

# Power-to-X

## Electrolysis and synthetic fuels

### Electrolysis

Electrolysis means splitting by means of electricity. In an energy context, the substance that is split is most often water forming hydrogen and oxygen, but several other processes are to be mentioned such as chlor-alkali electrolysis for the production of chlorine and NaOH and production of a range of metals that cannot be manufactured by direct reduction by carbon. In all cases, the overall process is divided into an oxidation process (anodic) and a reduction process (cathodic) each taking place at separate electrodes. This way the products are formed in different compartments and there is no need for subsequent separation. Some of the industrial electrolysis processes are listed in **Table 1**. In the following, focus will be on electrolysis of water although electrolysis processes for direct production of other fuels is also possible, e.g., by electrochemical reduction of CO<sub>2</sub>.

**Table 1.** Selected important electrolysis processes in the industry.

Electrolysis process	Overall reaction	Oxidation product	Reduction product
Water electrolysis	$2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$	O <sub>2</sub>	H <sub>2</sub>
Chlor-alkali process	$2\text{NaCl} + 2\text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{H}_2 + \text{Cl}_2$	Cl <sub>2</sub>	H <sub>2</sub>
Aluminium production (the Hall-Heroult process)	$2\text{Al}_2\text{O}_3 + 3\text{C} \rightarrow 4\text{Al} + 3\text{CO}_2$	CO <sub>2</sub>	Al
Magnesium production	$\text{MgCl}_2 + \rightarrow \text{Mg} + \text{Cl}_2$	Cl <sub>2</sub>	Mg
Sodium production	$2\text{NaCl} \rightarrow 2\text{Na} + \text{Cl}_2$	Cl <sub>2</sub>	Na

### The electrolyzer cell

#### *Functionality*

The overall process for the electrolysis of water is given as



regardless of the type of water electrolyzer. The oxidation and reduction processes are leading to evolution of oxygen and hydrogen, respectively.

It may not seem obvious that the formation of oxygen and hydrogen are oxidation and reduction processes when the reactant is water, but if we for a moment regard  $\text{H}_2\text{O}$  as a compound of one  $\text{O}^{2-}$  ion and two  $\text{H}^+$  ions, then it becomes self-explaining that  $\text{O}^{2-}$  (two of) is oxidized to  $\text{O}_2$  and that  $\text{H}^+$  (two of) is reduced to  $\text{H}_2$ . Note that strictly speaking,  $\text{H}_2\text{O}$  is not an ionic compound, only a highly polar covalent molecule. However in the oxidation process, it is oxygen from which electrons are withdrawn in the oxidation process and thus it is oxygen that is oxidized.

The electrode processes depend on the type of electrolyzer. Here they are illustrated for an electrolyzer working in an acidic environment, i.e., where protons ( $\text{H}^+$ ) are present in high concentration, since it is the least complicated. The corresponding processes for other types of electrolyzers will be explained when these types are introduced later.

The cathode is by definition the electrode where a reduction process takes place, here reduction of hydrogen. The process is also called the *hydrogen evolution reaction* (HER)



Protons are consumed and hydrogen gas is evolved. The other electrode process taking place on the anode, the anodic process, is oxidation of oxygen called the *oxygen evolution reaction* (OER):

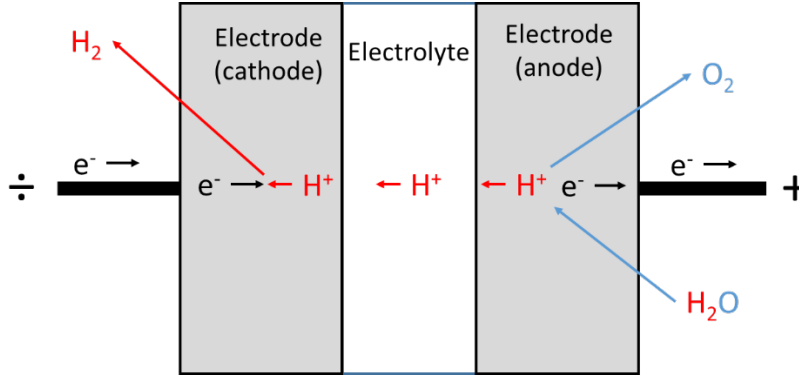


In order for (2) and (3) to add up to the overall equation (1), the protons produced at the anode must be transferred to the cathode. Otherwise the process would lead to exhaustion of protons at the cathode and accumulation of protons at the anode. This is facilitated by the electrolyte i.e., the component that separates the electrodes. It is an ion conductor, in this case a proton conductor.

The electrolyte has three purposes

1. It separates the electrodes and prevent a short circuit for the electrons, which would not bother splitting the water if they could pass through directly. The electrolyte must thus be a good electronic isolator.
2. It prevents the produced gasses from mixing. If hydrogen and oxygen could mix in the electrolyzer, it would lead to an extremely dangerous situation. Recombination into water would not only set the system back to start, it would also release all the chemical energy that has been stored in the hydrogen during the electrolysis process.
3. It transfers the ions formed on one electrode to the other electrode where they are consumed. It must thus be a good ion conductor.

The principle of the cell and the passage of current through are shown in **Figure 1**.



**Figure 1.** Schematic of a water electrolyzer cell with a proton conducting electrolyte. The current through the cell is carried first by electrons,  $e^-$ , then protons,  $H^+$ , and finally electrons again.

### *Thermodynamics and energetics of electrolyzers*

The total energy required to convert water into hydrogen and oxygen is given by the enthalpy of the reaction,  $\Delta H_r$ . At standard conditions<sup>1</sup>, it is the same as minus the standard enthalpy of formation of water,  $-\Delta H_{f,H_2O}^0$ .

