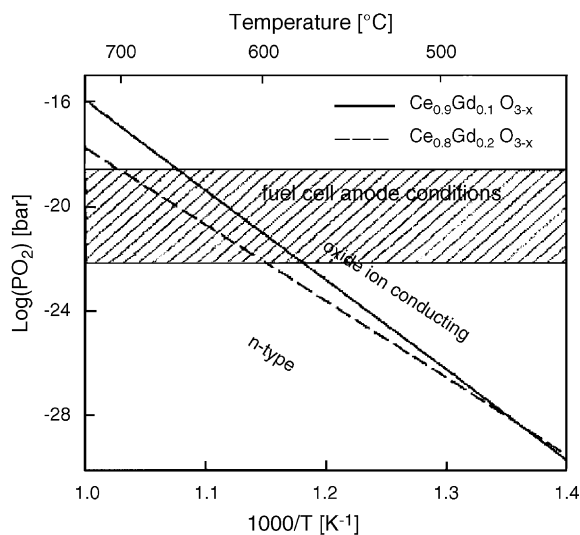

Fig. 10. Electrochemical properties of gadolinium doped ceria: electrolytic domain boundary at which ionic conductivity equals electronic conductivity (reproduction from [14]). Reprinted with permission from Elsevier.

function of temperature and oxygen partial pressure [14]. At temperatures below 700 °C, GCO is nearly a pure ion conductor and therefore can be regarded as electrolyte candidate for the SOFC and other applications.

In an SOFC unit, the anodic electrode material is typically Ni–cermet, which is a combination of metallic Ni and the electrolyte YSZ. The metallic nickel has several important functions: being an excellent catalyst for hydrogen oxidation and steam reforming of hydrocarbons simultaneously it works as a current collector. However as a drawback, it catalyses the competitive catalytic cracking of hydrocarbons and in such a way that is enhances the undesired deposition of carbon on the catalyst. The high activity in coke forming reactions makes its usability questionable especially for the desired direct oxidation of hydrocarbons [15]. The direct oxidation of hydrocarbon without any – internal or external – hydrocarbon steam reforming would be beneficial by decreasing the cost and complexity of SOFC power plants, especially for mobile applications where the hydrogen transport is complicated. Park et al. developed $Cu/CeO_2/YSZ$ anode composites, which were tested successfully for the direct oxidation of various hydrocarbon fuels operating for some hours [16,17].

A novel idea in the field of SOFC technology based on the partial oxidation of hydrocarbon deviates from the strict separation of fuel and oxidant [18,19]. Fig. 11 illustrates a schematic of a single-chamber SOFC being fed with a gas mixture of hydrocarbons and air. The working principle of this cell is based on the different catalytic activity of the two electrodes with respect to the partial oxidation of ethane forming hydrogen and carbon monoxide:

$$C_2H_6 + O_2 \rightarrow 2\,CO + 3\,H_2 \tag{1}$$
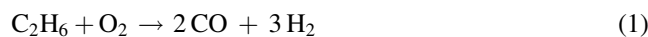
A large amount of hydrogen and carbon monoxide is formed over the Ni-based electrode due to its high catalytic activity for reaction 1. This allows the Ni-based electrode to work also as the anode for the following electrochemical oxidation reactions:

$$H_2 + O^{2-} \rightarrow H_2O + 2\,e^- \tag{2}$$

$$CO + O^{2-} \rightarrow CO_2 + 2\,e^- \tag{3}$$

The $Sm_{0.5}Sr_{0.5}CoO_3$-based electrode on the other side of the disc does not catalyze reaction (1) but it is active for
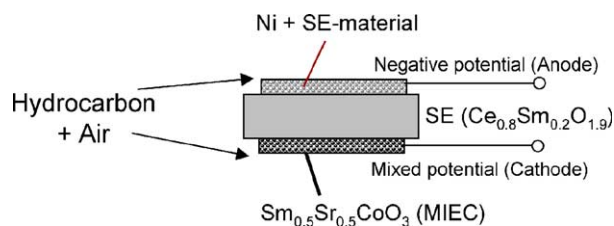

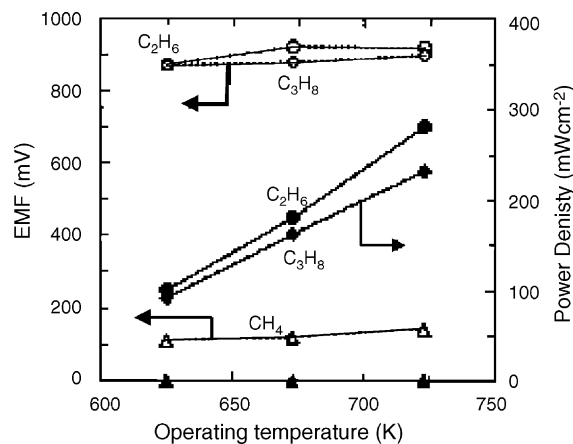Fig. 11. Schematic illustration of single-chamber SOFC in a flowing mixture of hydrocarbon and air.

Fig. 12. Temperature dependence of electromotoric force (EMF) and power density of single-chamber SOFC exposed to different hydrocarbon fuels (reproduction from [18]). Reprinted with permission from Science.

electrochemical oxygen reduction. Therefore, it acts as cathode for the following reaction:

$$0.5O_2 + 2e^- \rightarrow O^{2-} \tag{4}$$

This results in a difference of the oxygen activity between the two electrodes producing a cell voltage. When the single-chamber SOFC was supplied with a mixture of ethane and air at 500 °C, the cell generated an electromotoric force EMF = 920 mV [18]. The EMF and the power density of single-chamber SOFC in a mixture of different hydrocarbons and air as functions of temperature are presented in Fig. 12.

