

Hydrogen Production and Fuel Cells as the Bridging Technologies towards a Sustainable Energy System

Dr. F.A. de Bruijn

Ing. G. Rietveld

Dr. R.W. van den Brink

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Hydrogen Production and Fuel Cells as the Bridging Technologies towards a Sustainable Energy System

Dr. Frank A. de Bruijn*

ECN Hydrogen and Clean Fossil Fuels

Westerduinweg 3, 1755 LE Petten, the Netherlands

email: debruijn@ecn.nl

University of Technology Eindhoven, Department of Chemical Engineering and Chemistry

Den Dolech 2, 5612 AZ Eindhoven, the Netherlands

Ing. Bert Rietveld

ECN Hydrogen and Clean Fossil Fuels

Westerduinweg 3, 1755 LE Petten, the Netherlands

email: g.rietveld@ecn.nl

Dr. Ruud W. van den Brink

ECN Hydrogen and Clean Fossil Fuels

Westerduinweg 3, 1755 LE Petten, the Netherlands

email: vandenbrink@ecn.nl

* Corresponding author

Introduction

Today's energy use, based on the conversion of fossil fuels, is not sustainable on the long term. Global warming, security of supply and local air quality are strong driving forces to change the present energy system. Given the huge global demand for energy, no single solution can be imagined to make this energy supply more efficient, less carbon intensive and more sustainable, i.e. using renewable sources to a large extent.

Hydrogen plays a pivoting role in all strategies to lower CO₂-emissions, improve the air quality of urbanised areas and increase the possibilities of covering the energy demand with energy sources other than petroleum.

In the European Union, the Hydrogen and Fuel Cell Platform has set up a Strategic Research Agenda [1] aiming at the development of technologies needed for hydrogen production, storage, transport and application in stationary and mobile systems. In addition, a Deployment Strategy [1] has been made for the market introduction of these technologies. A program of over 2 billion euros is foreseen in the 7th Framework Programme. In the United States, the Freedom Car Initiative [2] and the FutureGEN [3] projects are just two examples of a huge program on hydrogen and fuel cell technologies. The Department of Energy has a well-organised program in which clear technology development targets are set, and progress is frequently assessed. In California, demonstration fleets of fuel cell vehicles are on the road, and state legislation on emissions pose a strong driving force to clean vehicles.

In Japan, being completely dependant on fossil fuels imports, a long tradition exists in developing stationary and mobile fuel cell applications. Programs funded by the NEDO and METI departments have already resulted in hundreds of small scale micro Combined Heat and Power Units as well as fuel cell vehicles running in road demonstrations [4].

The hydrogen energy chain

The energy chain for hydrogen is schematically drawn in Figure 1. For each step in the chain, several options exist or are in development. The energy efficiency and CO₂ emission of the complete hydrogen energy chain should be taken into account when considering the introduction of hydrogen into certain applications. Optimisation of each step will be necessary to maximise the benefit of this fuel for the future. At the same time the energy use and CO₂ emissions in society as a whole must be minimised. The consequence is that selection of a primary energy source for in this case the hydrogen energy chain alone is not sufficient. The optimal selection of the use of that primary energy source is as important as well.

From the perspective of hydrogen in transport for instance, hydrogen obtained by using wind power in combination with an electrolyser leads to a near zero-emission hydrogen chain. When this wind power can be used directly to substitute fossil fuel powered electricity generation, while the hydrogen for transport is generated by methane steam reforming, the benefit for society in terms of CO₂ reduction and energy savings is two times larger.

Hydrogen Sources and Production

Hydrogen can be produced by reforming natural gas and petroleum derived fuels, by gasification of biomass and coal, and by using renewable electricity to power water electrolyzers. Longer term options as thermo-chemical splitting of water, bacteriological hydrogen production and photo-electrochemical splitting of water are investigated as well.

In this chapter we limit ourselves to a number of mid-term options that can be used when the large scale use of hydrogen needs to be supplied by cost effective

production routes using available sources, being reforming of natural gas, with CO₂ capture, and the use of electrolyzers which can be powered by renewable electricity.

The use of hydrogen in stationary and mobile applications

For road transport, fuel cells are the most efficient conversion devices for using hydrogen. For the average drive cycle, which is dominated by a power demand which is only a fraction of the maximum available power, hybrid fuel cell systems offer a clear advantage in comparison to Internal Combustion Engines, hybridised or not, when energy use, CO₂ emissions and non-greenhouse pollutants are considered.

For stationary power production, small systems (1 – 200 kWe) in which heat and power demand can be provided by fuel cells provide an opportunity to save large amounts of energy in comparison to central electricity production, where waste heat is in general not used. These systems would preferably run on natural gas, which is converted on site to hydrogen. For large scale power production, the CO₂-free production of hydrogen from natural gas and coal, with the subsequent burning of this hydrogen in the power plant, can offer the first step to reduce the CO₂ emissions from power production significantly.

We discuss both the Proton Exchange Membrane as well as the Solid Oxide Fuel Cell in this chapter (PEMFC and SOFC). Both types are in full development, the PEMFC for mobile and stationary applications, the SOFC for stationary applications as well as for auxiliary power generation for transport as well.

Hydrogen production from Natural gas

The production of syngas and hydrogen is one of the older large-scale industrial catalytic processes. The first steam reforming plant was commissioned by BASF in 1925 [5]. The worldwide annual hydrogen production is 1 billion m³/day [6].

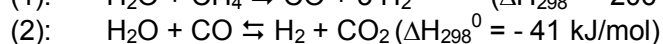
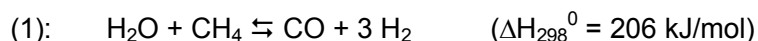
Hydrogen is mainly used in ammonia synthesis for fertilizer production (700 million m³/day) and in hydrotreating of transportation fuels. In recent years, with hydrogen being envisaged to play a very major role as a sustainable transportation fuel and for CO₂-free power generation, new methods for hydrogen production in combination with CO₂ capture and storage (CCS) are being developed. In fact, the production of pure hydrogen already involves CO₂ removal, with the CO₂ being vented or used in the food industry. For bulk production of hydrogen for energy, however, more efficient and cheaper processes are needed. This involves new process steps and new demands on the catalysts used in these processes.

Below, we will first briefly describe conventional hydrogen production. Then the combination of hydrogen production and CCS will be described. Finally, we will elaborate on two of the technologies for more efficient hydrogen production with CO₂ capture that are currently in the R&D phase, hydrogen membrane reactors and CO₂ sorption enhanced reactors.

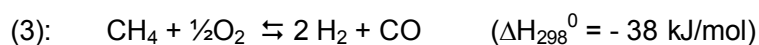
1. Conventional hydrogen production

1.1 Hydrogen production from natural gas

Steam methane reforming of methane (SMR) is the most widely practiced commercial process for the production of syngas and hydrogen: almost 50% of the world hydrogen production comes from natural gas. Two equilibrium reactions, steam reforming and the water-gas shift (WGS) reaction, are at the heart of the hydrogen production process.



Next to SMR, other technologies are used for syngas production from natural gas that involve addition of oxygen or air. The catalytic partial oxidation (CPO) reaction is given in equation (3) and in autothermal reforming (ATR) this reaction is combined with reactions (1) and (2).



ATR is used widely, although costs are relatively high due to the high capital and energy costs related to the cryogenic air separation plant (approx. 40% of the total capital costs). For large-scale plants, however, such as Gas-to-Liquid plants, but also possibly natural gas based power stations with pre-combustion CO₂ capture, ATR becomes more economic than SMR [7].

Figure 2 shows that for the production of 99% pure hydrogen, many catalytic processes are used. The desulphurisation section is used to reduce the sulphur content of the natural gas to 0.01 ppm to protect the SMR and WGS catalysts downstream. A supported Cobalt-Molybdenum catalyst (CoMoS) converts the sulphur compounds in H₂S, which is removed by a ZnO catalyst [5].

The subsequent steam reforming section is operated at very high temperatures: 850 - 900°C. The SMR catalysts themselves are already active below 400°C, but high temperatures are necessary to drive the strongly endothermic reaction forward [8]. In industry, Nickel catalysts are used in high-alloy reaction tubes, which are heated by external burners. This design is expensive and leads to heat losses, although much of the heat is recuperated. Next to Ni-catalysts, also noble metal catalysts such as supported ruthenium, platinum and rhodium are very active in steam methane reforming [9]. They are only used commercially in special applications, because their price is much higher than that of the Ni-based catalysts. Those applications are for example on-board hydrogen production for fuel cell vehicles or auxiliary power units, where compactness of the system is important.

Downstream of the reformer the CO is converted to hydrogen by two subsequent water-gas shift sections: a high-temperature shift (HTS) followed by a low-temperature shift (LTS). This is done because the equilibrium of the WGS reaction lies at the product side at lower temperatures (around 200 °C), but the reaction kinetics are faster at increasing temperature. Therefore, to reach high CO conversions, the majority of the CO is converted in a high-temperature shift (HTS) section and the remaining CO is converted in a low-temperature shift section. (LTS). HTS catalysts have magnetite (Fe₃O₄) as the active metal with chromium oxide (Cr₂O₃) added as a structure stabiliser. They operate between 320 and 500°C [10], which makes a relatively high CO-slip of a few mole% inevitable due to the thermodynamics of the shift reaction. At higher temperatures and lower steam to CO ratios, some methane may be produced as a by-product. High temperatures combined with low steam-to-CO ratios leads to reduction of the iron oxide, which causes sintering and deactivation of the catalyst. LTS catalysts contain copper as the active material, which is supported on zinc oxide (ZnO₂) and alumina (Al₂O₃). Operation temperature is between 185 and 275°C. High CO conversions can be reached at these temperatures, up to CO slip levels of 1000 ppm. As discussed above, the reaction proceeds slowly at low temperatures, so relatively large volumes of catalyst are needed. At temperatures above 275°C, the copper sinters and the catalyst loses its activity. copper is also very sensitive to sulphur poisoning, for safe operation the sulphur content of the gas should be below 0.1 ppm.

For the final steps, the purification of the hydrogen, several technologies are in use. Figure 2 shows CO₂ removal by either physical or chemical absorption followed by

conversion of the remaining CO and CO₂ into methane. Alternatively, pressure swing adsorption (PSA) is used to produce pure hydrogen and a purge second stream that contains CO, CO₂, CH₄ and hydrogen. This purge stream is used for underfiring of the reformer. A third option, which is used often in small-scale hydrogen production, is preferential oxidation of CO (PrOx). For use of hydrogen in a PEM fuel cell, CO must be removed to below 10 ppm. Some air is added to the gas exiting the LTS catalyst and at temperatures around 150°C, CO is combusted, while the hydrogen does not react. PrOx catalysts used are supported platinum catalysts and platinum-ruthenium catalysts [11].

1.2 Hydrogen production from other feedstocks

Approximately 30% of the hydrogen is produced from heavy oil and 20% from coal [6]. Lighter liquid hydrocarbons are – after desulphurisation – also converted by steam reforming on nickel catalysts. The downstream treatment of the syngas is the same as for natural gas.

Refinery residues, coke as well as coal are converted to syngas by gasification. Several gasification technologies exist, but for hydrogen and power production entrained-flow gasifiers are mainly used [12]. The two major commercially available entrained flow gasifiers are the dry-fed Shell gasifier and the slurry-fed Texaco gasifier (process is currently marketed by GE). The syngas coming out of the gas clean up section, which still contains up to 1 vol.% of sulphur compounds, can be further converted into hydrogen in two ways. Pathway A in Figure 3 shows that the sulphur containing, 'raw' gas first enters a sour gas shift catalyst.

The active components of this so-called CoMoS catalyst, Cobalt and Molybdenum, are only active as sulphides. This implies that sulphur should always be present in the gas to keep the metals in the sulphided state. The operating temperature window is between 250 and 500 °C. At higher temperatures, the metal sulphides are more easily converted into metal oxides, so the minimum necessary amount of sulphur in the feed increases with temperature. For operation at 400°C, sulphur content of the dry feed should be at least 300 ppm [13].

Subsequently, H₂S is removed from the syngas by a chemical or physical solvent. Upon regeneration of the solvent, the H₂S is fed to a Claus plant to produce elemental sulphur. CO₂ can be removed by the same solvent or in a separate absorber.

In pathway B in Figure 3, H₂S is first removed by absorption and then enters a clean gas shift section. Catalysts used are standard HTS catalysts. The use of LTS catalysts is only possible when sulphur is removed to very low levels (below 0.01 ppm), using a Rectisol (methanol) solvent [6]. Downstream the WGS section CO₂ is removed by absorption. When partial pressures are high (above 1.5 MPa, [6]) a physical solvent (e.g. methanol) can be used. Physical solvents can be easily regenerated by flashing at reduced pressures. At lower CO₂ partial pressures a chemical solvent (e.g. mono-ethyl amine (MEA)) is used, which requires energy input for steam regeneration of the solvent.

Pathway A, the sour shift case, is especially used for hydrogen production from slurry fed gasifiers. Those gasifiers produce syngas with a relatively high moisture content. Since steam is necessary in the water-gas shift section, this gas can be readily used. In addition, sulphur absorption is generally carried out at low temperature (ambient or even lower), which means that the steam is condensed out of the fuel gas. Therefore, from an efficiency point of view, the need to condense all of the steam from the fuel

prior to the sulphur removal unit would undoubtedly make the configuration in pathway B unattractive for slurry fed gasifiers.

Pathway B can be used for dry fed gasifiers, which produce a syngas with very little moisture. After sulphur removal the temperature of the syngas is increased by the addition of superheated steam.

2. Hydrogen Production with CO₂ Capture

As it is highlighted elsewhere in this book, CO₂ capture and storage (CCS) has attracted much attention as a possible opportunity to mitigate climate change. The recent publication of the special report on carbon dioxide capture and storage by the Intergovernmental Panel on Climate Change highlights the possibilities for capture of CO₂ from various sources and the storage of CO₂ in geological formations [14].

While the production of hydrogen is a relatively small source of CO₂ nowadays, it is usually produced in large installations with in many cases CO₂ separation technology already in place. Currently, the CO₂ produced from hydrogen production is used in the food industry or (in most cases) vented to the atmosphere. In the future hydrogen may well play an important role in two of the largest CO₂ emitting sectors, namely power production and transport.

2.1 CO₂ capture

For the power generation sector several options exist for the capture of CO₂ (see Figure 4). Post combustion capture removes the CO₂ from the flue gases of a power plant, using chemical solvents. Much progress is being made in reducing the energy consumption needed for the regeneration of the solvents [14], but the efficiency penalty remains relatively high. Alternatively, combustion of coal or natural gas can be carried out using pure oxygen or oxygen-rich air, in order to increase the partial pressure of CO₂ in the flue gas. Several industrial oxygen generation technologies exist, such as cryogenic air separation and PSA, but energy demands are relatively high [14]. Chemical looping combustion is an emerging technology in which a solid oxygen carrier is circulated between two beds. A combustor in which a metal oxide (typically NiO) is reduced by natural gas under formation of steam, CO₂ and a hot flue gas and a regenerator in which the depleted oxygen carrier is regenerated using air [15].