The equilibrium cell voltage is the voltage at which the applied electrical voltage maintains equilibrium between reactants and products in the electrochemical reaction, i.e., between water on one side and hydrogen and oxygen on the other. This is governed by the Gibbs free energy of reaction,  $\Delta G_r$ .  $\Delta G_r$  is also the minimum work (electrical work) required to run the process of splitting water. The reversible cell voltage,  $E_{rev}$ , is

$$E_{rev} = \frac{\Delta G_r}{nF} \quad (4)$$

Where  $n$  is the number of mole electrons transferred in the reaction and  $F$  is Faraday's constant (96485 C mol<sup>-1</sup>). It is the molar free energy divided by the molar charge transferred in the reaction. At standard conditions

$$E_{rev}^0 = \frac{\Delta G_r^0}{nF} = 1.23 \text{ V} \quad (5)$$

The values with respect to the higher and lower heating values of hydrogen are listed in **Table 2**. The reversible cell voltage is the same for fuel cells and electrolyzers since it is a characteristic of the equilibrium situation with no current. In principle, the cell can later be operated as a fuel cell or an electrolyzer starting from the same equilibrium point. The reversible voltage is the lowest possible voltage at which the electrolysis reaction can occur.

<sup>1</sup> The standard condition in chemical thermodynamics is the pressure 1 bar and normally the temperature 25°C. Values at standard conditions are marked with <sup>0</sup> at the symbol.

We see from **Table 2** that the minimum electrical energy is less than the total energy required. The missing energy can in principle be supplied from any source, but in practice it normally happens via additional electrical energy. Due to imperfections in the cell, the cell voltage is always higher than the equilibrium voltage anyway. If all the energy is to be supplied electrically, the cell voltage must be related to the enthalpy of the reaction,  $\Delta H_r$ , and we can calculate a cell voltage from that similarly to equation (5)

$$E_{TN} = \frac{\Delta H_r}{nF} \quad (6)$$

The obtained voltage is the *thermoneutral voltage*,  $E_{TN}$ . As the name indicates, a cell operated at this voltage is in thermal balance with its surroundings with no need for energy supplied as heat and no waste heat emitted. The electrical energy consumed matches exactly the chemical energy of the produced hydrogen.

The voltage and the enthalpy in (6) are not marked as a standard values, they can be if  $\Delta H_r^0$  is applied, but  $E_{TN}$  applied can apply at any temperature or pressure. It will vary slightly, but not much, since  $\Delta H_r$  is a very mild function of temperature and pressure. What matters more is the fact that  $\Delta H_r$  can be higher or lower heating value, giving very different values of  $E_{TN}$ . See **Table 2**. The choice of value depends on whether water is supplied to the electrolyzer as liquid or vapour.

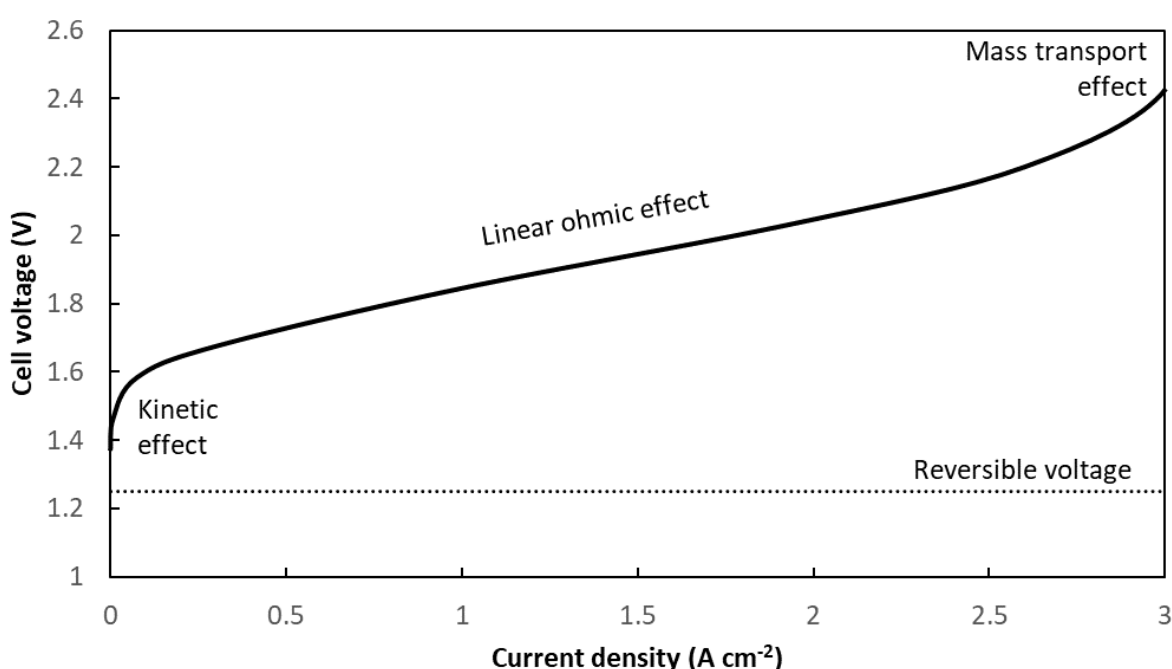
**Table 2.** Enthalpies and free energies for the water electrolysis process at standard conditions (all species at unit activity and 25 °C).

$H_2O \rightarrow H_2 + \frac{1}{2}O_2$	<b>Water as liquid</b> (Higher heating value)	<b>Water as vapour</b> (Lower heating value)
Enthalpy of reaction, $\Delta H_r$ .	285.8 kJ/mol	241.82kJ/mol
Free energy of reaction, $\Delta G_r$	237.1 kJ/mol	228.6 kJ/mol
Maximum conversion efficiency ( $\Delta H_r / \Delta G_r$ ), $\eta_{max}$	121%	106%
Reversible voltage, $E_{rev}$	1.23 V	1.18 V
Thermoneutral voltage, $E_{TN}$	1.48 V	1.25 V
Minimum total energy for producing $H_2$	39.38 kWh kg <sup>-1</sup>	33.32 kWh kg <sup>-1</sup>
(Nm <sup>3</sup> at 1 atm, 0 °C)	3.54 kWh Nm <sup>-3</sup>	3.00 kWh Nm <sup>-3</sup>

## Polarization curves

Polarization curves (voltage-current curves) of electrolyzers resembles those of fuel cells, but are as a first approach mirrored in a horizontal line at the reversible potential (1.23 V at standard conditions). This implies that the cell voltage increases with current, meaning that more energy has to be provided at large current density than at low current density (the energy carried by the electrons is proportional to the voltage by which they are driven through the electrolyzer).