2.2. Oxidative coupling of methane to C_2 and syngas production from methane

The conversion of methane into higher hydrocarbons, such as the C_2 coupled products, ethane and ethylene, or syngas production by partial oxidation, have significant commercial importance. The option of using solid oxide membranes for supplying the necessary oxygen for methane activation has several economical and environmental advantages over the direct use of air as oxidant. The membrane is impermeable to nitrogen and so it provides only oxygen for the reactions, thus avoiding NO_x formation. In addition, in a solid electrolyte process, there are the combined possibilities of electrochemical enhancement of products selectivity, simultaneous generation of electrical power and, in general, more control over the reaction pathway.

In the electrocatalytic oxidation of methane in a SE membrane reactor, methane feed stream does not contain oxygen. It is transferred directly into the reaction zone through the membrane by passing anodic current through the cell. The oxygen ions, O^{2-}, are formed at the air electrode (cathode). Then, these ions are transferred to the electrode–catalyst (anode) through the YSZ electrolyte. On the anode they can either discharge to produce O_2 or oxidize methane
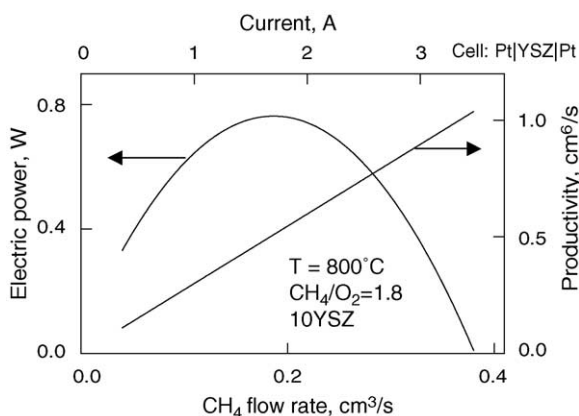
Fig. 13. Effect of methane flow rate (or current) on generated electric power and syngas productivity of SE membrane reactor for the reaction $CH_4 + 0.5\,O_2 \rightarrow CO + 2\,H_2$ (reproduction from [21]). Reprinted with permission from Elsevier.

Fig. 14. Electrocatalytic reforming of methane with carbon dioxide in an electrocatalytic cell NiO-MgO|YSZ|(La, Sr)MnO₃ at open-circuit and closed-circuit conditions at 800 °C: current density and reaction rates of CH_4 and CO_2 vs. time on stream (reproduction from [24]). Reprinted with permission from Elsevier.

[20,21]. The electrocatalytic oxidation of methane enables the simultaneous production of syngas and electricity. It prevents the reaction mixture from explosion, since CH_4 and O_2 (air) are separated by the YSZ electrolyte. In their paper, Semin et al. [21] present experimental results on the electrocatalytic conversion of CH_4 to syngas over a Pt-based electrode in an SE membrane reactor over a large geometric area of the electrode–catalyst. These authors used methane as feed without any diluents. Fig. 13 shows the electric power generated and the syngas productivity versus the methane flow rate on electrocatalytic methane oxidation.

Lapeña-Rey and Middleton [22] investigated the oxidative coupling of methane in an SE reactor incorporating trimetallic catalyst formulations such as $Mn/Na_2WO_4/SiO_2$ and $Mn/K_2WO_4/SiO_2$. For three investigated methane-to-oxygen ratios, the total C_2 selectivity decreased in the order $K > Na > Ag$. The potassium tungstate supported catalyst gave the best overall C_2 selectivity (86% at 4% C_2 yield).

2.3. Dry reforming of methane

Especially, the CO_2 reforming of methane, yielding synthesis gas, has received renewed interest today because of the possibility to enhance natural gas utilization and converting carbon resources inherently contained in CO_2 and CH_4 into syngas. The synthesis gas generated by dry reforming of methane has a low H_2/CO ratio so it can be used for methanol and Fischer–Tropsch synthesis. The electrocatalytic reforming of CH_4 by CO_2 in an SE membrane reactor has some advantages over conventional catalytic reforming. The syngas generated by electrocatalytic reforming in an SE membrane reactor can be used as fuel in a subsequent SOFC, thereby improving the overall energy utilization of methane. Catalyst deactivation by coking is suppressed by the oxygen ions being directly supplied to the catalyst which is on top of the SE membrane.
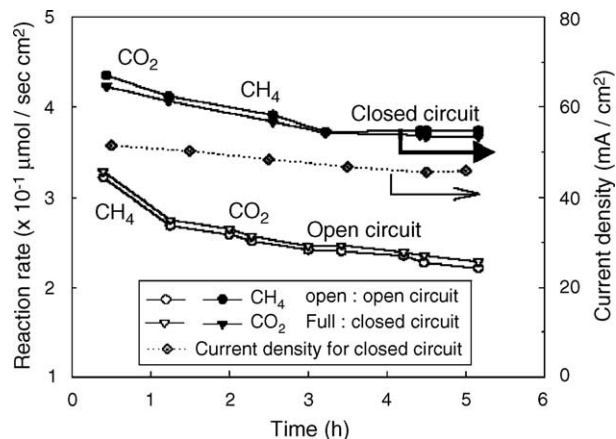
The feasibility of the cogeneration of syngas and electricity by electrocatalytic reforming of CH_4 with CO_2 has been first demonstrated by Belyaev et al. [23]. Recently, the same reaction was investigated over Ni-based catalysts with a cell NiO–MgO|YSZ|(La,Sr)MnO₃ by Moon and Ryu [24]. Fig. 14 shows the reaction rates of CH_4 and CO_2 and the current density of the electrocatalytic cell versus time on stream at open-circuit and closed-circuit conditions.