The third option, pre-combustion CO₂ capture, involves the conversion of the fuel into a hydrogen and CO₂ mixture and separating the two compounds prior to combustion. The CO₂ is compressed and made ready for transport and storage. The hydrogen is can either be compressed and transported for use as automotive fuel, or be used directly for power generation. The hydrogen production route can in principle be similar to the technologies described above: steam reforming or coal gasification followed by water-gas shift and CO₂ separation. There are, however, a few considerations that make the pre-combustion CO₂ capture different from conventional hydrogen production.

1. CO₂ must be relatively pure. The presence of non-condensables such as nitrogen or methane in the CO₂ stream make compression of the CO₂ to approx. 100 bar very difficult.
2. The efficiency and costs of the complete power production cycle or well to wheel cycle dictate the technology choices. Industrial hydrogen or ammonia synthesis are relatively high-value products compared to electricity and automotive fuel.
3. In a Natural Gas Combined Cycle (NGCC) or an Integrated Gasification Combined Cycle (IGCC), the steam produced from the waste heat boiler is

converted into extra electrical power in the steam turbines. So for hydrogen production, the steam use must be kept as low as possible.

3. Novel processes for hydrogen production with CO₂ capture

For combined hydrogen production and CO₂ capture several novel technologies are in development, most of them for the application in a pre-combustion CO₂ capture combined cycle. The main focus is to reduce the efficiency penalties and other associated costs of CO₂ capture. Below the most important technologies in the R&D phase, membrane reactors and sorption-enhanced reactors, are described and special attention is paid to the catalytic aspects.

3.1 Hydrogen membrane reactors

Hydrogen-selective membranes inside a reactor for reforming remove hydrogen from the reaction zone and, as a consequence of Le Chatelier's Principle¹, the equilibrium of reaction (1) is shifted to the product side. This makes it possible to reach high hydrogen conversions at lower temperatures than ordinary reforming. Hydrogen membranes are also applied in the water-gas shift reaction, which enables the use of just one shift reactor, which can be operated at higher temperatures than the LTS catalyst and still reach high CO conversions.

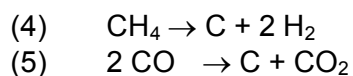
Hydrogen permeates through the membrane and the gases that do not permeate, the so-called retentate stream, contain high concentration of CO₂, next to some unconverted methane, CO and non-permeated hydrogen (see Figure 5). The driving force of the separation process is provided by the difference in partial hydrogen pressure on both sides of the membrane. This can be achieved by applying a pressure difference over the membrane or by using a flow of a sweep gas (typically nitrogen or steam) on the permeate side [14]. In most cases both a pressure difference and sweep gas are applied.

Membrane materials have to withstand a pressure difference and relatively high temperatures (500 °C and up). Microporous ceramic membranes have been used, but they have a relatively low selectivity for hydrogen [16]. Most commonly studied membranes are dense palladium or palladium-silver alloy membranes [17-22]. Alloying the Pd membrane with silver is necessary to prevent embrittlement of the Pd layer due to the phase change between the α - and β -phase upon cooling the membrane down from e.g. 500°C to ambient in a hydrogen containing atmosphere. Generally, the membrane consists of a thin (1-5 μm) layer of Pd-Ag-alloy, supported on a porous metal [18,22] or ceramic substrate [21]. Also high-temperature (700°C and higher) mixed proton conducting ceramic membranes have been developed for steam reforming applications [23].

Shu et al. [18] provides one of the earlier examples of experimental steam reforming in a membrane reactor. They used a commercial Ni/Al₂O₃ catalyst and two types of membrane: Pd and Pd-Ag on a stainless steel support. Methane conversion was 51% in presence of the Pd-Ag membrane at 500°C and 136 kPa, vs. 37% in absence of a membrane. Conversion with the pure Pd membrane was somewhat lower. Lægsgaard-Jørgensen et al [19] used an unsupported 100 μm wall thickness Pd-Ag membrane combined with a commercial Ni/MgO steam reforming catalyst. They observed a strong positive effect of pressure on methane conversion at 500°C, although thermodynamics of the SMR reaction are negatively influenced by pressure. At 1 MPa methane conversion was 61% and to reach this conversion without a membrane a temperature of 707°C is necessary.

¹ Le Chatelier's Principle states that "any inhomogeneity that somehow develops in a system should induce a process that tends to eradicate the inhomogeneity".

One of the possible problems in a steam reforming membrane reactor is the formation of carbon. Carbon can be formed either by cracking of methane (reaction 4) or the Boudouard reaction (reaction 5).



Whether a driving force for carbon formation exists is dictated by thermodynamics, so it is dependant on reaction temperature and pressure, and the H/C and O/C ratios in the system (see Figure 6). By removing hydrogen from the reaction zone, the H/C ratio is decreasing and the system moves closer to the thermodynamic area where carbon formation is likely. The arrow in Figure 6 labeled SMR is equal to a reforming mixture with a steam-to-carbon ratio of 3. When hydrogen is removed by a membrane the H/C ratio decreases, but stays out of the thermodynamic carbon formation region, even at 400°C (in contrast with autothermal reforming, ATR, however). Lægsgaard-Jørgensen et al. [19] calculated that at 500°C and 7 bar, a steam-to-carbon ratio of higher than 2.5 should be used to avoid carbon formation in a membrane reactor. It must be noted, however, that on Ni-catalysts even outside the thermodynamic region, carbon formation has been observed [5]. Carbon formation can be suppressed by adding promoters to the Nickel catalyst, such as potassium [8].

The point labeled DR in Figure 6 represents the conditions for dry reforming (reaction 6), with a CO₂/CH₄ ratio of 2.



For dry reforming, carbon formation is very likely, especially when carried out in a membrane reactor [24]. For this application noble metals are used, that are intrinsically less prone to carbon formation, because, unlike Nickel, they do not dissolve carbon. Irusta et al. [24] show above equilibrium methane conversion in a reactor equipped with a self-supported Pd-Ag tube. Small amounts of coke formation on their Rh/La₂O₃/SiO₂ catalyst were observed, but this is reported not to have any effect on activity.

Lægsgaard-Jørgensen et al. [19] calculated that the reaction rate of the reactions involved in SMR is much higher than the rate of penetration of methane through the membrane. Lin et al. [20] observed that the methane conversion strongly depends on the space velocity and the amount of methane per membrane surface area (load-to-surface ratio). Since the transport of hydrogen through the Pd-layer of a membrane is believed to be rate limiting [19], the development of thin, yet stable layers of Pd-Ag with a high permeability are important goals in membrane R&D. The Energy Research Centre of the Netherlands (ECN) has produced coated ceramic tubes of 80 cm length with a smooth 3-5 µm thick Pd-Ag layer on top made by electroless plating [21]. Sintef in Norway developed a novel method, magnetron sputtering, to make very thin Pd-Ag layers of 1-5 µm, with a very high permeance [22].

3.2 Sorption-enhanced reforming and water-gas shift

Like with the membrane reactors, in sorption-enhanced reforming (SER) or water-gas shift (SEWGS) reactors one of the products is extracted from the reaction zone, thus shifting the reaction equilibrium to the product side. In SER and SEWGS the SMR or WGS catalyst is mixed with a CO₂ sorbent ("acceptor"). The CO₂ produced during the reaction is absorbed and the reverse reaction cannot occur (Figure 7). The hydrogen stream also contains unconverted methane and CO. For production of pure hydrogen

an extra hydrogen purification step is needed, for application of SER in pre-combustion CO₂ capture for power generation, the gas can be fed directly to the gas turbine [25].

SER and SEWGS are batch processes: at some point the sorbent is saturated with CO₂ and the equilibrium reaction occurs again. The sorbent subsequently has to be regenerated by either reducing the pressure (pressure swing mode) or increasing the temperature (temperature swing mode). Purge gas is steam, because it can be easily condensed out of the CO₂ stream, yielding pure CO₂ ready for compression and transport (Figure 8). Table x1 gives an overview of the most important CO₂ sorbents studied for SER and SEWGS.

Table x1 *The three most studied classes of CO₂ sorbents in SER and SEWGS.*

Sorbent	Mode	T ads	T des	Reference
K-promoted hydrotalcite-based compound	PS	400 - 500°C	400 - 500°C	[25-29]
Ca-oxide, dolomite	TS	400 - 700°C	> 800 °C	[30-32]
Li-zirconates and silicates	TS	500 - 650°C	700 - 800°C	[33-34]

PS = Pressure Swing, TS = Temperature Swing

Hydrotalcites are layered double hydroxides with the general formula $Mg_6Al_2(OH)_{16}[CO_3] \cdot 4H_2O$. Loading these compounds with potassium carbonate strongly increases their CO₂ uptake [25,35]. It must be noted, that the hydrotalcite structure already breaks down below 400°C [26] into a mixed metal oxide. Air Products and Chemicals pioneered the use of these potassium carbonate promoted hydrotalcite-based materials (K-HTC) for sorption-enhanced reforming of methane [26]. Mixing the K-HTC with a SMR catalyst in a 2:1 ratio, gave high (90%+) conversions of methane at temperatures as low as 400°C. In first instance Ni-based catalysts were used, but they were not resistant to the environment during the regeneration (desorption) step of the cycle. Instead, noble-metal based catalysts were used.

Ding and Alpay also studied sorption-enhanced reforming with K-HTC as sorbent [28], using a commercial Ni-based catalyst. They found that the SER process benefits from higher pressures and that lower steam to methane ratios can be used than in ordinary reforming. Reijers et al. [25] show that K-HTC is an effective sorbent between 400 and 500°C, with an CO₂ uptake of approx. 0.2 mmol/g. This capacity is low compared to calcium oxides and lithium zirconates. Above 500°C, the CO₂ sorption capacity of K-HTC decreases rapidly to zero.

Reijers et al. [25], using a commercial noble-metal reforming catalyst, show that high methane conversions of more than 95% are reached at 400°C, while equilibrium conversion is only 54% at these conditions. Figure 9 shows that methane breaks through before CO₂, and that the regeneration part of the cycle is longer than the reaction part. The latter results in a high amount of steam necessary for regeneration, which is very detrimental for the overall efficiency of the system [37]. Using the thermodynamics of the SMR reaction, the conversion of methane can be calculated at a certain equilibrium CO₂ concentration at the exit of the reactor. It follows that for 99% CH₄ conversion at 400°C, the CO₂ concentration must be well

below 1 ppm, which only occurs for a short period in the beginning of an adsorption cycle [37]. At higher temperatures higher CH₄ conversions can be reached at more practical CO₂ output levels, but unfortunately K-HTC cannot be used above 500°C.

K-HTC is used more successfully for sorption-enhanced water-gas shift [27]. Breakthrough of CO occurs at the same time as breakthrough of CO₂ [37] and the amount of steam necessary for desorption can be kept relatively low [27]. A commercial high-temperature shift catalyst can be used. During desorption in steam, the catalyst can be oxidised, so it is necessary to add some hydrogen to the purge steam [27].

Calcium oxide, limestone or dolomite (a mineral composed of CaO en MgO) are used as CO₂ acceptors in SER [30] and SEWGS [38]. Calcium oxide acts as a CO₂ acceptor at a wide range of temperatures between 450 and 700 °C. For regeneration high temperatures are necessary: Balasubramanian et al. use a regeneration temperature of 975°C [30]. The energy released by the conversion of CaO into CaCO₃ is 170 kJ/mol [25], which is almost enough to supply the heat for the SMR reaction.

For WGS, commercial catalysts are only operated up to 550°C and no catalysts are available for higher temperatures, because adverse equilibrium conversion makes the process impractical in absence of a CO₂ sorbent. Han and Harrison [38] show that at 550°C dolomite and limestone have a sufficiently high WGS activity. For SMR a conventional Ni SMR catalyst is used in a 1:1 ratio with CaO [30]. Meyer et al. [32] also used a Ni-based catalyst in combination with limestone and dolomite, and achieved CH₄ conversions of 95% at 675 °C while the CH₄ conversion at equilibrium was 75%.

A general problem with CaO, limestone and dolomite is the limited lifetime of the CO₂ acceptor material [32]. The capacity for CO₂ is initially very high, but is depleted to almost zero after several cycles. Although the minerals are relatively cheap, this would imply a very considerable stream of waste material coming out of the hydrogen plant. Novel materials are in development with a higher stability [39].

Li-zirconates (Li₂ZrO₃) and Li-orthosilicates (Li₄SiO₄) are also active as high temperature CO₂ acceptors. The carbonation of Li₂ZrO₃ is accompanied by a heat release of 160 kJ/mol [34]. The theoretical absorption capacity is huge: 28 wt% CO₂ for Li₂ZrO₃. For Li₂ZrO₃ the kinetics of CO₂ uptake are slow, and modeling of the SER using Li₂ZrO₃ shows that this limits the applicability of these compounds [34]. Novel specifications of these materials, however, have a better CO₂ uptake kinetics [40]. Lithium orthosilicate has been developed by Toshiba and has more favorable CO₂ uptake kinetics than lithium zirconate [33], as well as reduced volume changes during the reaction-regeneration cycles.

4. Conclusions and catalytic challenges

To improve the efficiency of combined hydrogen production and CO₂ capture, several technologies are in development that combine catalytic reactions and separation of either hydrogen or CO₂. Major targeted area of application are the production of bulk hydrogen as a transport fuel and electricity production with pre-combustion CO₂ capture.

The following catalytic and material challenges can be extracted from the overview of the literature on membrane and sorption-enhanced reforming:

- There is a need for low-cost methane steam reforming catalysts that are active at low temperature and resistant to coke formation under membrane

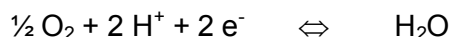
reactor conditions. Also low-cost (Ni-based) catalysts are needed that can withstand regeneration conditions in a sorption-enhanced reformer.

- Although in many WGS applications cases conventional HTS catalysts are used, for some applications water-gas shift catalysts may be needed that operate at temperatures above the current industrial standard. Also stability in a steam atmosphere, during regeneration of a SEWGS reactor, is an issue.
- CO₂ sorbents should combine a high CO₂ capacity, favourable CO₂ uptake kinetics, low-energy input for regeneration and high stability during cycling. For application of sorption-enhanced water-gas shift in coal gasification gas, sulphur resistance is an issue. Still much development work is needed in this area. Moreover, also the understanding of the underlying mechanisms of CO₂ sorption in especially promoted hydrotalcite-based materials, and Li-zirconates and orthosilicates is still very limited, which makes development of better sorbents more difficult.
- For Pd-Ag membranes the manufacture of defect-free thin layers, reproducible in production, and stability are major issues. Also sulphur resistance and the interaction of the membrane with the catalyst material is important.