The polarization curve of an imagined electrolyzer is plotted in **Figure 2** with the voltage loss mechanisms dominating different areas indicated. The *ohmic contributions* are linear and proportional to the current density. They originate primarily from the ion conduction resistance in the electrolyte and to a lesser extent from the electronic resistance in the electrodes (outside the catalytic layer).



**Figure 2.** Polarization curve of an arbitrary electrolyzer cell with the different contributions to the total overvoltage visualized. Current density normalized to the electrode area is normally preferred over absolute current to make curves comparable.

The two electrode overpotentials are non-ohmic, i.e., nonlinear with current and follow a logarithmic-like development, which means that they increase sharply at low current densities and become almost constant at higher current densities.<sup>2</sup> At high current density, a steeper rise of cell voltage due to mass transport limitations is shown in **Figure 2**. This is included for completeness of the theory, but is often not seen at all in cells fed with liquid water. In liquid water fed electrolyzers, the concentration and

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<sup>2</sup> Kinetic overvoltages are described by the Butler-Volmer equation and the Tafel equation, which are not treated here.

proximity of water is overwhelming and mass transport effects are rarely seen, even at several amperes pr. centimetre square (The concentration of molecules in liquid water is more than three orders of magnitude larger than in a gas at ambient temperature and pressure). Vapour fed electrolyzers working at high temperature are more prone to mass transport limitations, but still it is not a common problem. It should be added that water fed cells with poor bubble removal properties can run into mass transport problems because water is excluded by accumulated bubbles, but in that case, the polarization curve becomes too chaotic to be described by a simple model made up of kinetic and ohmic contributions anyway.

## *Electrical efficiency*

There are many efficiencies assigned to electrolyzers.

- Current efficiency. The current efficiency,  $\eta_{\text{cur}}$ , is the ratio between the ideal theoretical current,  $I_{\text{id}}$ , at any fixed hydrogen production rate,  $\dot{n}_{\text{H}_2}$ , and the real measured current,  $I_{\text{real}}$ .

$$\eta_{\text{cur}} = \frac{I_{\text{id}}}{I_{\text{real}}} \quad (7)$$

The lower the real current for a given production rate, the higher the efficiency (In other words, one needs to spend less current). In the ideal case, current and hydrogen production rate are related as

$$I = 2F \dot{n}_{\text{H}_2} \quad (8)$$

This is Faradays Law of Electrolysis.<sup>3</sup>  $\dot{n}_{\text{H}_2}$  is the molar hydrogen production rate,  $I$  is the current and  $F$  is Faraday's constant ( $96,485 \text{ C mol}^{-1}$ ). The digit 2 is inserted because it takes two mole electrons to make one mole molecular hydrogen. Alternatively, current density and hydrogen production rate pr. cm square can be used. The current efficiency,  $\eta_{\text{cur}}$ , is normally close to 1 (or 100 %), because side reactions are rare and limited. The most common source for a lowering of the current efficiency is gas crossover. If hydrogen to some extent diffuses through the electrolyte, it is lost from the hydrogen stream and moreover, oxygen crossing over may be reduced at the cathode consuming electrons in addition to those consumed by the hydrogen process, causing an unproductive current. A similar effect is present if crossover oxygen consumes hydrogen by recombination to water. Current efficiency is also called *faradaic efficiency*

- Voltage efficiency. Voltage efficiency,  $\eta_{\text{vol}}$ , is the ratio between the theoretical ideal cell voltage,  $E_{\text{id}}$ , and the real cell voltage,  $E_{\text{real}}$ . In contrast to the current efficiency, this is normally very different to 100%.

$$\eta_{\text{vol}} = \frac{E_{\text{id}}}{E_{\text{real}}} \quad (9)$$

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<sup>3</sup> Michale Faraday lends his name to other laws too, but among electrochemists, this is often just referred to as Faraday's Law.

Like above, the lower the real cell voltage, the higher the efficiency (In other words, one needs less voltage (energy) to push the electrons through). The theoretical ideal cell voltage can be chosen corresponding to the minimum work or the minimum total energy required to produce hydrogen. The question is thus if the most relevant as  $E_{id}$  is the reversible voltage,  $E_{rev}$ , or the thermoneutral voltage,  $E_{TN}$ .

To answer this question, it is appropriate to first define 100% efficiency. Efficiency is what you get divided by what you pay for it. What you get is the fuel and the energy value of the fuel is the heating value at standard conditions. What you pay is the electrical energy to run the cell. Then 100% efficiency is obtained when operating at the thermoneutral voltage as the energy of the fuel equals the energy of the electrical work. This view is challenged by the fact that an electrolyzer can be operated at voltages below thermoneutral as long as it is above the reversible voltage. This gives us efficiencies above 100%. The “missing” energy is then supplied as heat from somewhere, perhaps the cell housing. We can include that as part of what we pay, but then the efficiency will always be 100% and the concept of efficiency useless. The thermoneutral voltage is accepted as the reference and efficiencies above 100% are accepted too.

$$\eta_{vol} = \frac{E_{TN}}{E_{real}} \quad (10)$$

Had the reversible voltage been chose as reference, the efficiency would be electrical efficiency only relating to the minimum work (the free energy) of reaction and not the total energy (the enthalpy). The combination of the efficiencies, shown later in (11), would not be possible either.

- System efficiency. The system efficiency,  $\eta_{sys}$ , includes current efficiency, voltage efficiency and the efficiency of all the external system components (power electronics, electrolyte circulation, control devices etc.) and perhaps water processing (desalination and purification),  $\eta_{ext}$ .