Solid electrolyte membrane reactors have been recently tested also to the oxidation of C_2–C_4 hydrocarbons to valuable oxygenates [25]. The experiments were carried out at 500 °C under oxygen pumping conditions using MoO_3 as catalyst which was deposited on a Au anode. The evolution of gaseous oxygen was observed in the operation with alkanes. Alkenes were more active and they were oxidized with high selectivity without oxygen evolution. Ethane and propane were found to be inert in a cell configuration MoO_3/Au|YSZ|Ag, while isobutane was partially oxidized to methacrolein. The highest selectivity (73%) was obtained for methacrolein from isobutene. In comparing experiments using V_2O_5 as catalyst in the same cell under oxygen pumping conditions, both alkanes and alkenes were oxidized. Isobutane was oxidized to methacrolein with low selectivity, and propane formed propene by oxidative hydrogenation. Ethane was slowly oxidized to CO_2. With V_2O_5 as catalyst the evolution of gaseous oxygen was observed in all reactions. The lattice oxygen was found to be active for selective oxidations, while co-feed of gaseous oxygen with hydrocarbons resulted in decreased selectivities.

Another recent example of selective oxidation of hydrocarbon is the electrochemical synthesis of maleic anhydride in an SE membrane reactor [7]. A vanadium phosphorous oxide (VPO) catalyst was fixed on the Au electrode and the reactor was operated at temperatures between 730 and 773 K, in the oxygen pumping modus. The

chosen operation conditions were a compromise between a high reaction selectivity at low temperature, and a high oxygen transfer rate through the YSZ membrane at high temperature due to lower electrolyte internal resistances. At 751 K with applied current of 40 mA, the conversion of butane was 15 to 16% and the selectivity to MA was about 39%.

## 3. High-temperature proton conducting membranes

A typical proton conducting ceramic material such as $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ is a solid solution based on the perovskite-type oxide $SrCeO_3$, in which Ce is partly replaced by Yb. Other perovskite-type oxides – based on $SrCeO_3$ or $BaCeO_3$ – in which some trivalent cations are partially substituting cerium, show protonic conductivity, too. The general formulas are $SrCe_{1-x}MxO_{3-\alpha}$ or $BaCe_{1-x}MxO_{3-\alpha}$ where M stands for a certain rare earth element, x is less than its upper limit of solid solution formation range (usually less than 0.2) and α represents the oxygen deficiency per unit formula. The ceramics of these perovskite-type oxide solid solutions exhibit p-type electronic (hole) conduction under oxidizing atmosphere free of hydrogen or water vapor at high temperatures.

Proton conductivity of these oxides can be obtained if protonic defects exist. There are two mechanisms for proton conduction. The first is proton hopping, also called the Grotthus-mechanism, in which the proton jumps between adjacent oxygen ions. The second mechanism is hydroxyl-ion migration, also called the 'vehicle' mechanism.

Protonic defects can be formed by reaction between water molecules and oxygen vacancies according to the equation

$$O_o{}^x + V_o{}^{\bullet\bullet} + H_2O(g) \rightarrow 2\,OH_o{}^{\bullet}$$
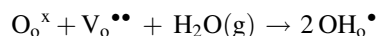
where two effectively positive hydroxyl-groups on regular oxygen positions are formed. Another important mechanism forming protonic defects is the reaction of hydrogen with electron holes according to

$$2\,h^{\bullet} + 2\,O_o{}^x + H_2 \rightarrow 2\,OH_o{}^{\bullet}$$
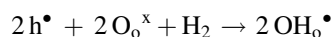
for which the presence of excess holes is obviously necessary.

The conductivities in hydrogen atmosphere are in the order of 10^{-3} to 10^{-2} S cm^{-1} at 873–1275 K. Proton conduction was validated by electrochemical hydrogen transport experiments in hydrogen- or water-vapor-containing atmosphere. The role of water vapor can be seen in Fig. 15 [26]. It was found that the hydrogen evolution rate obeyed Faraday's law up to very high current densities using humidified cathode carrier gases. Within the examined range of water vapor pressures, 6.6×10^2 to 2.3×10^3 Pa, the current efficiency was almost unity until current densities of 450–600 mA/cm^2 were reached which was about 10 times larger than in the operating case where dry carrier gas was used.
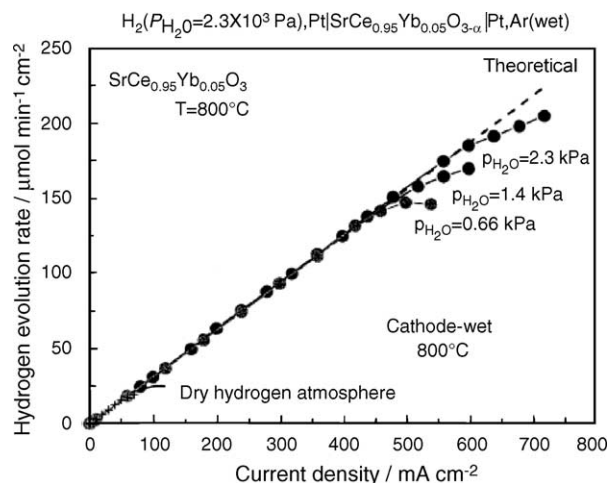

Fig. 15. Hydrogen pumping using proton-conducting ceramic: H$_2$ evolution rate at cathode vs. cell current density (reproduction from [26]). Reprinted with permission from the Electrochemical Society.