Electrochemical hydrogen production and conversion

Kinetics of the Electrochemical hydrogen-oxygen processes

Fuel cells and electrolyzers are each other's counterparts for the electrochemical conversion, respectively generation, of hydrogen and oxygen:



For the overall reaction:



The electrochemical rate of an oxidation/reduction reaction is expressed as:

$$I_{\text{ox}} = n \cdot k^0 \cdot F \cdot A \cdot C_{\text{ox},s} \cdot \exp[(1-\alpha) \cdot nF/RT] \cdot (E - E^0)$$

$$I_{\text{red}} = n \cdot k^0 \cdot F \cdot A \cdot C_{\text{red},s} \cdot \exp[-\alpha \cdot nF/RT] \cdot (E - E^0)$$

in which

I	=	current density of reaction, in $\text{A}\cdot\text{cm}^{-2}$
n	=	number of electrons in reaction
k^0	=	rate constant, in s^{-1}
F	=	Faraday's constant, 96484.56 C/mol
A	=	electrode surface area, in cm^2
$C_{\text{ox},s}$	=	concentration of species to be oxidized, in $\text{mol}\cdot\text{cm}^{-3}$, at electrode surface
α	=	transfer coefficient, giving the symmetry of the activation barrier, often taken to be 0.5
R	=	gas constant, 8.314
E	=	electrode potential, V
E^0	=	standard potential of electrochemical reaction, 0V for the H^+/H_2 couple and 1.229 V for the $\text{H}_2\text{O}/\text{O}_2$ couple

Electrochemistry is in many aspects directly comparable to the concepts known in heterogeneous catalysis. In electrochemistry, the main driving force for the electrochemical reaction is the difference between the electrode potential and the standard potential, $(E - E^0)$, also called the overpotential. Large overpotentials, however, reduce the efficiency of the electrochemical process. Electrode optimisation is therefore aimed at the maximisation of the rate constant k , which is determined by the catalytic properties of the electrode surface, maximisation of the surface area A , and by minimisation of transport losses, resulting in maximum concentration of the reactants.

Figure 10 gives a schematic presentation of the current-voltage characteristics of hydrogen and oxygen on platinum. The theoretical open circuit cell voltage at 25 °C and standard conditions is 1.229 V, for both the fuel cell and electrolyser.

For the reaction of hydrogen and oxygen to generate a current in a fuel cell, the anode needs to be polarised more positive than 0V vs NHE (Normal Hydrogen Electrode, the reference potential for all electrochemical reactions) for the oxidation of hydrogen, while the cathode needs to be polarised more negative than 1.229 V vs NHE for the reduction of oxygen.

As hydrogen oxidation is on a suitable electrode a very fast reaction, only a small polarisation is needed to generate a significant current density, typically 20 - 50 mV. The oxygen reduction is a slow reaction, even at the most suitable electrode. To generate a current which is the same as that of the hydrogen oxidation, a much larger polarisation is

needed, at least 300 - 500 mV. A fuel cell voltage of 0.5 - 0.7 V is obtained at normal operation.

For the electrolyser to generate hydrogen and oxygen by putting electric energy in the cell the polarisation is the mirror-image of the fuel cells: the polarisation needs to be negative relative to the standard potential for the facile hydrogen evolution while a polarisation to more positive potentials is required for the slow oxygen evolution. An electrolyser voltage of 1.6 - 2 V is obtained at the production rate that is often requested for practical purposes.

Hydrogen Production by water electrolysis

The electrolysis process is a well-known process dating back to the 19th century, in which DC electricity is used to split water into hydrogen at the cathode and oxygen at the anode. The principle is illustrated for an acid electrolyser in Figure 11. Electrolysis is the most obvious way to produce hydrogen from wind energy, solar energy and hydropower electricity. This does not necessarily mean that it is the best use of these renewable sources. Direct use of the electricity in fact leads to more avoided CO₂ emissions and primary energy use, as long as the electricity mix in most countries is dominated by fossil fuels. For the long term however, hydrogen production from renewable electricity is an attractive contribution in the overall mix of options for hydrogen production.

Current electrolyser technology was originally developed for local hydrogen production to meet industrial demand for high purity hydrogen. Using this technology for hydrogen vehicle fuelling stations leads to an estimated untaxed price of hydrogen of \$4-8 per kg [41] and more than \$10 [42] per kg hydrogen for local hydrogen production on fuelling stations, whereas the target retail cost is \$2.75 per kg hydrogen [43]. The cost breakdown shows that both capital cost as well as electricity cost are important contributors to the high overall cost.

The development of electrolyser technology for the production of hydrogen as a vehicle fuel is aimed at several issues:

1. increase of the electrolyser efficiency to reduce electricity cost
2. reduction of capital cost
3. increase of pressure level of hydrogen output of the electrolyser

Three types of electrolysers can be discerned:

1. alkaline electrolysers
2. solid polymer electrolysers
3. solid oxide electrolysers

For the efficiency calculation for the electrolyser, the operating cell voltage is to be divided by 1.48 V, which is the voltage corresponding to the higher heating value of hydrogen. Other often used numbers for efficiency calculations are the kWh needed for the production of 1 Nm³ of hydrogen, which is 3.54 kWh, or of 1 kg of hydrogen, which is 39.41 kWh. All electrolyser efficiencies with liquid water feed quoted below are higher heating value efficiencies.

Alkaline electrolysers are at an industrial stage, especially commercialised for on-site production of ultrapure hydrogen for industrial applications. In general, this hydrogen is needed at low to moderate pressure, and the cost demand is set in comparison to the alternative, which is in general the supply by tube trailers. High purity water is fed to the electrolyser. State-of-the-art commercial alkaline electrolysers typically operate at HHV systems efficiency of 60 - 75% [44]. Current densities of alkaline electrolysers lie between 0.2 - 0.4 A.cm⁻² [45,46]. Hydrogen production capacities are between 10 and 500 Nm³.hr⁻¹ [44,46]. It appears that alkaline electrolysers of the most-used designs are not very suitable for the variable input power [46] that is to be expected when using renewable electricity.

A clear advantage of alkaline electrolyzers is the use of nickel based electrodes, thus avoiding the use of precious metals. Catalytic research is aimed at the development of more active anodes and cathodes, primarily the development of high surface area, stable structures. Nickel-cobalt spinel electrodes for oxygen evolution and high surface area nickel and nickel cobalt electrodes for hydrogen evolution are shown at the laboratory scale to lead to a decrease in electrolyzer cell voltage [47]. More active electrodes can lead to more compact electrolyzers with lower overall systems cost.

For hydrogen production as an energy carrier, it is beneficial to produce the hydrogen at high pressure. The Solid Polymer Electrolyzer (SPE), or Proton Exchange Membrane Electrolyzer (PEME) offer the best opportunity to generate high pressure hydrogen. The polymer membrane can withstand the pressure differences that can always occur when working at elevated pressure much easier than the alkaline cells containing liquid electrolyte. By producing hydrogen at high pressure in the electrolyzer, the use of mechanical compression can be avoided, which poses high maintenance costs and extra capital investment. It is also more suitable to use with varying power conditions, in comparison to alkaline electrolyzers. Most R&D today is directed to SPE.

As the SPE is an acid electrolyzer, noble metal electrodes are preferred for high current density operation.

SPE electrolyzers are at present available at a scale of 0.5 - 10 Nm³ hydrogen per hour at an output pressure up to 200 bar. The available systems operate at a rather poor overall efficiency, between 50 - 70 % [44,48]. The projected price level of these systems, at industrial production level, is at least a factor of 3 - 5 too high.

Platinum on carbon is generally used for the hydrogen producing cathode, whereas iridium or iridium oxide is used as the oxygen producing anode [49]. At cell level, current densities of more than 1 A.cm⁻² at an electrolyzer voltage of 1.7 V (i.e. at 87% efficiency) are demonstrated, using noble metal loadings of 0.6 mg.cm⁻² at the cathode and 1.5 - 2 mg.cm⁻² at the anode [49].

Due to the high loading and cost of iridium, binary and ternary mixtures are used in alternative anodes, such as IrO₂/RuO₂ and IrO₂/RuO₂/SnO₂, thus decreasing the use of iridium [49]. One should however question the long-term stability of these anodes, taking into account the stability domains of ruthenium and tin in acid media [50]. For the hydrogen evolution, where corrosion conditions are less severe, nickel alloys are under investigation [51].

A concern for alkaline as well as solid polymer electrolyzers should be the sensitivity of the electrolyzers for contaminants in the feed water. The minimum required water quality of an industrial Solid polymer electrolyzer is ASTM type II water [48], which contains at maximum 5 µg.l⁻¹ of sodium and chlorine, and 3 µg.l⁻¹ SiO₂ [52]. It should have a maximum conductivity of 0.25 µS.cm⁻¹. Clean drinking water meeting Dutch standards contains around 60 mg/l of sodium, 80 mg/l of chlorine and has a conductivity of 55 µS.cm⁻¹ [53]. For both electrolyzers, contaminating ions can inhibit the electrochemical reactions, leading to lower power densities and/or efficiencies. In addition, the contaminants can react themselves, leading to poisoning of the electrodes and/or contaminating the product gases. In case of the SPE electrolyzer, ions are easily exchanged with the protons of the membrane, leading to lower membrane conductivity. For hydrogen production for industrial processes, it is not an issue to process the feed water to meet the water quality requirements. When hydrogen is to be produced as an energy carrier, all systems components adding to systems complexity, cost and energy use are highly unwelcome. These new requirements could lead to the need for alternative electrode materials, which are less sensitive to specific adsorption of foreign ions. Poisoning of the membrane is a non-catalytic issue but should be addressed as well.

For both low temperature electrolyzers, the biggest gain in efficiency is to be expected from improvement in Balance of Plant components, taking into account the big gap between cell efficiency, in the 80-90% range, and the system efficiency, in the 50-60% range. In the case of SPE electrolyzers catalytic research should therefore be directed

tomaking the catalysts, more tolerant to contaminants,. In the case of alkaline electrolyzers, in addition to this more active electrodes could lower capital costs.

Solid Oxide Electrolyzers, SOE, are in development for steam electrolysis. As electrolysis is an endothermic process, supply of waste heat can be used beneficially to reduce the electrolyser voltage, and thus increase its electrical efficiency. Combination with nuclear power generation and geothermal heat sources is often encountered in development programs for the SOE.

The simplest SOE electrolyser splits water into hydrogen and oxygen. Another option is electrolysis of CO₂ and H₂O, which yields syngas, a mixture of CO and H₂ [54]. The syngas can be synthesized further into ethanol or methane. In the conventional steam electrolyser, air is supplied to the anode side. Increased efficiency can be achieved by supplying CH₄ (natural gas) to the anode which reduces the required electricity for driving oxygen ions against the concentration gradient across the membrane [55]. In the case of total oxidation of methane, the cheap natural gas just replaces expensive electrical energy. In an advanced device, a catalyst could promote partial oxidation and produce syngas. In this option hydrogen is produced at both the anode and the cathode.

Generally state-of-the-art, zirconia based fuel cells are investigated for SOE operation, with LSM (strontium doped lanthanum doped manganite) for the anode and nickel zirconia cermets for the cathode [56]. A specific problem of Ni-based cathode is oxidation at high oxygen (steam) partial pressures. Adding hydrogen to the steam solves this problem but reduces efficiency and increases system complexity. Alternative materials, providing high catalytic activity for the electrolysis reaction and high chemical stability would simplify the system and reduce costs.

The ultimate catalysis challenge is provided by the reversible SOFC, which can be switched between electrolyser and fuel cell mode. In this case, for achieving high efficiency in both modes, the electrodes should combine catalytic activity for both reactions, apart from chemical stability in reducing and oxidising gas environments.

Proton Exchange Membrane Fuel Cells

The PEMFC (Proton Exchange Membrane Fuel Cell) is a fuel cell with a proton conducting fluorinated polymer as electrolyte. A schematic drawing of the PEMFC is given in Figure 12. At the anode, hydrogen is oxidized to protons. At the cathode, oxygen from air is reduced to water. The PEMFC is in development for various applications. Transport is the main driving application for the development of the PEMFC, with the toughest specifications with respect to cost, power density and operating conditions. Most car manufacturers aim at fuel cell systems for drivelines operating on pure hydrogen. For auxiliary power systems for passenger cars, trucks, ships and aircrafts, on board hydrogen generation from diesel and kerosine is still the preferred option. In this case, hydrogen is fed to the anode as part of a mixture with carbon dioxide, water, nitrogen and small amounts of carbon monoxide and other contaminants. Such a mixture is generally called "reformat".

For the stationary generation of heat and power the PEMFC is in development as well. Fuel Cell systems for combined heat and power generation mostly run on natural gas, and sometimes on biogas. Reformat is fed to the anode in these stationary systems. Only for backup power systems, which are designed for only a limited operating time, pure hydrogen is often used as fuel for the anode.

The development for stationary applications is aimed at different specifications, but the materials development mainly coincides with that for transport applications. The operating life time for stationary fuel cells is however much longer than for use in cars, 40,000 hours or more versus 5,000 hours for passenger cars. Fuel cells in cars on the other hand will experience more voltage cycling as well as atart/stop cycles.

The PEMFC is technically in quite an advanced status. Fuel Cell systems for both transport as well as stationary applications exist in a wide variety and are being operated

in demonstration programs under practical conditions [57]. For large scale market introduction, cost has to be reduced significantly, and durability must be improved. Both items cannot be solved by clever engineering only, but require new materials as well.

The PEMFC and its components are displayed in Figure 13. The electrodes, where the catalytic reactions take place, have a complex structure, as is displayed in Figure 14 for the cathode. Note that although the reactants and products for the anode differ from that at the cathode, the anode structure is similar to that of the cathode.

For a fast catalytic reaction, free access of gas, electrons, protons and water is needed. This leads to a best compromise of the volume fractions of proton conducting polymer, electron conducting carbon, active sites and void space.

A current-voltage curve of a PEMFC is displayed in Figure 15. It gives for a given composition at one set of conditions the relation between the current density and the cell voltage. The fuel cell electrical efficiency is directly proportional to the fuel cell voltage

ΔE_{cell} :

$$\text{Eff}_{\text{FC, LHV}} = \Delta E_{\text{cell}} / 1.23 \text{ V}, \text{ or } \text{Eff}_{\text{FC, HHV}} = \Delta E_{\text{cell}} / 1.48 \text{ V},$$

for the lower heating efficiency and the higher heating efficiency respectively.

There is a clear trade-off between power density (voltage * current density) and efficiency. Operating the fuel cell at a high efficiency leads to such a low power density that the investment factor becomes too high. Therefore most fuel cells are operated at a maximum cell voltage of 0.7 V, giving a cell LHV efficiency of 57%. Opposed to internal combustion engines, the operation at low power demands, e.g. when idling, leads to higher efficiencies of the fuel cell.

In the current voltage curve in Figure 15, three different regions can be discerned. At low current densities, the performance is kinetically limited. In the linear part, determined by ohmic losses are significant. At high current densities, the mass transport losses dominate.

The PEMFC uses platinum on carbon catalysts for the anode and the cathode. State of the art electrodes contain around 0.2 - 0.4 mg.cm⁻² platinum, generating a power density of 0.5 - 0.7 W.cm⁻². Using a total loading of 0.6 mg.cm⁻² and a power output of 0.5 W.cm⁻², the platinum usage amounts to 1.2 g.kWe⁻¹. It has however been demonstrated that fuel cells with 0.4 g Pt.kWe⁻¹ are achievable when using clean hydrogen and air [58]. The long term stability of such cells is however not known yet, and the use of reformate prescribes higher loadings of PtRu at the anode, 0.2 mg_{PtRu}.cm⁻² at minimum. The ultimate goal is to lower the platinum usage to 0.2 g Pt.kWe⁻¹.

The use of noble metals is an important factor in the cost of the fuel cell. Whereas the cost of many components drop when the scale of manufacturing increases, this is not the case for the noble metal catalysts. The concern of a real shortage of platinum in case of large scale use of fuel cells in vehicles has been proven not to be substantiated [59], but this is based on a significant reduction of its use to 15 g/vehicle, corresponding to the 0.2 g Pt.kWe⁻¹ mentioned before. The key issue is to minimize the amount of platinum per kW fuel cell power, while maintaining the power density of the present state-of-the-art. It makes no sense to substitute platinum by another metal which leads to a reduction of the power density of several factors.