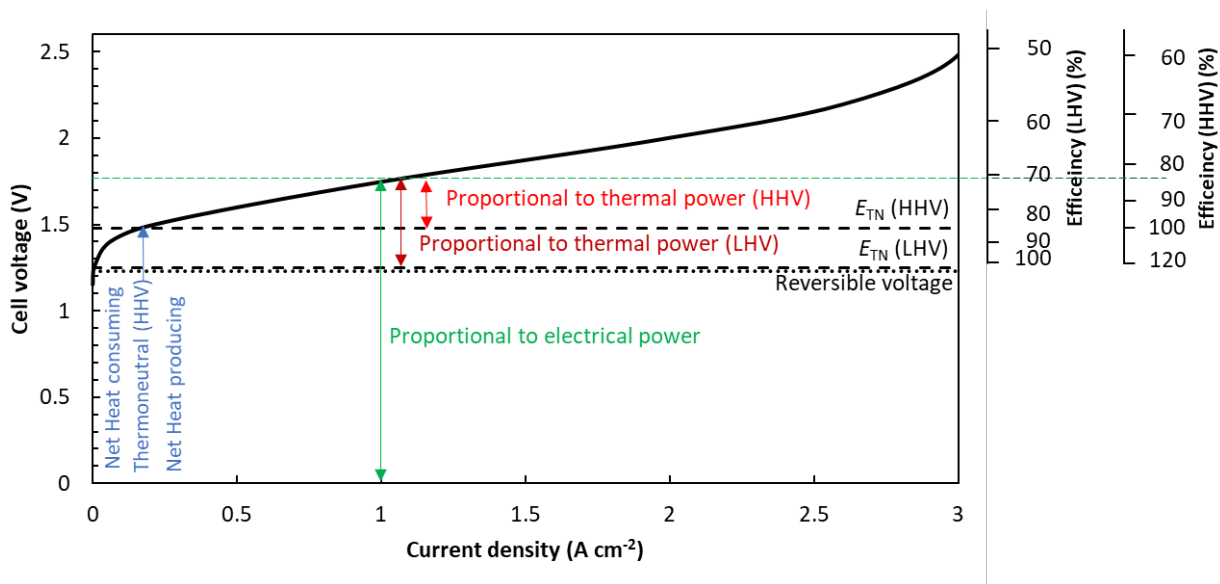
The total system efficiency is the product of all the described efficiencies.

$$\eta_{sys} = \eta_{cur} \eta_{vol} \eta_{ext} \quad (11)$$

All the efficiencies above depend on several factors and in particular on the current density, i.e., the hydrogen production rate. To the user, the hydrogen producer, the total system efficiency is most interesting. That is how much electrical energy is required to produce a given amount of hydrogen. It is often stated by the supplier on a total system level and given at kWh pr. normal  $m^3$  ( $Nm^3$ ) of hydrogen produced. This practice eliminates the need for clarification on which energy value (heating value) is assigned to hydrogen. However, it introduces a new ambiguity since it is not necessarily clear in all contexts what a normal  $m^3$  is. Pressure and temperature must be defined and different organization work with different standardized values for pressure (1 bar and 1 atm) and for temperature (0 °C, 15 °C, 20 °C or 25 °C), called either “standard” or “normal”. Most commonly in the electrolyzer community, a normal cubic meter is defined at 1 atm and 0 °C. A more consistent indicator would be kWh  $kg^{-1}$  hydrogen. **Table 2** has the values. Note that the values of  $\Delta H$  and  $\Delta G$  are positive showing that the

energies are supplied to the system during electrolysis. System efficiencies as a percentage can easily be calculated by division of the relevant minimum value in **Table 2** by the actual energy consumption.

If the waste heat (if any) can be used for something, then it becomes more complicated, but that is most relevant for electrolyzers operated at high temperature because of the quality of the heat, but then again, high temperature electrolyzers are generally so efficient due to excellent kinetics that they are rather in need for an external heat supply than being a heat supplier themselves. This, among other things, is illustrated in **Figure 3**. It can be seen that at high current densities,  $E_{\text{cell}} > E_{\text{TN}}$  and consequently,  $\eta_{\text{con}} < 100\%$ . At low current densities,  $E_{\text{cell}} < E_{\text{TN}}$  and then  $\eta_{\text{con}} > 100\%$ . The required energy quantity that exceeds the electrical energy must naturally be supplied as heat from an external source.



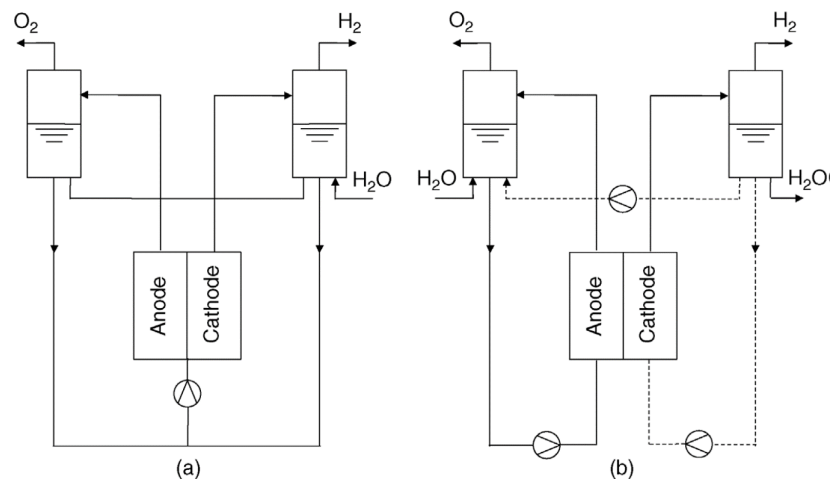
**Figure 3.** Polarization curve of an arbitrary electrolyzer. At a specific current density, the curve crosses the hatched line of the thermoneutral voltage. At lower current densities, it is a net consumer of heat and heat must be supplied to the cell to maintain the temperature. At high current densities, the cell voltage is above thermoneutral and the cell produces more heat by the internal processes than it needs. The cell then becomes net heat producer and must be cooled. At thermoneutral, the cell is thermally balanced. At an arbitrarily chosen working point (here close to  $1 \text{ A cm}^{-2}$ ) the voltage proportional to the electrical power supplied is highlighted by the green hatched line and the net thermal power evolved are indicated depending on whether water is supplied as liquid or vapour. To the right, the voltage efficiency can be read with respect to higher and lower heating value.