A high-temperature proton conducting membrane can be used in various applications, as a sensor of hydrogen or hydrocarbons, for separation of hydrogen, energy conversion and synthesis of chemicals as will be discussed briefly in the following sections.

3.1. Hydrogen sensors and pumps

In the open circuit mode (OCM), proton conducting electrolyte membranes can be used in hydrogen, steam, alcohol or hydrocarbon sensors (e.g. leak detector for chemical plants or for coal mines). The working principle of a sensor with proton conducting membrane is based on the principle of electrochemical hydrogen concentration cell (see Fig. 16) where the theoretical open circuit cell voltage (OCV) is $E_{cell}^0 \sim \ln(P_{H2}(I)/P_{H2}(II))$, where $P_{H2}(I)$ and $P_{H2}(II)$ are the partial pressures of hydrogen in each electrode compartment. Therefore, the OCV can be used as a signal for hydrogen activity if $P_{H2}(I)$ or $P_{H2}(II)$ is known. For hydrocarbon or alcohol sensors both one-chamber and two-chamber constructions are used [27]. In the one-chamber sensor, there are two different electrodes with different activity. Only one electrode is active for hydrocarbon oxidation in air. Therefore, separation of electrode compartments is not necessary and no standard gas is needed, which are the major advantages of this sensor variant.

As a further application of proton conducting membranes, hydrogen can be selectively separated from gas mixtures, e.g. containing compounds such as water and hydrogen disulfide, by proton pumping at close-circuit conditions [2].

3.2. Fuel cells

During the last two decades, researchers in the field of solid oxide fuel cells paid much attention to the preparation

$$p_{H2}(I) \quad > \quad p_{H2}(II)$$
$$1/2\,H_2 \leftrightharpoons H^+ + e^- \qquad H^+ + e^- \leftrightharpoons 1/2\,H_2$$

$$E^0_{cell} = \frac{RT}{2F} \ln \left(\frac{p_{H_2}(I)}{p_{H_2}(II)} \right)$$
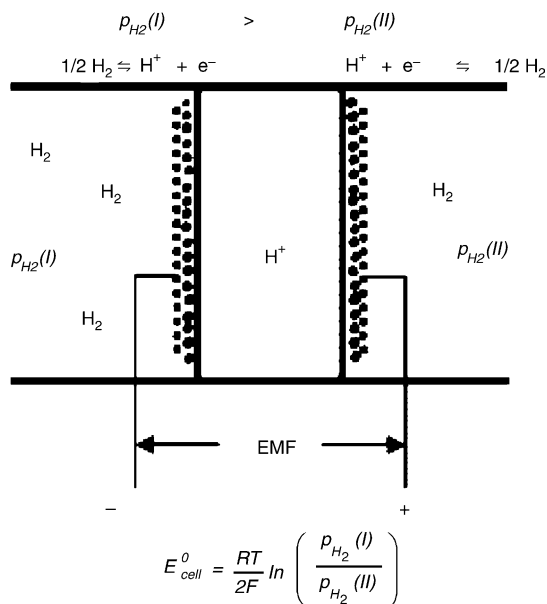
Fig. 16. Working principle of hydrogen concentration cell using a proton-conducting membrane (reproduction from [2]). Reprinted with permission from Elsevier.

and characterization of solid oxide materials with protonic conductivity [28–30]. Historically, one of first works on high-temperature proton-conducting fuel cells was published by Iwahara et al. in 1981 [31].

The interest in protonic conductors and their utilization in fuel cells is very high because complete hydrogen utilization could easily attained in a SOFC based on a protonic electrolyte. Protonic ceramic fuel cells are targeted for operation at 55–65% electrical efficiency with pipeline

natural gas as feed. This can only be achieved with greater than 90% direct methane fuel utilization. Such a high fuel utilization is made possible by two major factors. First, high thermochemical efficiency of reforming and water shift reactions at the anode is possible at the high operating temperatures of 700–800 °C. Second, water vapor is produced at the cathode where it is subsequently swept away by the air flow, rather than at the anode where it would dilute the fuel (carbon dioxide is the only anode exhaust gas).

3.3. Electrocatalytic membrane reactors

Moreover, proton conducting membranes are applicable in electrocatalytic reactors for hydrogenations and dehydrogenations of organic compounds. Several reactor concepts are illustrated in Fig. 17. Unique features of proton conducting membrane reactor concepts compared to traditional catalytic reactors are:

- hydrogen and the compounds to be hydrogenated or dehydrogenated are kept separated by the membrane,
- the chemical potential of hydrogen at the reaction sites and the reaction rate can be controlled via the electrode potential or via the electric current, and
- hydrogenation and dehydrogenation of organic compounds on either side of the membrane can be carried out simultaneously in a single unit.