The catalysts used as a base for electrode manufacturing, consist of high loadings of noble metal on carbon, of 40 wt% or even higher. These high loadings are used to render a thin electrode with high enough amount of active sites, typically 10 μm thick. The platinum particle size are even at these high noble metal loadings in the range of 2-3 nm [60]

Catalysts for hydrogen oxidation (anodes)

When using pure hydrogen as fuel, low amounts of platinum can be used at the anode, as the oxidation of hydrogen has a high exchange current density. Lowering the loading of platinum at the anode to 0.05 mg.cm^{-2} is possible without a significant loss in performance [58]. When reformed fuel is used, platinum cannot be used, as it is too easily poisoned by CO. Even CO_2 has a negative impact, through the reverse water gas shift reaction which leads to CO formation [61].

Platinum alloys offer better tolerance towards CO. Especially PtRu and PtMo alloys show superior tolerance towards CO [62]. Nonetheless, performance of the presently known catalysts is far from satisfactory.

Figure 16 shows fuel cell stack performance of a 1 kWe atmospheric PEMFC stack using PtRu anodes, operating on various gas compositions. As can be clearly seen, already small concentrations of CO lead to a large decrease of fuel cell performance. An air-bleed of 1.5% air in hydrogen is able to mitigate this effect completely. Such an air-bleed leads to the direct oxidation of CO by O_2 on the noble metal surface. This is a procedure that is frequently used in practice. However, this solution is not ideal. The addition of air needs to be accompanied by careful sensing of the oxygen concentration, thus leading to increased system complexity. Second, the selectivity of CO oxidation is poor: 1.5 % air is needed to oxidize 10 ppm CO. The remainder of the oxygen is reacting with hydrogen, leading to lower efficiency and local heat formation. This heat formation is likely to have a negative effect on catalyst and membrane lifetime [63].

Catalyst development has led to formulations more effective than PtRu, especially at higher CO concentrations. As shown in Figure 17, which gives the drop in performance for different anode formulations when increasing amounts of CO are added to hydrogen, both PtPd [64] as well as PtRuMo [65] lead to strong improvement of the tolerance towards CO.

Another concept, first introduced by Johnson Matthey [66], is the "bilayer" concept. In this concept, the CO oxidation function is separated from the hydrogen oxidation function. Figure 18, measured by using home-made electrodes at ECN, shows the benefit of this bilayer concept. Using the bilayer electrodes composed by a PtRu layer closest to the membrane, and a PtMo layer on top of that, a CO concentration of 200 ppm in a gas consisting of 75% H_2 and 25% CO_2 leads to a voltage decline of 50 ppm at 350 mA.cm^{-2} versus more than 250 mV for PtRu electrodes [67].

Still, the CO tolerance is too low for practical purposes. Ideally, 1000 ppm CO or more should be tolerated without a voltage loss exceeding 20 mV. Moreover, the stability of binary and ternary catalysts under fuel cell operating conditions is an issue.

The strategy towards CO tolerance has therefore been changed, towards the development of proton conducting polymers suitable for high temperature operation of the PEMFC, i.e. $120 \text{ }^\circ\text{C}$ and higher. It is already demonstrated [68] that at this temperature, 1000 ppm CO leads to only minor loss of performance. In the last section the topic of high temperature operation will be further addressed.

Finally, the anode catalyst can be exposed to very high potentials when a lack of hydrogen occurs in certain parts of the cell. This is known as fuel starvation. The fuel cell, as part of a large series, is intended to generate a high current density anyhow, resulting in electrochemical processes that can generate this current. This often leads the oxidation of the carbon support [63], leading to loss of noble metal. Catalyst formulations that are capable of water oxidation can limit the risk of carbon oxidation.

The catalytic challenges for PEMFC anodes can be summarised as:

- minimisation of the use of platinum to $0.05 \text{ mg Pt.cm}^{-2}$, enabling fuel cell power density of 1 W.cm^{-2}
- tolerance towards impurities at the ppm level, even when using hydrogen as fuel
- for operation on reformat, tolerance towards at least 100 - 200 ppm CO, as well as to CO_2 in the 10 - 25% range

- stable for 5,000 hours for automotive and 40,000 hours for stationary applications under operating conditions as well as open circuit and shut down conditions

Catalysts for oxygen reduction (cathodes)

At the cathode, the reduction of oxygen requires higher amounts of platinum. Figure 10, showing the individual contributions of the hydrogen oxidation and the oxygen reduction to the overall rate, clearly illustrates that optimising the cathode has the highest priority for hydrogen/air fuel cells. On top of that, mass transfer at the cathode is much more hindered than at the anode. Whereas hydrogen is generally fed as a pure gas, oxygen is fed as part of air. In addition, water is produced at the cathode by the electrochemical reduction of oxygen. Insufficient removal of this product water severely hinders the transport of oxygen to the reaction site.

As a result of poor ionic and electronic conduction the utilisation of the platinum surface area at the cathode is much less than 100%.

Strategies towards optimisation of the cathode structure consist of improving the removal of water, lowering the ionic and electronic resistance and by preventing the deposition of platinum in inaccessible catalyst pores.

Improving the intrinsic activity of platinum has been tried by many researchers so far. Alloying with chromium has been proven to be very effective [P4]. It leads to higher exchange current densities, the challenge is to translate these to higher current densities at the operating voltage [60]. The most promising alloy published recently is a PtCo catalyst [69]. It has a three fold higher intrinsic activity in comparison to platinum, and its stability is promising. Pre-leaching of PtCo prior to the manufacturing of the fuel cell electrode keeps the leaching during fuel cell operation under control. Other alternative active metals are often not stable at the operating conditions, i.e. a rather high potential in combination with a highly acidic environment, leading to leaching of many less noble components from the catalyst surface.

In the search for cheaper materials, the often encountered problem is that the intrinsic activity is so low that it leads to much thicker electrodes, which in turn is counterproductive as it leads to high mass transfer losses.

The catalytic challenges for PEMFC cathodes can be summarised as:

- minimisation of the use of platinum to 0.15 mg Pt.cm⁻², enabling fuel cell power density of 1 W.cm⁻²
- tolerance towards air impurities at the ppm level
- stable for 5,000 hours for automotive and 40,000 hours for stationary applications under operating conditions as well as open circuit and shut down conditions

High temperature operation of the PEMFC

The first generation of commercial PEMFC's will use presently known components, consisting of a perfluorosulfonic acid membrane as electrolyte and catalyst compositions as cited above. The electrolyte determines that the fuel cell needs to be operated at fully humidified conditions and limits the operating temperature to 80 - 90 °C.

There is a strong driving force towards operation at higher temperatures and lower humidity levels: it will make the fuel cell system simpler, heat transfer from the fuel cell will become easier, and tolerance towards impurities will improve [70]. Operation for automotive applications is targeted towards 120 °C, while stationary systems could be operated at even 150 °C and higher. The key component needed to enable this higher operating temperature is the electrolytic membrane. The consequences for the electrocatalysts are however important as well.

Already in the present set-up, there is concern on the long term stability of the noble metal particles in the electrodes. Especially during shut-down, high voltages can occur,

leading to the corrosion of both the noble metals as well as the carbon support. At higher operating temperatures, these phenomena will be accelerated exponentially. More stable supports(carbon or other), as well as more stable deposited noble metal particles are needed. The benefit of operation at high temperature could be that water removal at the cathode becomes a less critical issue, as its evaporation will take place much faster. The introduction of new electrolytes, to be used in the electrodes as well for ionic accessibility at high temperature operation, can have a negative impact on electrode kinetics as well. In the present high temperature fuel cells, using phosphoric acid doped Polybenzimidazole, the phosphoric acid leads to poor oxygen reduction kinetics caused by the specific adsorption of phosphoric acid on platinum. As the state-of-the-art PEMFC electrodes are optimized for the operation below 100°C and the use of perfluorosulfonic acid as electrolyte, significant new R&D will be needed when a new electrolyte emerges with high temperature operation as a consequence.

Solid Oxide Fuel Cells

As the name states, Solid Oxide Fuel Cells (SOFC) consist mainly of metal oxide materials. The electrolyte is a dense oxygen ion conducting ceramic material, typically yttrium-stabilised ZrO₂ (YSZ), which is sandwiched between the porous anode and cathode. The most common type of cathode material is strontium doped lanthanum manganite (LSM), an ABO₃ type compound having the perovskite crystal structure. The cathode can be mono-phased LSM, but two-phase cathodes, where the LSM is mixed with a good oxygen conductor like YSZ or CeO₂ are also possible. Generally, the anode is nickel based. At the operating conditions the nickel is metallic. YSZ or ceria is mixed with the nickel to prevent sintering during operation, matching of the thermal expansion coefficient of anode and electrolyte and for providing oxygen conductivity of the anode structure.

SOFCs are produced in two geometries, tubular and planar. A further distinction between SOFC types is based on the mechanically supporting structure, which is the thickest component of the cell. The oldest type of SOFC is electrolyte supported, in which case the YSZ electrolyte has a typical thickness around 0.1 mm. Because of the high electrolyte thickness this type of cell must be operated at high temperatures, around 950°C, for achieving a high oxygen ion conductivity and thereby limiting the losses. Cell types suitable for reduced temperature operation (700-850°C) are the anode-supported, Figure 19, and the cathode-supported SOFCs. In these cells the porous anode or cathode structures are relatively thick components while the thickness of the electrolyte layer is reduced to 5-15 microns.

SOFC are operated with a hydrogen containing fuel and air. Oxygen from the air is reduced at the cathode. The resulting oxygen ions migrate through the electrolyte to the anode. At the anode the hydrogen is oxidised and reacts with the oxygen ions to water. In contrast to low-temperature fuel cells, the SOFC can also directly oxidise CO, reacting to CO₂. Whereas low-temperature fuel cells require clean hydrogen as the fuel, SOFCs can be fuelled by carbon containing gases, which may even contain methane, which is steam-reformed internally, either by water added to the fuel stream and/or by the water generated at the anode itself. Figure 20 shows a schematic representation of a SOFC cell with two-phase electrodes and the relevant cell reactions.

The supporting structure of tubular cells is commonly manufactured by extrusion of a paste containing the actual electrode ceramic material and additionally an organic binder, solvents and additives for achieving the required rheological properties of the paste. After drying the extrudate is subjected to a two-stage firing process. In the first phase, up to about 300°C the organic materials are burned off. In the second phase at temperatures between 1300 and 1500°C, the ceramic powder particles are sintered together into a solid structure, still with open porosity in case of electrode-supported cells, fully dense in case of electrolyte-supported cells. The thin layers are generally deposited to the tube by dip-coating, after which again a sintering step is applied. Generally, tape-casting of a slurry, containing essentially the same type of components as the paste for extrusion, is applied for manufacturing the mechanically supporting component of planar cells, while the thin layers are applied by screen-printing. The mostly immature processes applied for SOFC manufacturing today, consist of a high number of deposition and sintering steps, involving significant labour. Achieving cost targets for commercial applications will necessitate combining these into a limited number of manufacturing steps (co-extrusion, calendaring etc) and co-firing of all the cell components in combination with a high degree of automation. An important aspect in the manufacturing of SOFC cells is matching the sintering shrinkage and thermal expansion coefficients of the components that constitute the cell. Not doing so causes warpage and even cracking of cells. This and other manufacturing requirements put severe restrictions on the freedom of implementing new and improved materials into SOFC cells. It is worth mentioning that, although the nickel in the anode is the only metallic material in the SOFC, it is present as nickel oxide in all manufacturing steps. It is only at the start-up of the SOFC that NiO is reduced to Ni.

Catalysis issues in SOFC

Catalytic processes play an important role in the operation of particularly the SOFC anode and cathode, and the major challenges for the further development of SOFC towards a commercial project are for a large part related to improving catalytic activity and robustness. The critical technical issues for SOFC are reliability and lifetime, while economic requirements impose low manufacturing and materials costs.

A general issue addressed by virtually all major SOFC developers is decreasing the operating temperature. Virtually all SOFC cell degradation processes, including the ones involving catalysis, are thermally activated. At operating temperatures around 600°C, lifetimes in the range of 10 to 15 years are deemed achievable, which is required for commercialisation. In the alternative scenario SOFC stacks will be produced at low cost, which might economically enable stack replacement each five years. Furthermore the reduced temperature will enable the use of cheaper, commercially available materials for the steel interconnects in stacks and system components.

Apart from lifetime, costs requirements demand the use of low amounts of the more expensive materials or the use of low cost materials for cells (preferably both), in addition to low manufacturing costs. As an indication, considering full commercialisation of SOFC based systems, cost studies result in required cell production costs around 100 Euro per kW_e.

Robustness requires a low sensitivity in causing permanent damage or degradation of the SOFC system and hence the cell, for excursions outside the normal operating window, contaminants in the fuel and the air, thermal and reduction-oxidation (redox) cycling of the anode.

The following paragraphs will address catalysis challenges for each of the cell components separately.

Anode

The primary functions of the anode is catalysing the oxidation of hydrogen and facilitating the reaction with O²⁻ from the electrolyte to H₂O. For hydrogen oxidation Ni appears to be an excellent catalyst, not excelled by any other, relatively cheap, material up to now. In the Ni-YSZ type anode mentioned in the introduction the actual reaction takes place at the triple (gas, YSZ and Ni) phase boundary (TPB) of the anode and hence increasing the TPB length by optimising the anode microstructure is essential for achieving high performances. Nickel also provides electronic conductivity to the anode which is essential for leading the electrons to the interconnect of the stack. Similarly YSZ provides oxygen conductivity throughout the anode structure.

Additionally, nickel is a well established steam-reforming catalyst. An ideal SOFC system operated on natural gas applies internal steam reforming, that is the reforming of the methane takes place in the anode compartment of the stack. This type of system is favoured for system simplicity and costs (no external reformer), and for system efficiency because the heat generated by the cell reaction is directly used by the reform reaction, and hence the cooling requirements of the stack (by air at the cathode side) are significantly reduced.

The main drawbacks of the Ni-based anode are:

- The low tolerance to sulphur compounds which are present in every practical fuel and requires gas cleanup to below 1 ppm.
- The low redox cycling tolerance. Redox cycling occurs when the fuel flow to the stack is interrupted. Air leaking in from the environment will oxidise the nickel. Upon recovery of the fuel flow the nickel oxide will reduce again. Such a cycle will cause considerable performance loss due to coarsening of the nickel particles in the anode.
- Catalytic promotion of carbon deposition from carbon containing fuels. Carbon deposited in the anode will generally cause irreversible damage (disintegration) of the anode structure.

Alternative materials potentially capable of solving these issues would be the full oxide anodes. Many compounds in this class have been evaluated. Best properties have been achieved by compounds like La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O₃ [71,72] and La_{0.35}Sr_{0.65}Ti_{1-y}Ce_yO₃ (where y = 0.05 -0.8) [73]. However cell performances were still well below these of Ni-

cermet anodes, even at high (around 900°C) operating temperatures, making them unlikely candidates for low-temperature SOFC. The low performance is mainly attributed to the low electronic conductivity of these materials.

Improvements of the Ni-cermet type anodes have been achieved by substituting the YSZ by ceria, gadolinium doped ceria (GDC) and samarium doped ceria (SDC). Ceria seems to increase the catalytic activity of the cermet for hydrogen oxidation, while SDC and GDC improve the ionic conductivity of the anode. Ni-ceria cermets are considered the main candidate for low-temperature SOFC [74].