### *Stacks and systems – common principles*

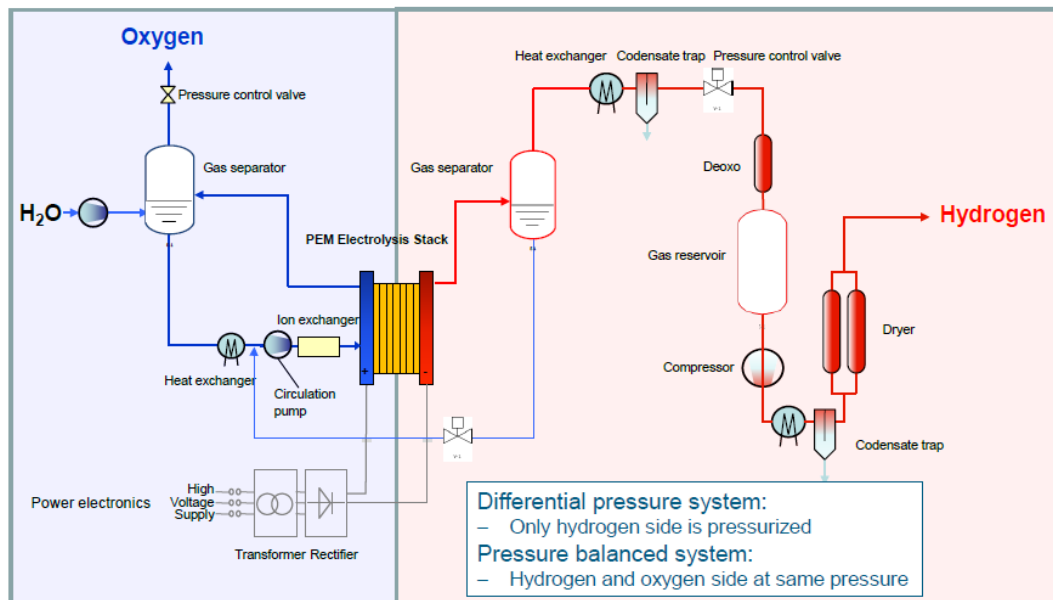
Assembly of multiple cells in stacks is always done to reach useful hydrogen production capacities. With rates in the order of 0.4 to a few ampere pr.  $\text{cm}^2$ , it is obvious that a large electrode area is needed, and this is only practical by stacking many cells. Stacking is very similar to the stacking of fuel cells, but the



system around, the balance of plant (BOP) is different. The first task is to get the produced gasses out of the cell and this is done by circulating of the fluids. In low temperature cells, a mixture of liquid and gas bubbles is pumped to separator tanks after which the liquid phase is pumped back to the electrode compartments. It can be done in a common system where the fluids are mixed after degassing or it can be via two separate loops. The advantage of the common loop system is that any change of concentration in the fluid (e.g., KOH in case of an alkaline electrolyte) due to consumption of water is averaged. The disadvantage is that remaining dissolved hydrogen and oxygen are mixed. The latter can be avoided with dual circulation loops, but that requires an extra circulation pump. See **Figure 4**. Additional components of the system are heat exchanges, a catalytic oxygen trace removal unit, a dryer, a compressor and power electronics. See **Figure 5**. Water processing, i.e., desalination and purification is also mandatory prior to electrolysis.



**Figure 4.** Fluid circulation architectures. Common (a) and separate (b) circulation of electrolyzer fluids.



**Figure 5.** A full system for a PEM electrolyzer.

## Types of electrolyzers

Electrolyzers are classified after the electrolyte, just like fuel cells. In principle, any of the fuel cells types can be operated as an electrolyzer, but the optimization of the components is directed by slightly different needs and the system around, the balance of plant, is very different. The dominating electrolyzer systems are the alkaline electrolyzer the PEM electrolyzer and the solid oxide electrolyzer. They are listed in **Table 3** with their most common abbreviation. In the following, the three electrolyzers are described in more detail.

**Table 3.** The main types of electrolyzers. The short names are the most common abbreviations with alternatives in brackets. “EC” stands for “electrolyzer cell” and “WE” for “water electrolyzer”.

Name	Short	Electrolyte	Ions conducted	Operating temperature	Characteristics	State of development
Alkaline electrolyzer	AEC (AWE)	Aqueous KOH in porous separator	OH <sup>-</sup>	60-90 °C	Traditional proven technology	Mature traditional technology.
Proton exchange membrane electrolyzer	PEMEC (PEMWE)	Proton conducting polymer	H <sup>+</sup>	60-80 °C	Recent advanced and compact technology	Recent market introduction
Solid oxide electrolyzer	SOEC (SOWE)	Oxide ion conducting ceramic	O <sup>2-</sup>	700-900 °C	Very high conversion efficiency	Mostly under development. Some demonstration