In the dehydrogenative coupling of methane, the formation of ethane and ethylene was enhanced by applying an electric potential difference to the reactor [32]. Another application was the reduction of NO occurring in automobile
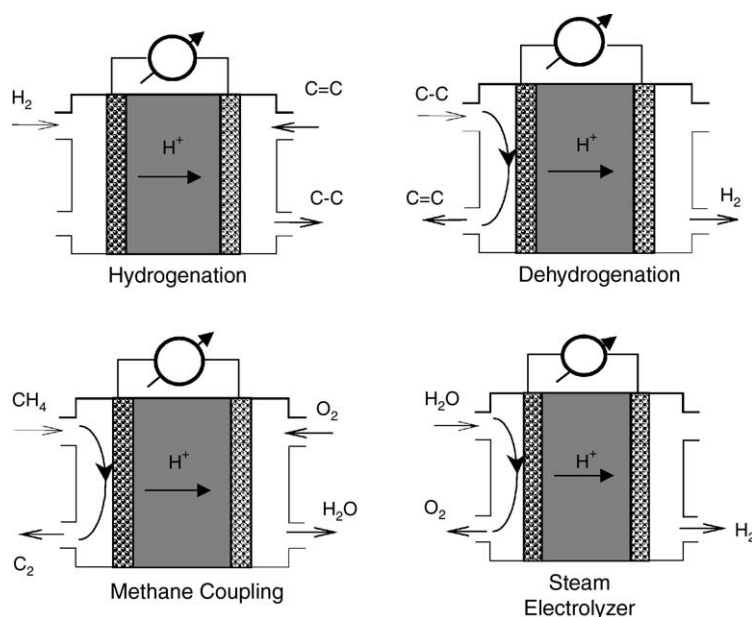

Fig. 17. Examples for the use of proton conducting membranes in electrocatalytic membranes reactors.
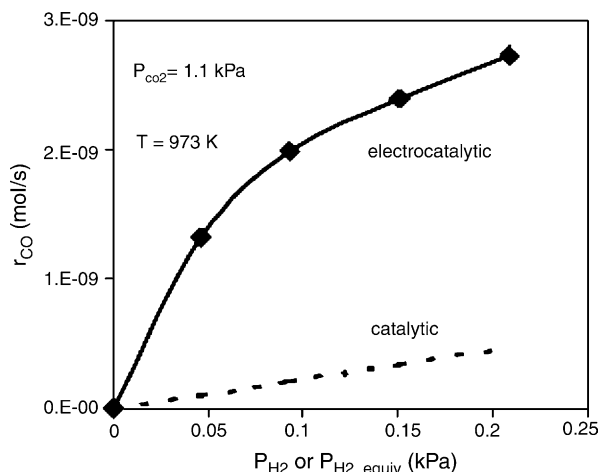
Fig. 18. Hydrogenation of carbon dioxide ($CO_2 + H_2 \rightarrow CO + H_2O$): CO formation rate vs. (equivalent) partial pressure of hydrogen (reproduction from [34]). Reprinted with permission from Elsevier.

exhaust lines [33]. The reduction of NO by hydrogen, which was produced by a steam electrolysis cell, was tested with different catalysts on the cathode side. A mixture of Pt-sponge and Sr/Al_2O_3 was found to be the most active catalyst for the preferred reduction of NO in excess of O_2. Recently, the hydrogenation of CO_2 has been demonstrated successfully with proton-conducting membranes strontia–zirconia–yttria perovskite and the working (cathodic) electrode was a polycrystalline copper film [34]. The observed reaction rates are about one order of magnitude higher than under normal catalytic conditions, if hydrogen is supplied electrochemically as presented in Fig. 18. A very recently proposed application of a high-temperature proton-conducting membrane is the dehydrogenation of propane over Pt and Pd to produce propylene and hydrogen [35].

4. Low-temperature proton conducting membrane reactors

The most established low-temperature proton conductor is the polymer electrolyte membrane (PEM) material Nafion which is commercially available from DuPont. This membrane is a fully fluorinated polymer–ether backbone having sulfonic acid groups. After solvatisation of the acid groups with water, the PEM exhibits protonic conductivity. Due to the necessity of humidification and due to limitations regarding maximum operating temperatures ($<120\,^\circ$C) of Nafion-type materials, intense research activities are nowadays going on, aiming to develop new proton conductors. The operation of PEM-based reactors, especially fuel cells in transportation, would be clearly simplified if the membranes could work without any humidification and at higher temperatures up to 200 $^\circ$C. A promising material being suitable for higher temperatures (up to 200 $^\circ$C) is polybenzimidazole (PBI) from PEMEAS (former Celanese). The humidification-free operation of PBI membranes at

higher temperatures allows higher CO concentration in hydrogen fuel cells (PEMFC) fed with reformate gas because at higher temperatures CO-adsorption at the anode catalyst (Pt) is of less importance. Other possible membranes for PEM fuel cells are polymer–ceramic composite protonic conductors [36,37], and polyaromatic polyheterocyclic materials as polysulfones (PSU), poly-ethersulfone (PES), polyetherketone (PEK), polyetherether-ketone (PEEK), and polyphenyl quinoxaline (PPQ) [38]. The latter materials have to be doped with appropriate acids to achieve the desired proton conductivity.