Alloying the nickel of the anode for improving tolerance for fuel contaminants has been explored. Gold and copper alloying decreases the catalytic activity for carbon deposition, while dispersing the anode with a heavy transition metal catalyst like tungsten improves sulphur resistance. Furthermore, ceria cermets seem to have higher sulphur tolerance compared to Ni-YSZ cermets [75].

It is claimed that Cu-Ceria cermet anodes amply meet targets on sulphur and carbon tolerance, and furthermore is capable of direct oxidation (no water added to the fuel) of methane and many other higher-carbon fuels, while having high electrochemical performance. Still a debate is going on whether the direct oxidation is not actually internal reforming using the water generated by the cell reaction. Irrespective this debate, the reported performances with various fuels and high sulphur contaminant levels are impressive [76, 77]. However, because of the low melting point of copper and copper oxide, the manufacturing of this type of anodes is a very complex and vulnerable process, being the main reason the vast majority of cell developers disregards this anode option.

The main catalysis challenges related to SOFC anodes can be summarised as the specification of an anode material or mix of materials having the following properties:

- High catalytic activity for hydrogen oxidation at 600°C.
- Controlled catalytic activity for the steam-reforming of methane.
- Improved sulphur tolerance related to the catalytic activity for oxidation as well as reforming.
- Reduced catalytic activity for carbon deposition.
- Sufficient electronic and oxygen-ion conductivity.

These already complex challenges are further complicated by the restrictions imposed by requirements of low cost materials and manufacturing, and chemical and TEC compatibility with the other cell and stack components.

Cathode

The primary functions of the cathode are catalysing the O₂ reduction and transporting the O²⁻ ions to the electrolyte. Furthermore, the cathode should possess sufficient electronic conductivity for leading the electrons from the interconnect to the reaction sites. At practical operating conditions, the ionic conductivity of LSM is several orders of magnitude lower than its electronic conductivity. Therefore, in the single-phase and two-phase LSM type cathodes presented in the introduction the reaction sites are essentially at the TPBs of air, YSZ and LSM. Mixing the LSM with YSZ is one means, apart from refining the microstructure, of increasing the TPB length and extending the reaction sites through a larger part of the cathode structure. In the single-phase cathode the reaction sites are restricted to the electrode-electrolyte interface. LSM type cathodes perform satisfactorily at operating temperatures over 800°C.

Due to low catalytic activity of the LSM type cathodes at operating temperatures below 800°C, alternative cathode materials need be used. Many materials have been investigated, Figure 21. For temperatures as low as 700°C, La_xSr_{1-x}CoO₃ (LSC) and (La_xSr_{1-x})(Co_yFe_{1-y})O₃ (LSCF) are rather established, while Ba_xSr_{1-x}Co_yFe_{1-y}O₃ (BSCF) and Sm_xSr_{1-x}CoO₃ (SSC) [78] are materials quite recently identified as potentially high-performance cathodes for operation at even lower temperature. The chemical and

physical properties of these oxides vary significantly with the value of x and y, and these parameters are selected for the optimum tradeoff between catalytic activity, thermal expansion coefficient (should match with that of the applied electrolyte), electron and ion conductivity and chemical stability.

During the cathode sintering phase at high temperatures, these materials tend to react with zirconia electrolytes to $\text{La}_2\text{Zr}_2\text{O}_7$, which has low ion conductivity and hence will result in low performance cells. The reaction is generally prevented by sandwiching a thin ceria layer between the electrolyte and the cathode.

The intermediate and low-temperature materials exhibit both, significant oxygen ion and electron conductivity. This means that the oxygen reduction can take place everywhere in the cathode and is not restricted to the TPBs as in the LSM-type cathodes. An option for compensating the relatively low oxygen ion conductivity of LSC and LSCF at operating temperatures around 600°C is by mixing the material with (doped) ceria [79, 80].

A serious problem of all currently known cathodes is Cr poisoning. SOFC stacks are built with ferritic stainless steel interconnects. This class of steels obtains its high-temperature corrosion resistance by the formation of stable chromium oxide or spinel layers. At the SOFC operating conditions Cr reacts with water in the air to $\text{CrO}_2(\text{OH})_2$, which decomposes to Cr_2O_3 at the reaction sites of the cathode. The Cr_2O_3 reacts locally with the cathode and deactivates the site. Because of the higher number of reaction sites it is shown that the mixed conductivity oxide cathodes are less sensitive to Cr poisoning, compared to the cathodes that depend on TPBs. However, both cathode types need significant improvement concerning their Cr resistance for achieving lifetime targets.

Hence the catalysis related challenges for SOFC cathode are the development of cathode specifications, that is material and microstructure, having high catalytic activity for oxygen reduction at 600°C , high electron and ion conductivity, and a low sensitivity for poisoning by volatile Cr species. Again, as for the anode, considering cost and compatibility related requirements.

Electrolyte

The challenges for electrolyte developments are of non-catalysis nature. However, because anode and cathode development activities have to consider compatibility and interaction with the electrolyte, the most important issues are mentioned here. First of all, the oxygen ion conductivity of the electrolyte should be sufficiently high at 600°C . This can be achieved by materials selection and by reducing the thickness of the electrolyte layer. Additionally the electrolyte layer has to be mechanically reliable and chemically stable. Although there are much better oxygen conducting materials compared to the zirconias, particularly at 600°C , mechanical and stability requirements cause the majority of SOFC developers basing their technology on zirconia. Most common compositions are 3YSZ for electrolyte supported cells and 8YSZ for electrode-supported cells. Scandium doped zirconia could offer an attractive combination of conductivity and mechanical properties, but uncertainties on future price and availability of scandium forms a serious drawback. Double layer electrolytes of YSZ and doped ceria, with ceria at the cathode side, might also prove a viable option, particularly for 600°C operation.

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Figure Captions

Figure 1. *Energy chain for hydrogen*

Figure 2. *Process diagram for hydrogen production.*

Figure 3. *Hydrogen production from coal.*

Figure 4. *Pathways for CO₂ capture, Redrawn from IPCC [14].*

Figure 5. *Operating principle of a hydrogen membrane reactor for SMR.*

Figure 6. *Thermodynamic boundaries for carbon formation at different temperatures and 40 bar.*

Figure 7. *Principle of Sorption-enhanced reforming.*

Figure 8. *Schematic representation of Sorption-enhanced reforming. The topmost reactor is in reforming mode, the bottom one is being regenerated using steam.*

Figure 9. *Sorption-enhanced reforming experiment. Originally published in Reijers et al. in Industrial and Engineering Chemical Research, 2006 [25], republished with permission from the American Chemical Society.*

Figure 10. *Current voltage characteristics of hydrogen oxidation and oxygen reduction in a fuel cell, and hydrogen and oxygen evolution in an electrolyser.*

Figure 11. *Principle of an acid electrolyser.*

Figure 12. *Principle of a Proton Exchange Membrane Fuel Cell (PEMFC)*

Figure 13. *Main components of a PEMFC*

Figure 14. *Structural composition of a PEMFC electrode, in specific for a cathode*

Figure 15. *Current density-cell voltage plot for a PEMFC, at 80 °C, 1.5 barg, Pt on carbon electrodes.*

Figure 16. *Averaged current density-voltage characteristics of 30 cells for an atmospheric PEMFC stack on various anode feed compositions*

Figure 17. *Relative current density for various anode compositions as a function of increasing CO concentrations added to a pure hydrogen feed to the anode. $j_{ref} = 840 \text{ mA.cm}^{-2}$, at 0.5 V, for platinum/carbon*

Figure 18. *Cell potential at a current density of 350 mA.cm^{-2} for a carbon supported PtRu, a PtMo and a PtRu/PtMo bilayer anode. In the bilayer, PtRu is on the membrane side. Originally published in G.J.M. Janssen et al., Fuel Cells 2004 [67], republished with permission from Wiley-VCH Verlag GmbH & Co.*

Figure 19. *Fracture surface of a anode-supported cell. From left to right, the porous Ni-YSZ anode, the dense 8YSZ electrolyte and the porous LSM-YSZ cathode.*

Figure 20. *Schematic representation of the relevant SOFC reactions. The steam reform reaction needs nickel as the catalyst. Oxidation of H_2 and CO takes place at the TPBs (represented as red dots) in the anode, and is catalysed by the Ni. At the cathode O^2 reduction also occurs at TPBs and is catalysed by LSM.*

Figure 21. *Polarisation resistance (partly determined by the catalytic properties of the electrode) of cathode materials, measured by impedance spectroscopy of symmetrical cells. The area enclosed by the red box represents the target area for low-temperature cathode development.*

Figure 1.

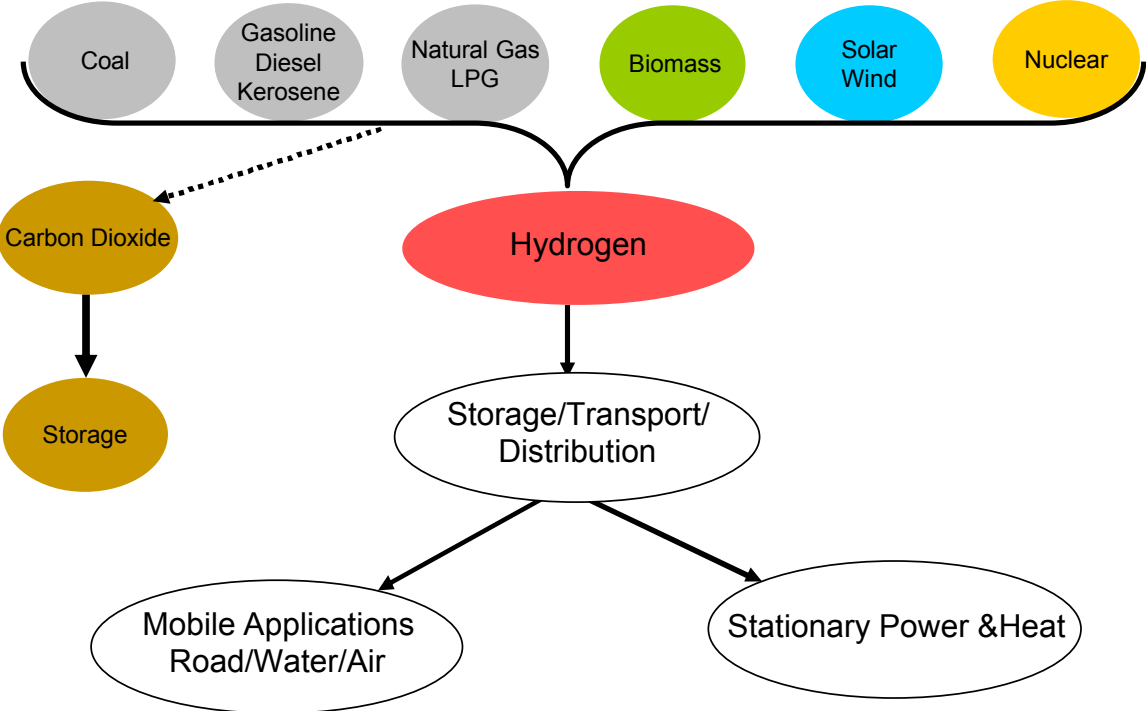


Figure 2.

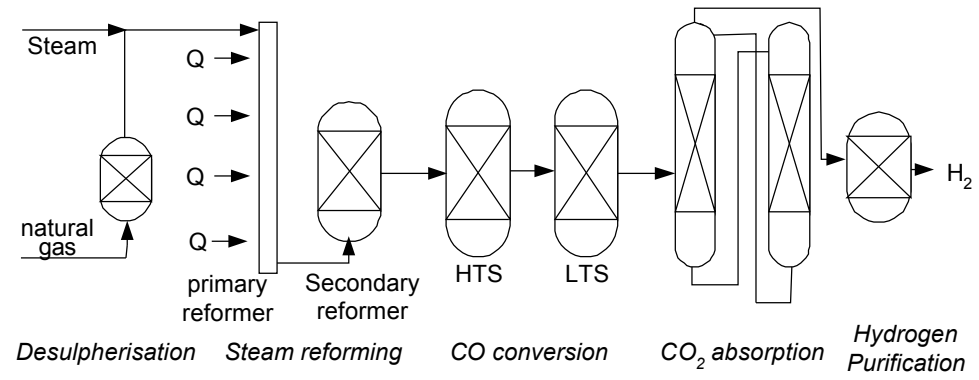


Figure 3.

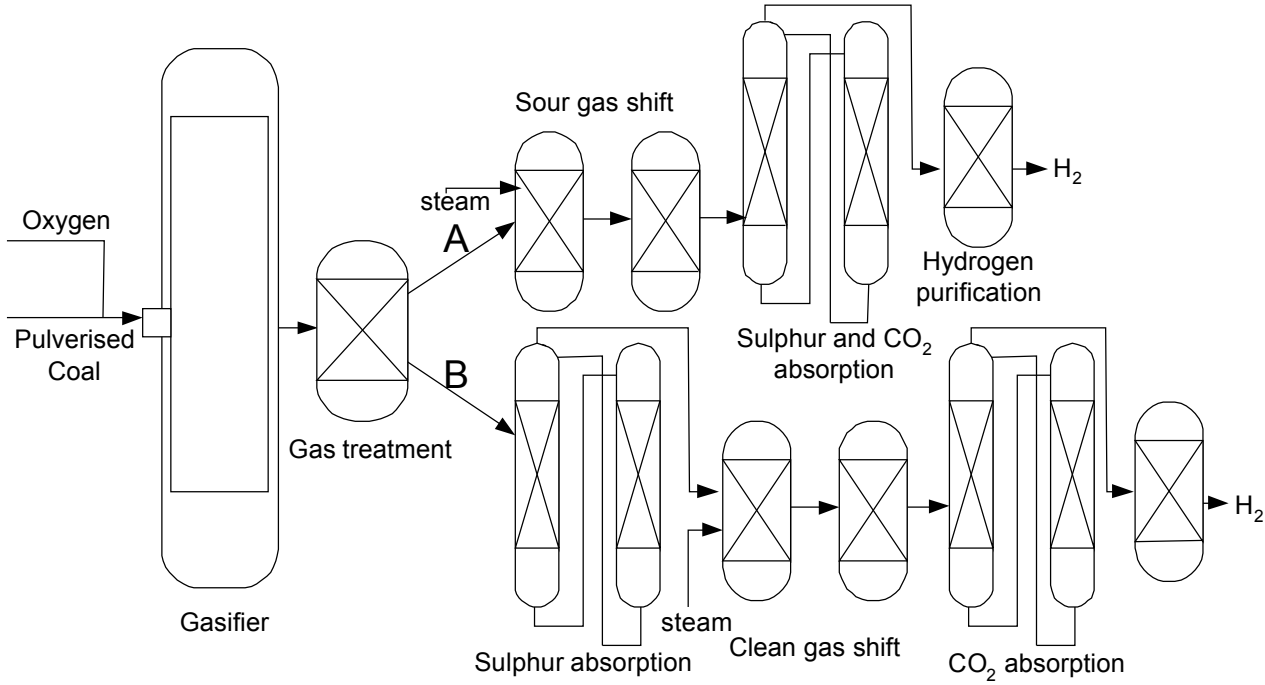


Figure 4.