### *The alkaline electrolyzer (AFC)*

The alkaline electrolyzer (AEC) is the traditional well-proven technology, which has been available over many decades. It is known for high reliability, but also for a large footprint due to low current density, typically in the range of 0.2-0.5 A cm<sup>-2</sup>. Stacks can be large, producing hydrogen at rates close to 4000 Nm<sup>3</sup> h<sup>-1</sup> (ca. 15 MW<sub>e</sub>) and with electrode diameters up to between 1 and 2 meters (**Figure 6**). Size and robustness of the technology has been demonstrated convincingly by industrial installations mainly in connection with the production of ammonia and fertilizers. Sable Chemical Industries in Zimbabwe has operated 28 stacks from IHT with a total hydrogen production capacity of 21,000 Nm<sup>3</sup> h<sup>-1</sup> (ca. 100 MW<sub>e</sub>) from 1973 and until recently. The largest electrolyzer plant was in Glomfjord, Norway, with 168 AEC stacks by Norsk Hydro. It produced over 30,000 Nm<sup>3</sup> h<sup>-1</sup> (ca. 135 MW<sub>e</sub>) and the installation was in operation from 1953 to 1991. Before that, from 1929, Norsk Hydro operated 3 plants in Rjukan with 440 electrolyzers and a capacity of over 60,000 Nm<sup>3</sup> h<sup>-1</sup>. The AEC stacks can be manufactured from reasonably inexpensive materials and do

not depend on noble or strategic elements for the catalysts or for internal coatings. Nickel and nickel alloys are the key materials for the interior components including the catalysts. The construction of the traditional AEC is rather simple and this is what makes it so robust.



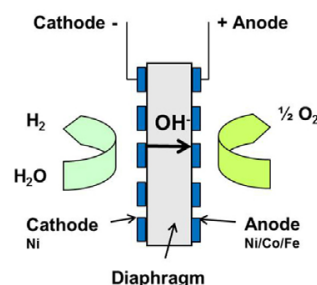
**Figure 6.** Large alkaline stacks from IHT.  $760 \text{ Nm}^3 \text{ h}^{-1}$ . Ca.  $3.5 \text{ MW}_e$ . The long tanks above the stack are the separator tanks.

The electrode reactions are the following:

Anode (oxygen evolution):  $4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$

Cathode (hydrogen evolution):  $4\text{H}_2\text{O} + 4\text{e}^- \rightarrow 2\text{H}_2 + 4\text{OH}^-$

Total:  $2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$

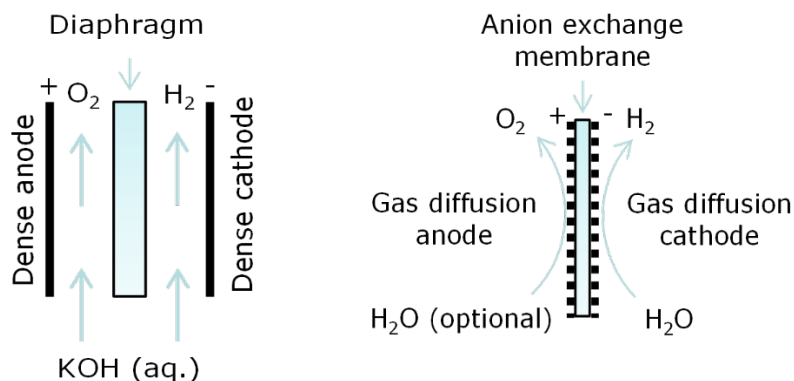


**Figure 7.** An alkaline electrolyzer cell.

We don't have any free protons in a highly alkaline environment (remember that at pH 14 the concentration of  $\text{H}^+$  is  $10^{-14}$  molar). The protons reduced are protons in the water molecule and the remainder is an  $\text{OH}^-$  ion, which is the charge carrier across the electrolyte. The electrolyte is concentrated aqueous potassium hydroxide, KOH, in a porous matrix between the electrodes. Originally, a rather thick mat of asbestos fibres was used because of its excellent stability in hot KOH. Today asbestos has been phased out in most countries due to its carcinogenicity and the state-of-art material is a porous polymer diaphragm with the trade name Zirfon Pearl from Agfa.

The interior of the alkaline cell is made from nickel or nickel coated metals. Nickel forms easily a dense oxide layer which is insoluble in the alkaline environment and this layer protects the metal from further corrosion. Fortunately, nickel and many of its oxides are also catalytically active for HER and OER. At the cathode where hydrogen is evolved, the conditions are reducing due to the low potential and nickel is metallic (not an oxide). A classic catalyst material is the Raney nickel, which is a highly porous, almost spongy form of nickel. It is made from a Ni-Zn or Ni-Al alloy from which the alloying metal is leached out in strong base leaving behind the porous nickel structure. The high surface area increases the number of catalytic sites pr. volume. On the anode electrode where the potential is high, nickel is in an oxide (or oxide-hydroxide) form, which is also active. The electrocatalytic activity can be improved by mixing in other metals forming alloys at the cathode and mixed oxides at the anode. Some of the most active catalysts in the alkaline system are based on Ni-Mo for HER and Ni-Fe for OER, but the choices are plenty.

The main reason for the low rate capability is the high internal ohmic resistance especially in stacks with gaps of several mm between the electrodes (Figure 8, left). Some improvement has been made with zero-gap or partly zero gap designs around a porous diaphragm, but such a porous separator, e.g. Zirfon Pearl from Agfa, still needs a certain thickness to prevent crossover or blowout of the electrolyte. A great step forward would be a viable separator or membrane with low area-specific resistance. Attempts to develop alkaline ion exchange membranes inspired by their acidic counterparts, the perfluorinated sulfonic acid membranes, have been plenty, but yet most materials are insufficient in terms of conductivity and especially stability.



**Figure 8.** The principles of the gap (left) and zero-gap (right) configurations of the alkaline electrolyzer. The zero-gap configuration provides a much shorter transport way for the ions and thus a much smaller internal ohmic resistance.

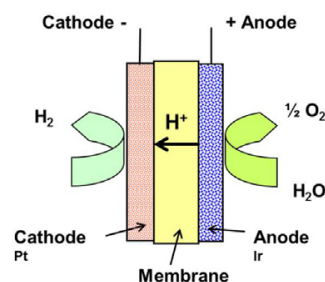
### *The PEM electrolyzer (PEMEC)*

The AEC has been the state of art electrolyzer technology until recently when the PEM electrolyzer (PEMEC) was introduced to the market (**Figure 9**). The latter has gained high popularity due to a much higher rate capability (1-2 A cm<sup>-2</sup>) and thus a smaller footprint. Moreover, since the electrolyte is a membrane conducting without addition of ions, only pure water is flooding the electrode compartments, and the fluid circulation for separation of the products gas from the liquid is only a flow

of pure water. Actually, only the anode compartment needs to be flooded because this is where water enters the process (see Figure 9), but the membrane is highly permeable to water so the cathode chamber might be flooded too.