4.1. PEM fuel cells

Today, PEM materials are fed as low temperature proton conducting membranes in energy production where the total oxidation of the fuel with maximal energy production is the primary goal. The applications of low temperature fuel cells have reached semi-commercial stage and several test units have been launched to the market. The operation of low temperature proton conducting membrane fuel cell using hydrogen as feed is effective, and high current densities can be reached. However, the use of gaseous hydrogen as feed brings many logistic and safety problems to solve and therefore research efforts were focused over several decades to develop safe storage and transportation systems for various forms of hydrogen.

Due to the mentioned difficulties in the operation of hydrogen fuel cell, a competitive fuel cell technology operating at low temperature is the direct methanol fuel cell (DMFC), where liquid methanol-water solution is directly used as an anode feed. Handling of liquid methanol is less complicated than that of gaseous hydrogen, and therefore the DMFC is a very promising low temperature fuel cell technology especially for transportation applications. The working principle of this fuel cell is presented in Fig. 19. In a recent review [39], the status and trends of DMFC technology are discussed in detail. Severe limitation of DMFC operation is caused by the deactivation of anodic electrode catalyst (Pt/Ru) due to the irreversible adsorption of the reaction intermediate CO on the catalyst active sites. Another limitation comes from the undesired transport of methanol from the anodic compartment through the membrane to the cathodic side (methanol cross-over). The cross-over and the direct oxidation of methanol on the cathode lead to a reduced cathode potential and thereby to a reduced overall cell voltage. Detailed mathematical analysis of methanol cross-over and the transport mechanisms in PEM have been reported by Sundmacher et al. [40] and Schultz [41].

4.2. PEM reactors

The application of polymeric proton exchange mem-branes (PEM) in chemical reactors at low temperatures ($<120\,^\circ$C) is not common. Only a few examples of such
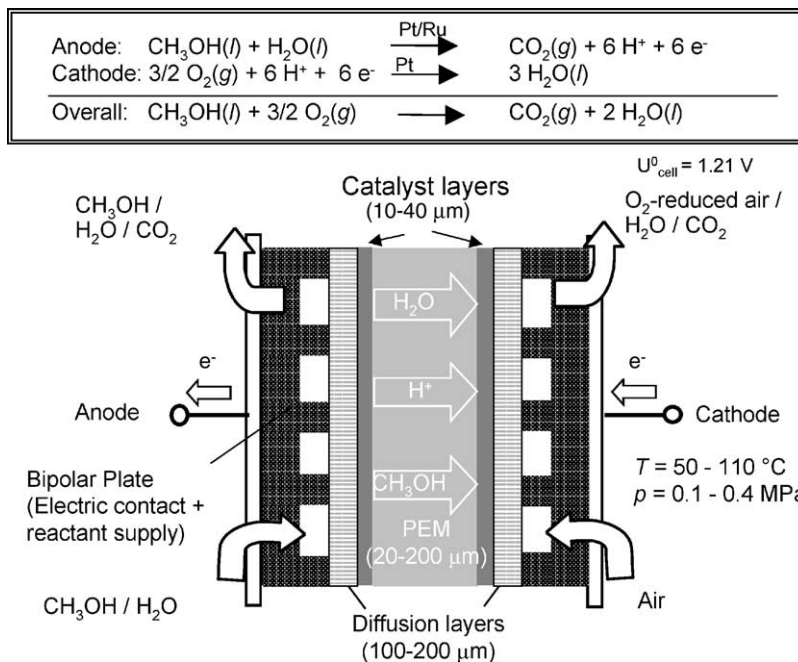
Fig. 19. Working principle of Direct methanol fuel cell (DMFC).

PEM reactors - operated in electrolysis modus or in fuel cell modus—can be found in the open literature. Theoretically these reactors can be used for specific oxidation, dehydrogenation and hydrogenation reactions, as some interesting examples in the literature show. The operation modi of these reactors depend on the reactions applied. In an optimal case, the co-generation of electrical energy and valuable chemical products has been successful. Fig. 20a and b
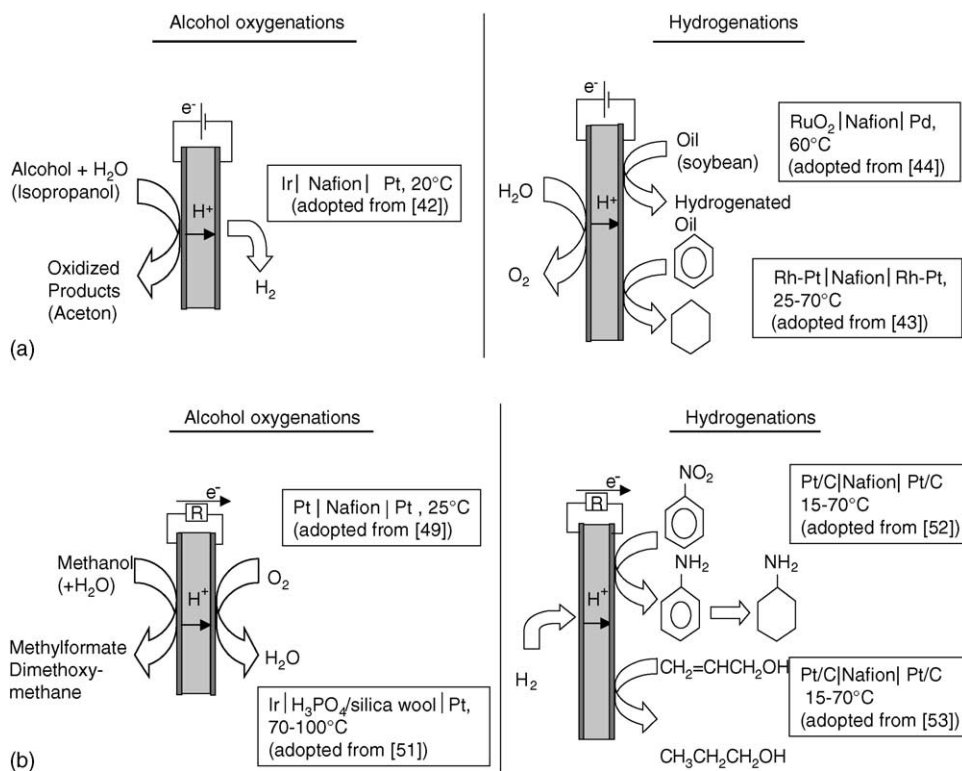