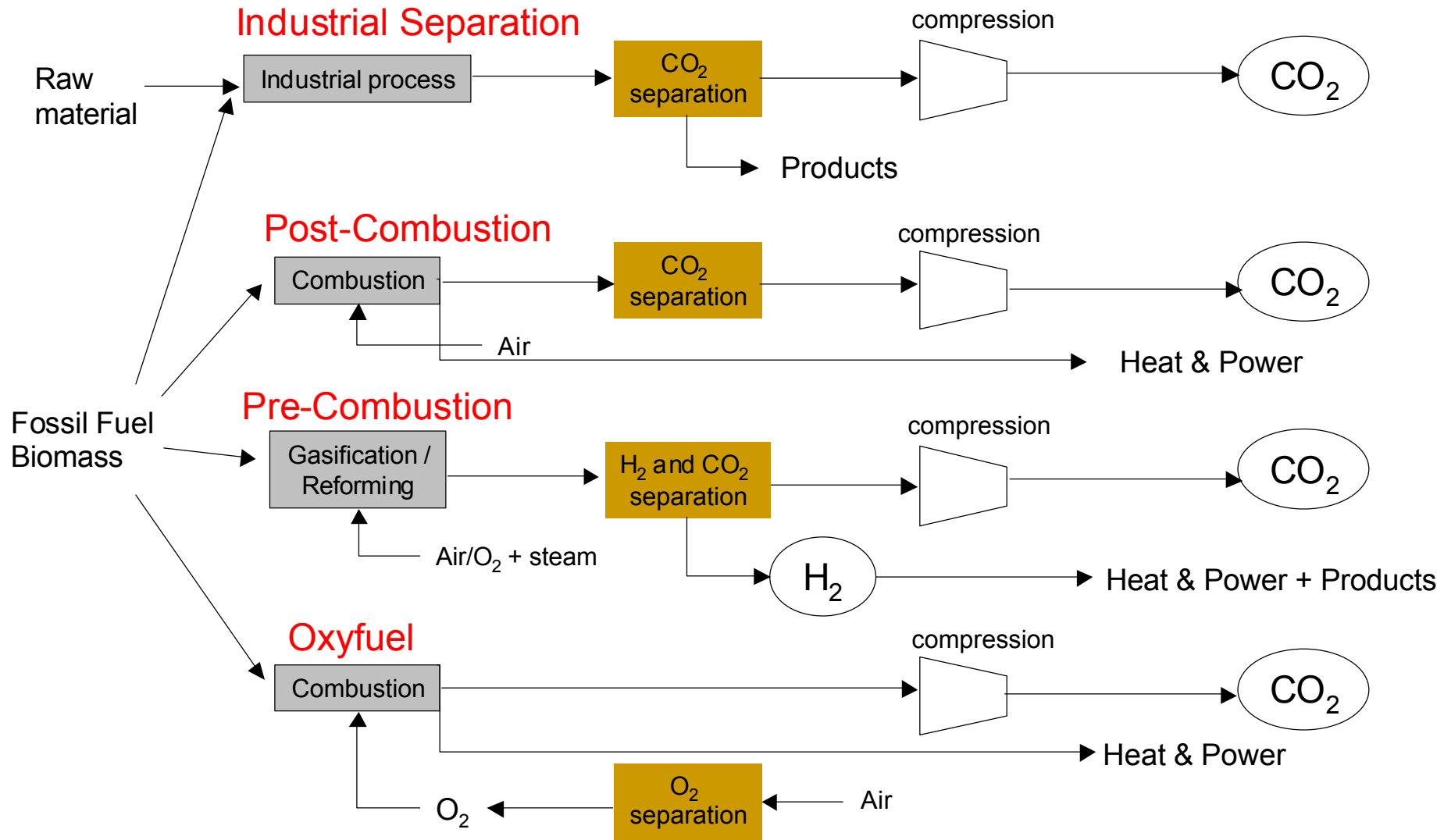


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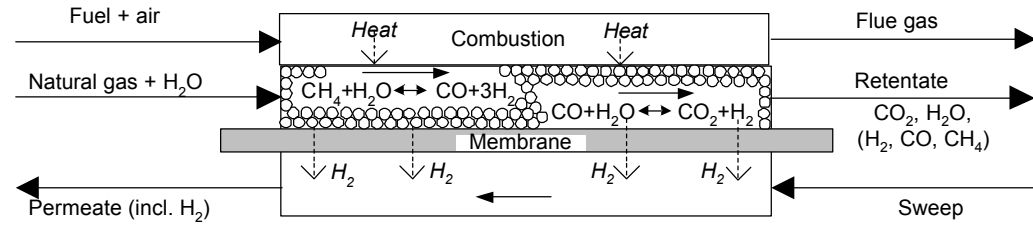


Figure 6.

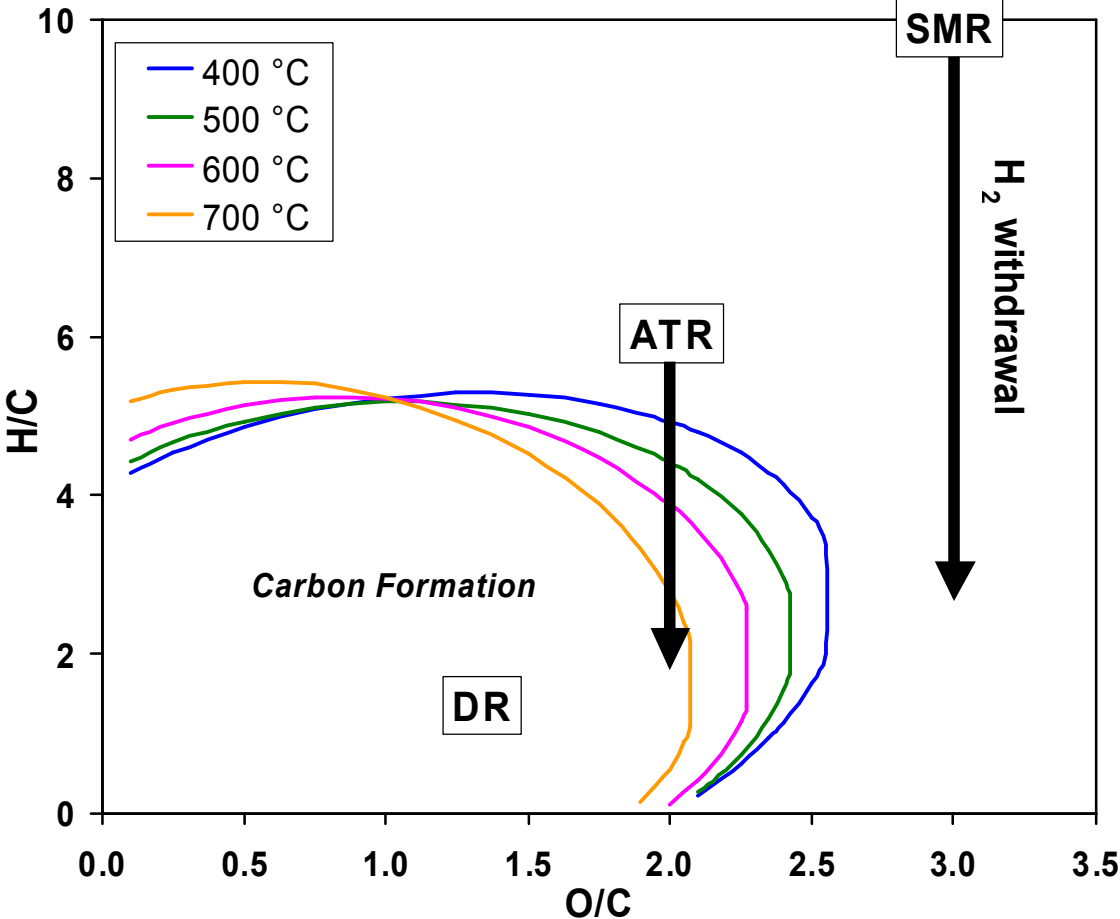


Figure 7.

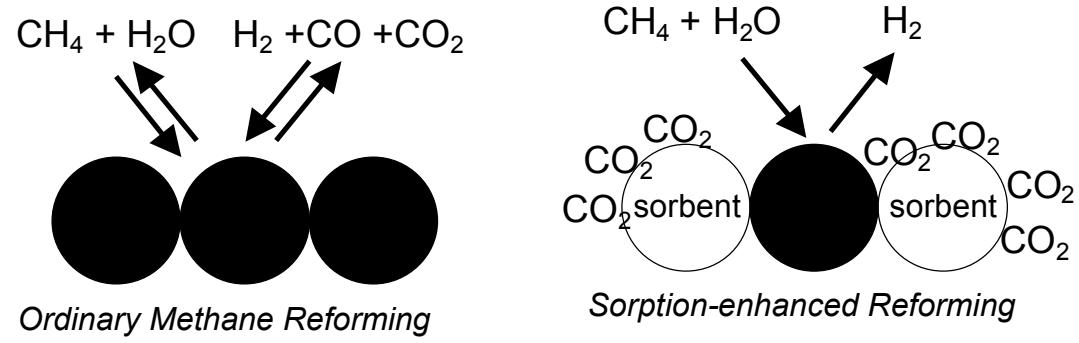


Figure 8.

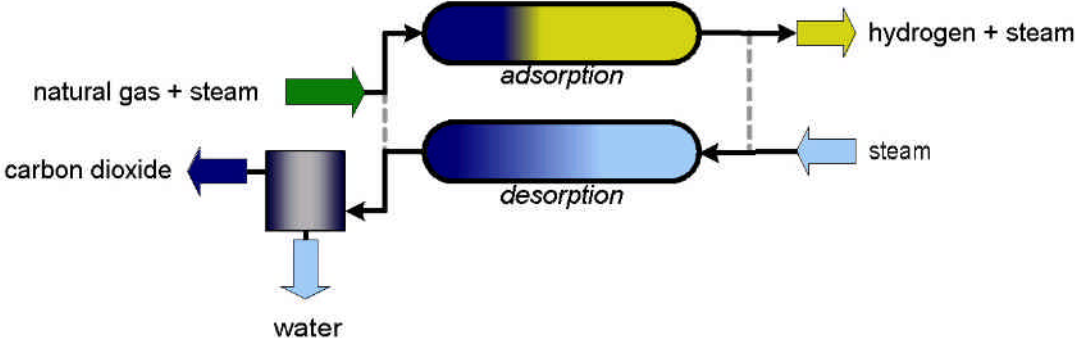


Figure 9.