The PEMEC is named by the proton exchange membrane it uses for electrolyte. It is the same proton conducting membrane as the one used in PEM fuel cells (a perfluorinated sulfonic acid, often the commercial products Nafion or Aquivion). The catalysts are entirely noble metal based, but the PEM electrolyzer differs from the equivalent fuel cell by having platinum only in the hydrogen electrode. The OER catalyst is iridium oxide ( $\text{IrO}_2$ ). The overpotential generated by the oxygen process causes an increase of the oxygen electrode potential for the electrolyzer and a decrease for the fuel cell. Consequently, metallic Pt is the stable form under normal operating conditions in the fuel cell, but Pt oxide, had it been used in the electrolyzer, is not a very good catalyst for the ORR. Ir is also in the oxide form, but  $\text{IrO}_2$  is a good catalyst and moreover, reasonably stable towards dissolution.

The electrode reaction are the following:



**Figure 9.** A PEM electrolyzer cell.

The membrane is highly acidic due to the immobilized sulfonic acid ions that liberated protons. Few materials are stable in the acidic environment and some only at the low potential of the cathode, the hydrogen electrode. Carbon fibre materials with a Pt catalyst can be used for the hydrogen electrode, just like in PEM fuel cells, but for the oxygen electrode with the high potential, carbon is not stable. Instead, the bulk of the flow plates and the oxygen electrode are made from titanium because it is protected by a stable dense oxide layer in the acidic environment. The corrosion problem is not only that materials corrode away, but if an oxide layer (as the initial corrosion product) has poor electrical conductivity, severe contact resistances emerges where current is supposed to pass between cell components. The solution is to coat flow plates and porous transport layers of the electrodes with noble metals. One might ask why it is necessary to use expensive titanium if the components are coated with noble metals anyway. The reason is that imperfections in the coating might lead to local corrosion of the material underneath. In terms of contact resistance this would not be a big problem to begin with as most of the surface will still be intact and provide pathways for conduction. The problem is that if the bulk material is steel for instance, iron will be dissolved and iron ions are harmful to the membrane.

The PEMEC has a number of advantages that are often stressed. It is well suited for dynamic operation and responds fast to transients in the current. This is a strong advantage for applications like grid

stabilizing services. It is also the most suited system for high pressure operation. If hydrogen is produced at high pressure, the need for subsequent compression before storage is reduced. Even if a subsequent mechanical compression step is needed, the advantage of the compression by the electrolyzer can be significant. The minimum energy needed for compression of a gas from 1 bar to 10 bar is the same as for compression the same amount of gas from 10 bar to 100 bar or from 100 bar to 1000 bar (only exact for a perfect gas). Pure oxygen at high pressure is very reactive and the handling of it is not as trivial as it might seem. Therefore asymmetric operation with only the hydrogen side pressurized is desirable, and it is possible with the PEMEC due to the tight membrane without pores from which the electrolyte can be blown out.

It is often said that the PEMEC is more efficient than the AEC, but in terms of energy efficiency, the two systems are similar, because they are operated at very different current densities dictated by the acceptable energy efficiency, say 65-80 % (HHV). It is fairer to say that the PEMEC is more *effective* in the sense that one gets more out of a given size of the device.



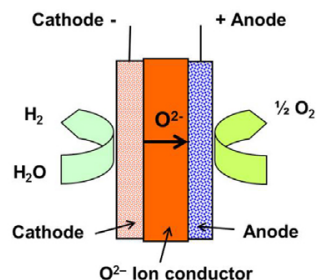
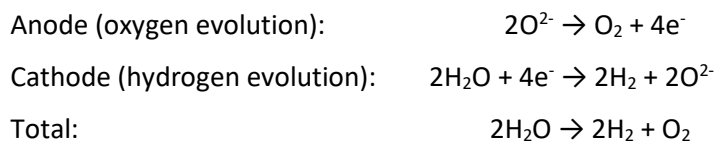
Figure 10. A 2 MW stack from Giner (US) (now Plug Power). Produces up to 900 kg H<sub>2</sub> a day.

### *The solid oxide electrolyzer (SOEC)*

The single cell of the solid oxide electrolyzer (SOEC) is made entirely from ceramic materials. The electrolyte is an oxide ion conductor (**Figure 11** and **Figure 12**). Solid state oxide ion conductors are

metal oxides especially optimized for this purpose. The metal oxides are crystalline, i.e., ordered, compounds of one or more types of positive metal ions ( $M^{n+}$ ) balanced by negative oxide ions ( $O^{2-}$ ). The positive and negative ions occupy specific positions neighbouring each other. In some tailored compositions, some of the oxygen positions are left empty (called vacancies) and this opens the possibility for a neighbouring oxide ion to take the place leaving behind another vacancy, which can be filled by the next oxide ion. This is the mechanism for the oxide ion conduction. One can imagine that it takes energy for the oxide ion to break loose from its position among metal ions and move before it can find rest in the new position and liberate the energy again. This energy is the activation energy for the process and only ions with that amount of energy (vibrations) can shift position. At room temperature the average thermal energy of the ions in the crystal lattice is much too low and even though the energy is unevenly distributed, the likelihood that a particular ion has enough thermal energy to move, is extremely low. Consequently, oxide ion conduction at room temperature is correspondingly slow, or practically absent. The oxide ion conductors used today need temperatures of at least 600-700 °C to have sufficient conductivity for an SOEC. Often SOECs are operated at 750-900 °C. The standard electrolyte material is yttria stabilized zirconia (YSZ) (yttria is yttrium oxide,  $Y_2O_3$  and zirconia is zirconium oxide,  $ZrO_2$ ). If some of the  $Zr^{4+}$  are replaced by  $Y^{3+}$  in the  $ZrO_2$  crystal lattice, it is clear that the amount of positive charge becomes too small to balance the charge of all the oxide ions and some positions have to be left as vacant to ensure charge balance. The term “stabilized” refer to the fact that yttria stabilizes a certain high temperature structure of zirconia.