Fig. 20. (a) Proton exchange membrane (PEM) reactors: Examples for water electrolysis operating modus. (b) Proton exchange membrane (PEM) reactors: examples for fuel cell operating modus.

present schematic illustrations of PEM reactor configurations, which are discussed more detailed in the following.

4.2.1. Electrolysis operating modus

The oxidation of various aliphatic alcohols with oxygen which is produced by in situ water electrolysis can be taken as an example of electrolysis carried out in polymer electrolyte membrane reactor [42]. Water was fed together with the various aliphatic alcohols to the anodic side of Nafion 117 membrane reactor, where IrO_2 deposited on the porous titanium layer worked as anode. The hydroxyl radicals formed in the electrolysis were interacting with the anode forming the higher oxide IrO_3, which was either reactive in the alcohol oxidation or evolved gaseous oxygen in the catalyst redox reaction (IrO_3/IrO_2). The tested alcohols showed remarkable differences in reactivities, secondary alcohol, isopropanol being the most reactive, followed by ethanol and methanol, and n-propanol having clearly the lowest reactivity.

The electrolysis of water can be applied also in hydrogenation reactions, as two examples show: hydrogenation of benzene [43] or soya oil [44,45]. In both systems, the electrolysis of water was carried out on the anode, where O_2 and H^+ were formed electrochemically. Protons migrated through the membrane, and on the cathode either atomic or molecular hydrogen was consumed for hydrogenations. Initially electrochemical and non-electrochemical hydrogenation of benzene (co-feed) were compared when hydrogen was pumped as protons through the membrane, and it was evident that the production rate of cyclohexane was much higher during electrochemical reactor operation. The preliminary test of simultaneous anodic water electrolysis and cathodic benzene hydrogenation showed rapid rise in current when benzene was conducted to the cathode compared to the case of water electrolysis without benzene, as shown in Fig. 21. However, after about 10 min the electric current started to decrease gradually due to deactivation processes running at the cathodic Rh–Pt electrode.
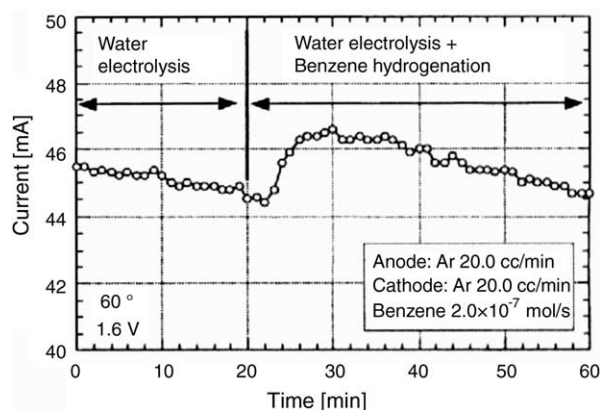

Fig. 21. Effect of simultaneous cathodic benzene hydrogenation in a PEM reactor operated in water electrolysis modus (reproduction from [43]). Reprinted with permission from Elsevier.

4.2.2. Fuel cell operating modus

The contributions of the research group of Otsuka has been considerable in the field of proton conducting membrane reactors, see e.g. [46–48]. In their first study in 1988, Otsuka et al. used a Pt-bounded Nafion 117 membrane as electrolyte at room temperature in a PEM-type membrane reactor. The studied reaction was the partial oxidation of methanol in the gas phase [49]. Under open circuit conditions ($E_{cell}^0 = 0.2$ V) the main product was CO_2 (>95% selectivity). In the electrochemical operation the valuable intermediates methyl formate and methylal were formed as main products, and only traces of CO_2 were observed. However, due to high internal cell resistances, the attained electric current and accordingly the rate of oxygenates formation remained low.

The low productivity due to the low conductivity of solid polymer electrolyte membranes in the preliminary study gave the researchers the impulse for developing a new ion conducting membrane from phosphoric acid impregnated silica wool. They have reported both successful oxidation of alkanes [50] and methanol in this system [51]. The configuration allowed them to increase the temperature, which resulted in increased conductivity. The partial oxidation of methanol was studied at temperatures between 70 to 100 °C with a cell configuration CH_3OH|noble metal|H_3PO_4 on silica wool|Pt|O_2. As catalytic electrode materials the metals Pt, Rh, Pd, Ru and Ir were tested, and the best performance was observed using Ir (anode)–Pt (cathode) for the oxidation of methanol to dimethoxy methane and methyl formate. The selectivity to the oxygenates was 72–78%, while some methanol was oxidised to CO_2. The optimal temperature was around 80 °C with regard to the oxygenate selectivity. The maximal current (34 mA cm^{-2}) was obtained however at a slightly higher temperature of 100 °C. The operation was carried out under short circuit conditions without a resistance in the external circuit. The cell performance was strongly deteriorated by the cross-over of methanol from the anode to the cathode. The methanol on the cathode is likely hindering the adsorption of oxygen on the electrocatalyst and so retards the electrochemical reduction of oxygen. The cross-over of methanol was measured to be about 5% of the feed methanol.