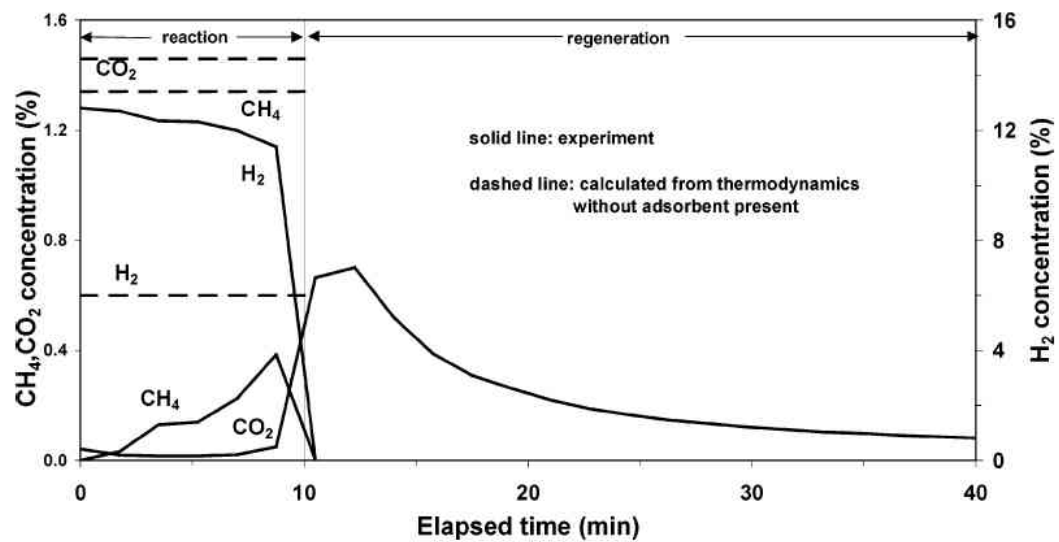


Figure 10

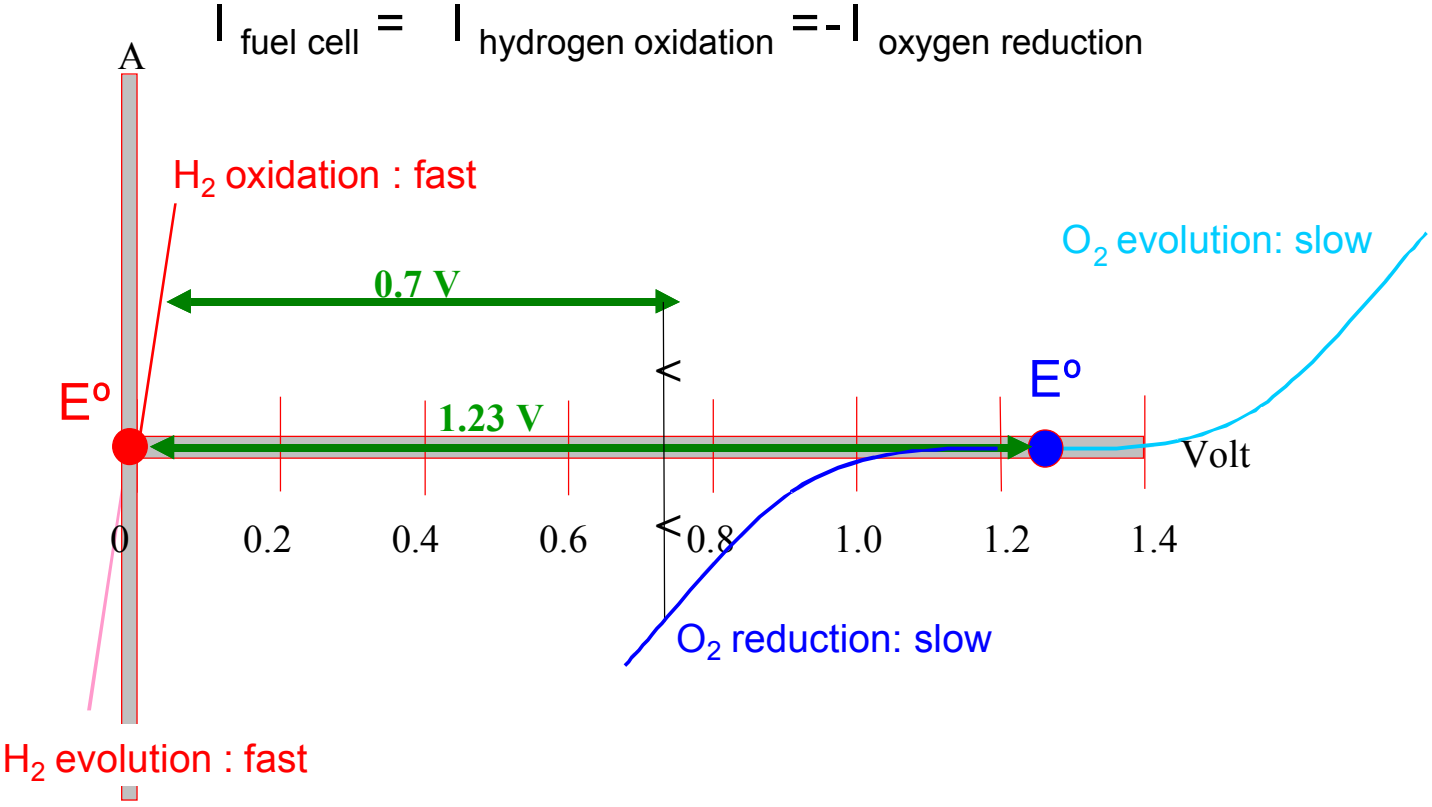


Figure 11

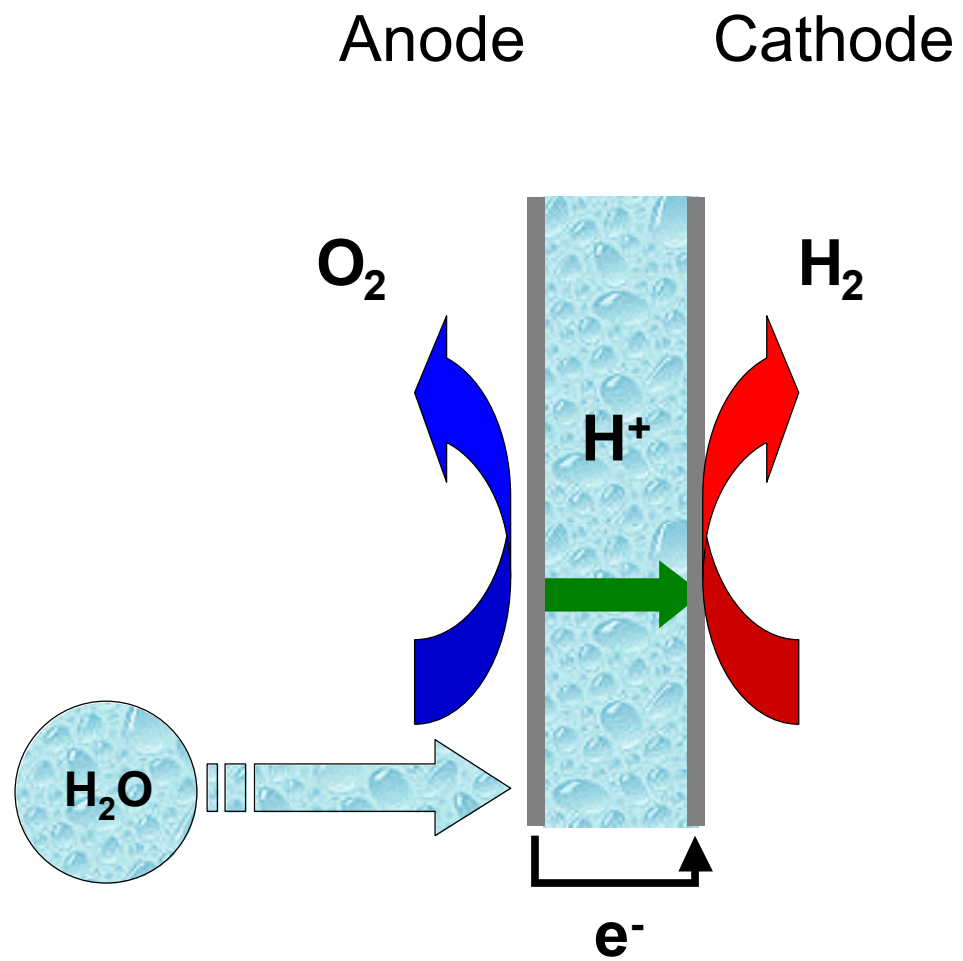


Figure 12.

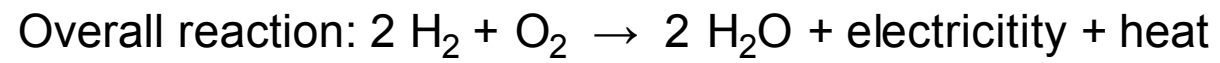
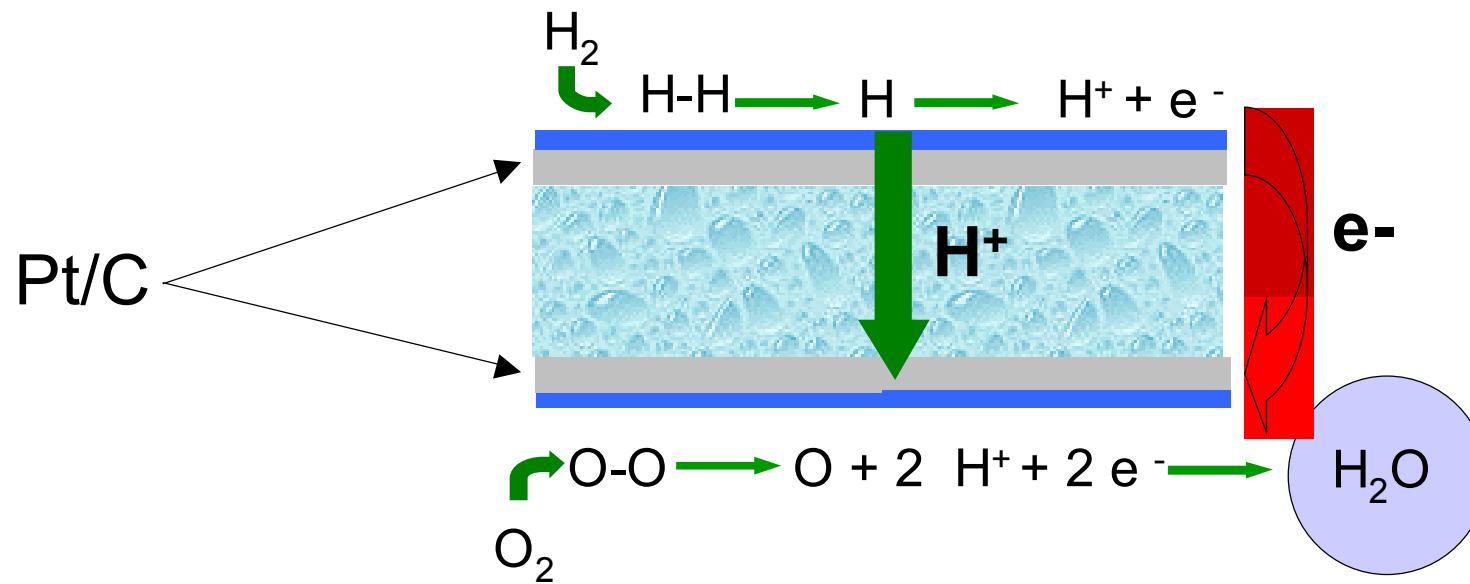


Figure 13.

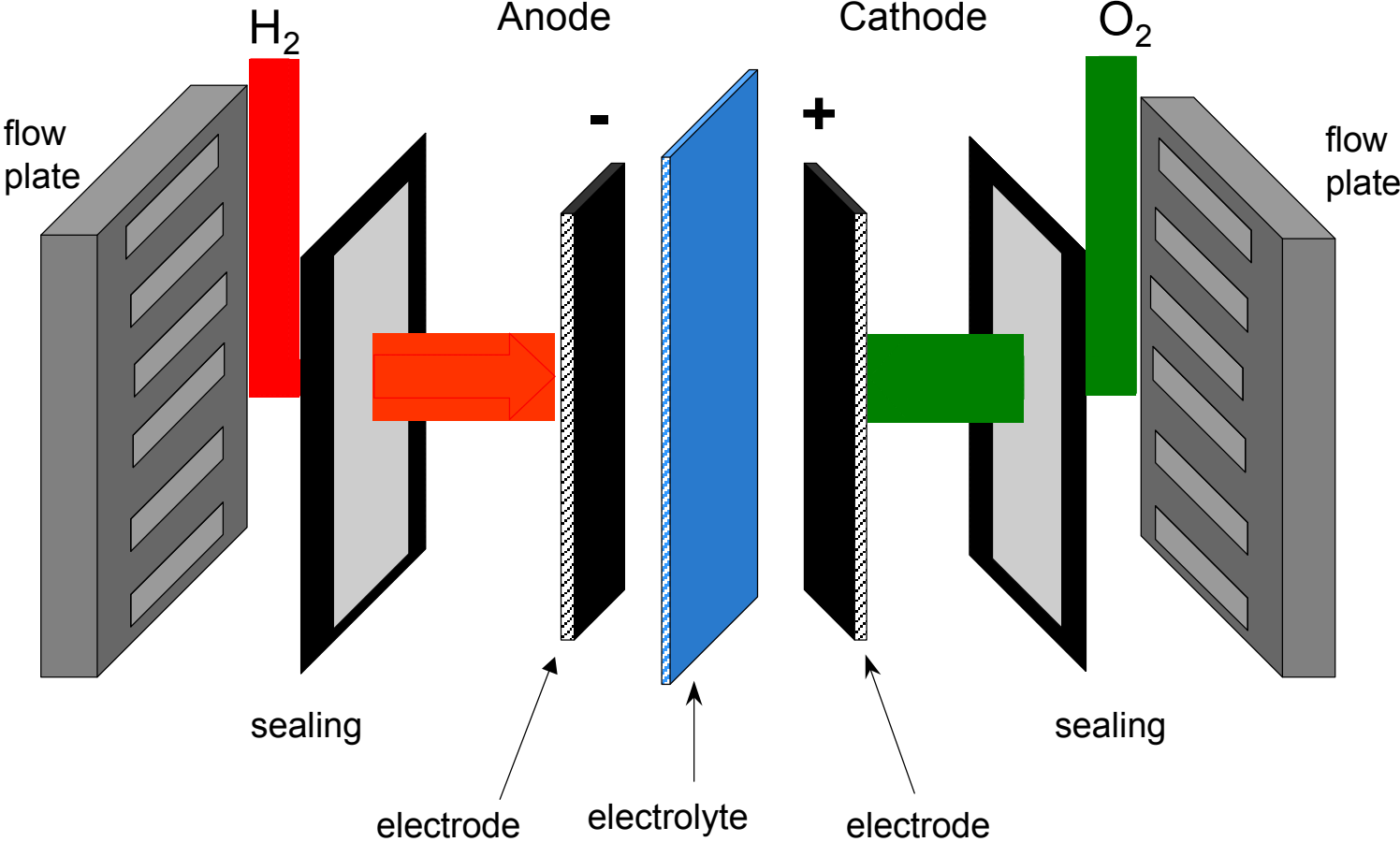


Figure 14.

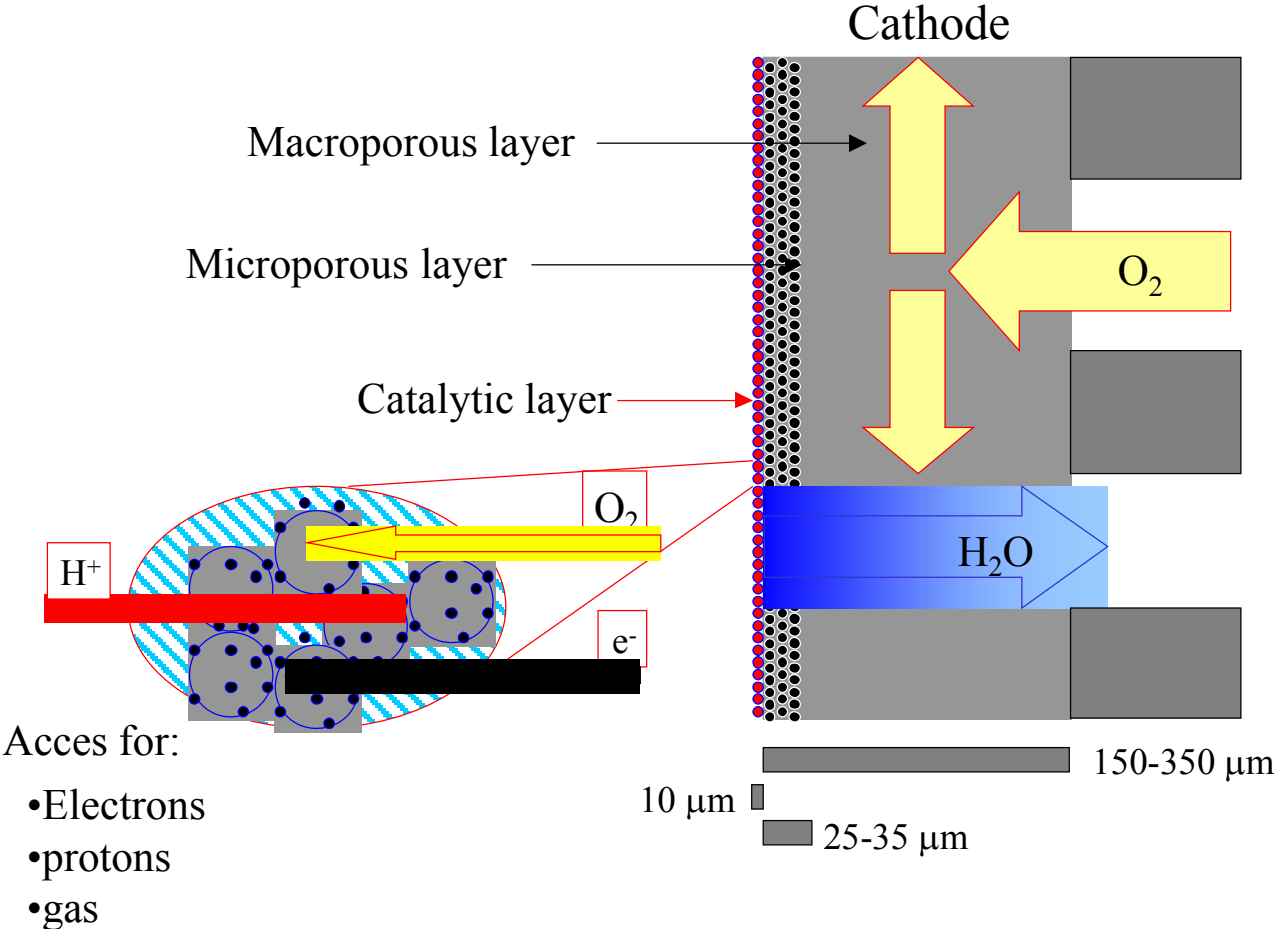


Figure 15.