One successful co-generation of energy and valuable products has been published by the group of Yuan et al. [52]. The selective hydrogenation of nitrobenzene to cyclohexylamine was carried out in the fuel cell modus simultaneously producing electric power. Anode and cathode were prepared by hot pressing of carbon supported Pt-catalyst on the Nafion 117 membrane. The measurements were carried out in a batch recycle mode for nitrobenzene, obtaining an open circuit voltage of 0.32 V at 343 K. In fuel cell operation the maximum power density was 1.5 mW cm^{-2} obtained at a current density of 15 mA cm^{-2}. After a reaction time of 2 h, 8.2% conversion of nitrobenzene, the selectivities being 57.3 and 28.2% to cyclohexylamine and aniline were
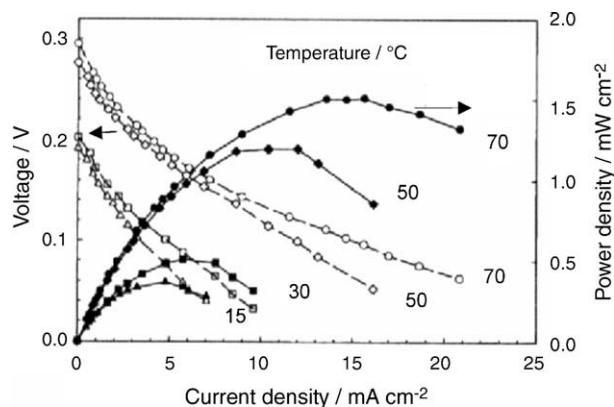
Fig. 22. Operating characteristics of PEM reactor applied for nitrobenzene hydrogenation to cyclohexylamine (reproduction from [52]). Reprinted with permission from Elsevier.

observed. In Fig. 22, the cell performance is presented as a function of current density.

Another example of fuel cell operation in chemical reactor from the same group is the hydrogenation of allyl alcohol to 1-propanol accompanied by co-generation of electrical energy [53]. The selected hydrogenation reaction might not be reasonable in the economic sense, but it can be seen as an interesting model reaction for co-generation in a PEM reactor. The open circuit potential was experimentally determined to be between $E_{\text{cell}}^0 = 0.23 - 0.27$ V although the standard open circuit potential was calculated to be 0.477 V. The maximum power density was 6.2 mW cm^{-2} at a current density of 66 mA cm^{-2}. Rather low conversions of allyl alcohol are reported (2.22% in 6 h), but the selectivity to 1-propanol was very high.

One special application of membrane reactors working in a fuel cell modus was reported by Sundmacher and Hoffman [54]. The electrochemical chlorine separation from a nitrogen stream was carried out in a PEM reactor. The reactor operated as a H$_2$/Cl$_2$ fuel cell having the open circuit voltage 1.36 V. A thin polymer electrolyte membrane layer was applied as barrier layer between anode and the liquid electrolyte (HCl) to prevent the break-through of H$_2$ bubbles into the liquid electrolyte layer. High mass transfer rates and current efficiencies were obtained when withdrawing the product HCl continuously from the electrolyte layer.

5. Concluding remarks

Solid ion conductors can be used as gas-dense membranes in various technological applications. The most important fields are electrochemical gas sensors, fuel cells, electrolyzers and electrochemical reactors where ions are pumped through the membrane by an electric field applied between the two electrodes. Solid electrolytes (SE) are distinguished by a very high selectivity with respect to mass transport of the ionic species. Concerning permeability,

these materials have to compete with porous membranes and with mixed ion electron conductors (MIEC).

With respect to high-temperature oxygen ion conductors, Solid Oxide Fuel Cells (SOFC) are still the most important field of research and application. However, nowadays new applications are investigated intensively such as the partial oxidation of light hydrocarbons to oxygenates. High-temperature proton conducting membranes offer new possibilities for designing electrochemical reactors. The thermodynamic analysis shows that hydrogen-fed SOFCs based on a proton electrolyte may have essential advantages compared to SOFCs based on oxygen ion conductors, regarding the efficiency of the transformation of chemically stored energy to electrical energy. Therefore, there is need for research on stable protonic electrolytes having high conductivity, and active electrodes working in atmospheres with a low level of humidity, both in hydrogen (anodes) and in air (cathodes).

Low-temperature proton conductors (PEM) are well-established membrane materials in hydrogen fuel cells (PEMFC) and in direct methanol fuel cells (DMFC). In this area, material optimization has to focus on the reduction of the undesired membrane cross-over fluxes of water and methanol. Composite membranes will play an important role for future generations of fuel cells. Moreover, interesting new application has been proposed where PEMs are used to carry out selective hydrogenation or selective oxidation reactions at mild conditions. In the future, PEMs might be also good candidates for the realization of microbial fuel cells (see e.g. [55]) being based on mediator-less direct electron transfer. This will require intense collaboration of biochemists and electrochemical engineers.

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