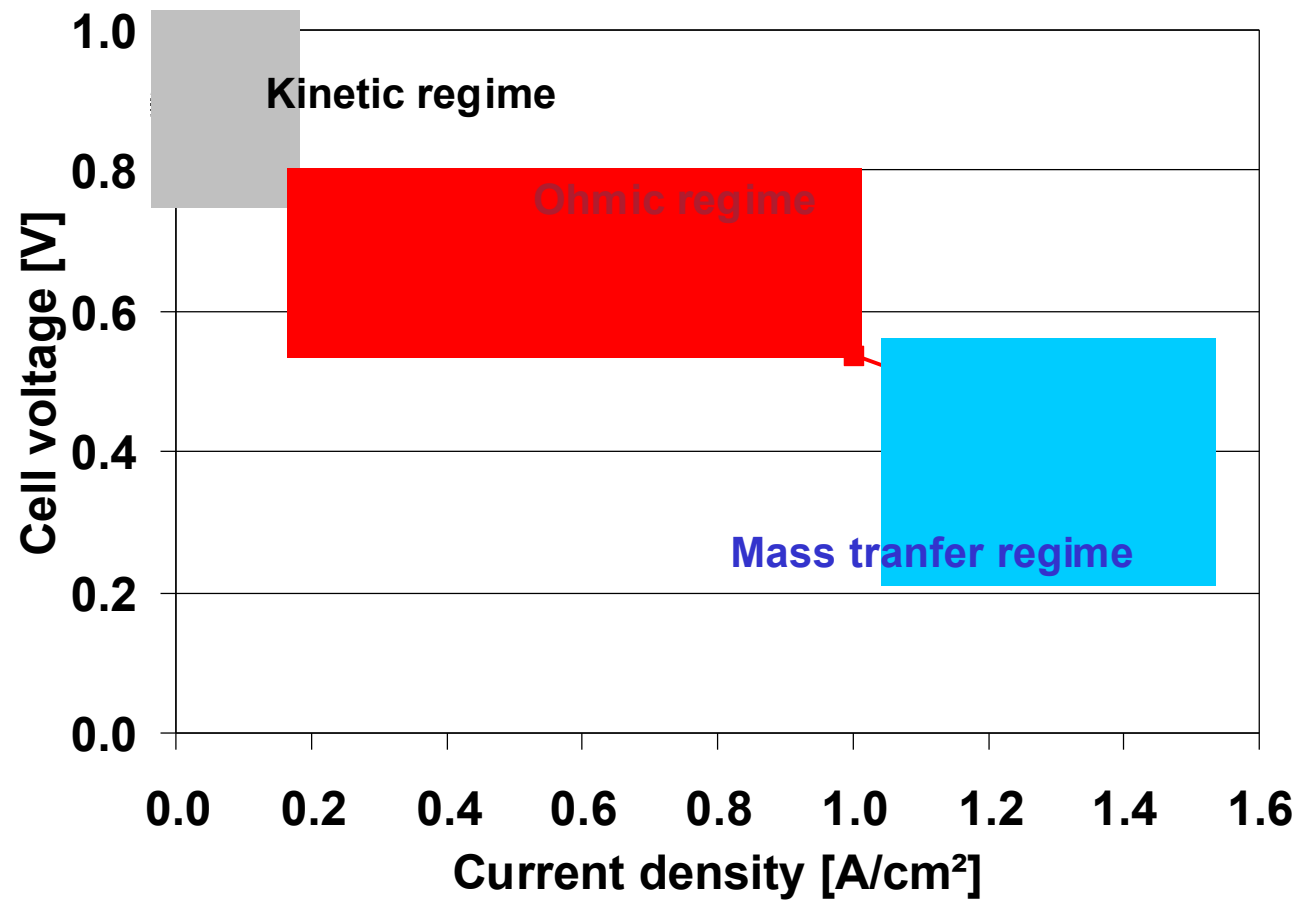


Figure 16.

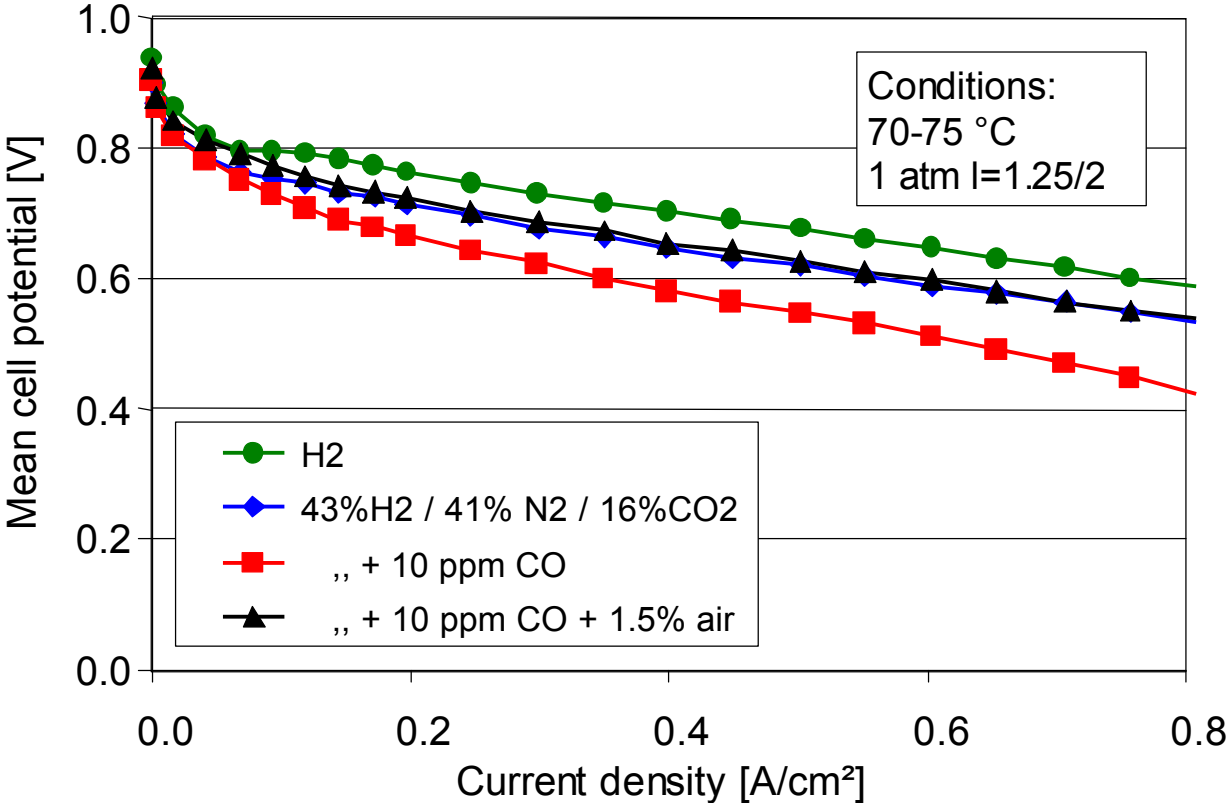


Figure 17.

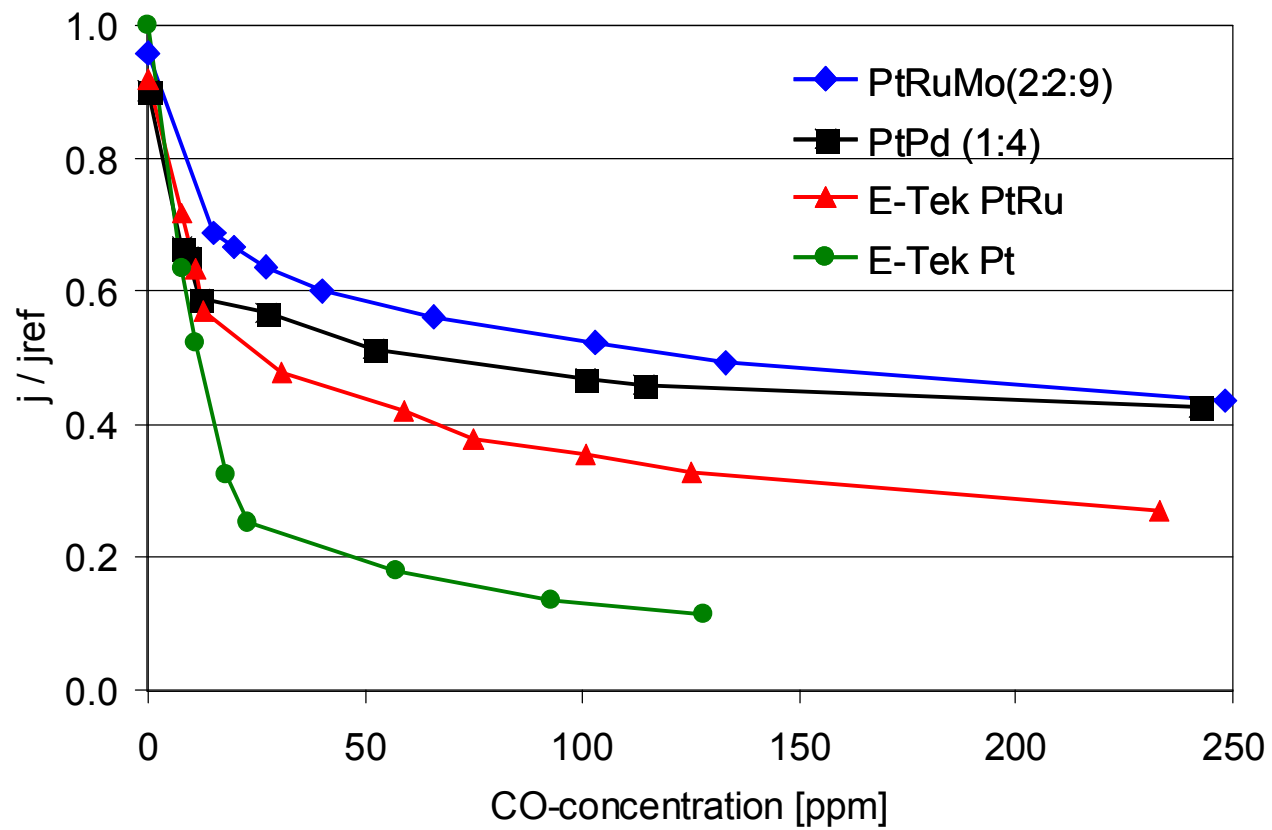


Figure 18.

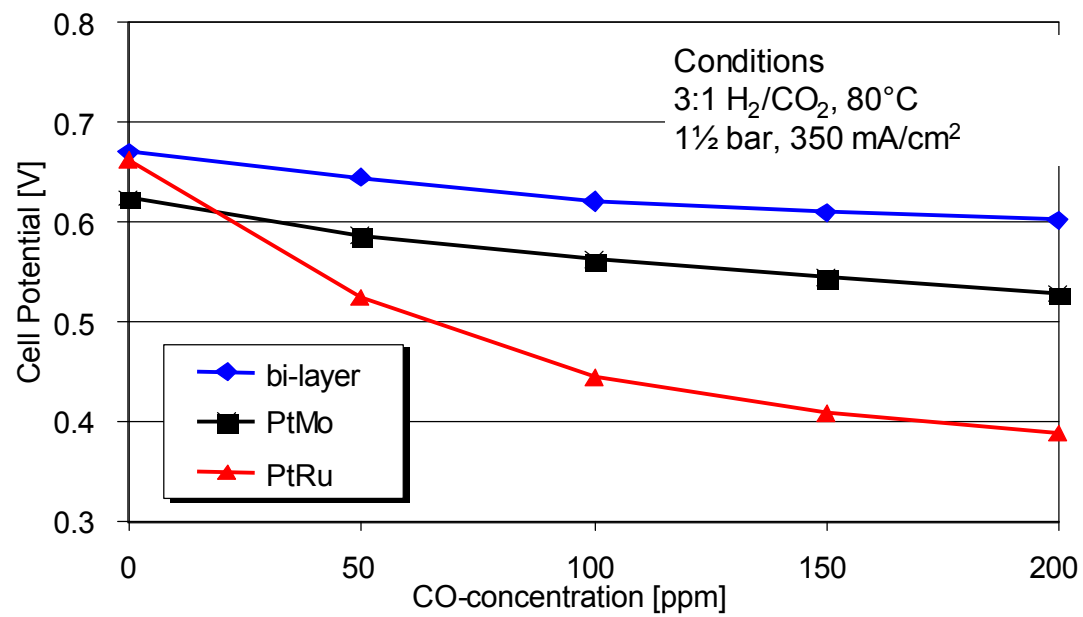


Figure 19.

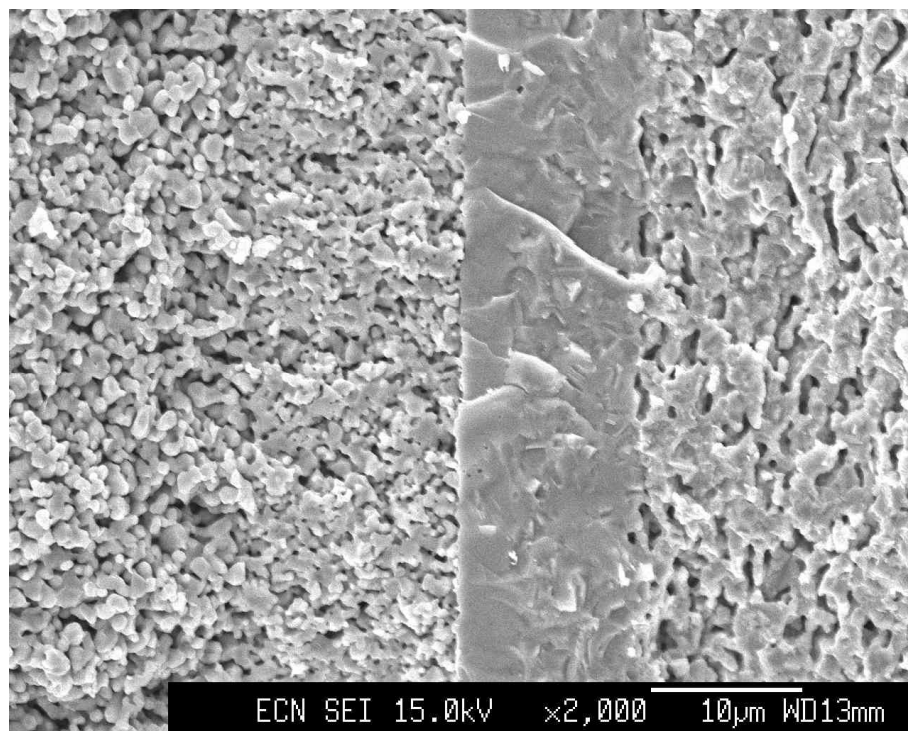


Figure 20.

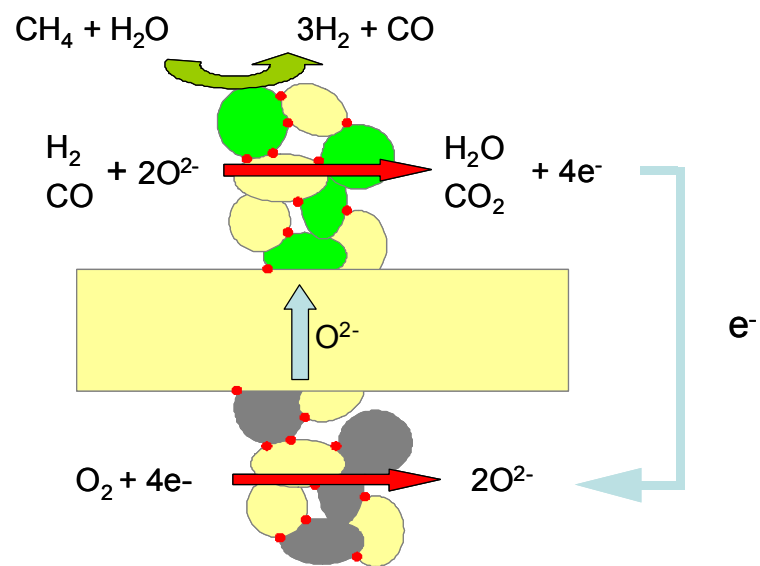


Figure 21.