The electrode reactions in an SOEC are

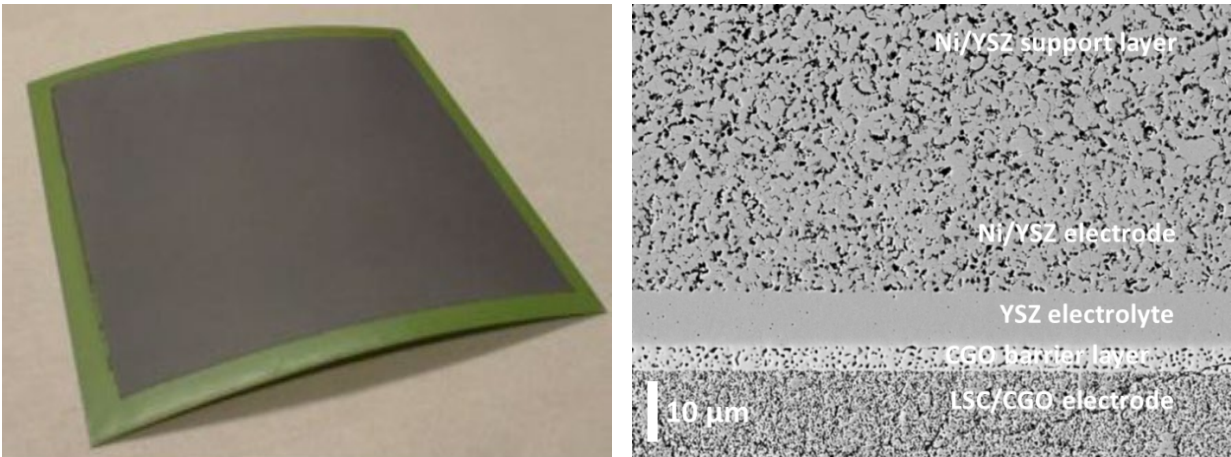


**Figure 11.** A solid oxide electrolyzer cell.

The electrodes are also ceramic. The hydrogen electrode is a cermet, a composite of a ceramic and a metal. The ceramic component is again YSZ, but here it is mixed with finely distributed nickel domains which serve as both catalyst and electron conductor. Everywhere the hydrogen evolution shall take place, the gas phase, the ion conducting phase and the electron conducting phase must coexist locally. Water vapour must have access, electrons must be supplied and the formed oxide ions must be transported to the electrolyte. These places constitute the three-phase boundaries. The YSZ conducts the ions and the water vapour enters through the pores by which the produced hydrogen escapes.

The oxygen electrode is made with mixed oxides of the perovskite structure and common choices are lanthanum strontium manganite (LSM,  $La_{1-x}Sr_xMnO_{3-d}$ ), Lanthanum strontium cobaltite (LSC,  $La_{1-x}Sr_xCoO_{3-d}$ ) and Lanthanum strontium cobaltite ferrite (LSCF,  $La_{1-x}Sr_xFe_{1-y}Co_yO_{3-d}$ ). These materials are at the same time ion conductors, electron conductors as well as good OER catalysts.





**Figure 12.** Solid oxide fuel cell or electrolyzer cell. Left: one single cell. Right: cross section of a cell.

### *Regenerative cells*

The idea of operating the same cell as an electrolyzer at times and as a fuel cell at other times is naturally very tempting. Such cells are called regenerative cells or reversible cells. The latter term can be misleading if understood in a thermodynamic sense, since no electrochemical cell is reversible in the sense that it doesn't generate entropy during operation. What is meant is only that the process can be reversed. Developing such regenerative cells is not as straightforward as one might expect, at least not for the low temperature systems with liquid water (alkaline and PEM).

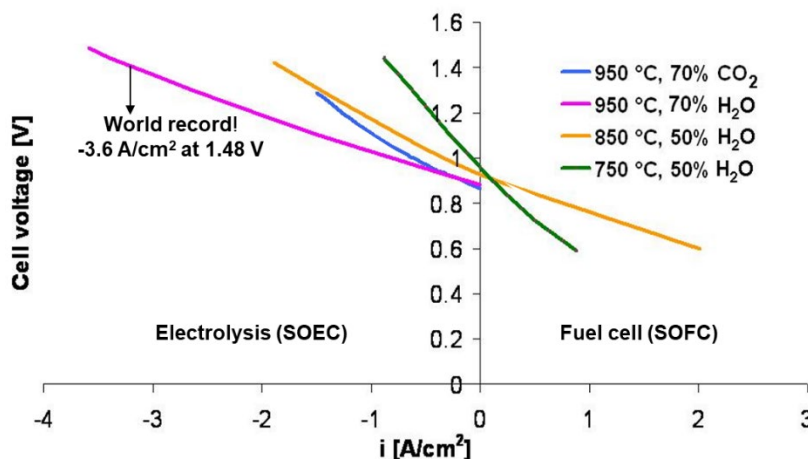
The low temperature cells face two fundamental problems. First, in electrolyzer mode we like the electrodes to be wetted well at all time and bubbles should be released and only occupy the electrode surface as little as possible. The electrode should be flooded. Consequently, the electrode must be hydrophilic (water loving). In fuel cell mode, on the other hand, we like the reacting gasses to cover the electrode and not the produced water, and we certainly don't want electrode flooding. The solution is to make the electrode sufficiently hydrophobic (water repelling). It is difficult if not impossible to optimize the electrode in to opposite directions at the same time.

The other problem is the catalysts. The very difference in electrode potentials, especially for the oxygen electrode with the largest overvoltage, makes it likely that the catalyst changes oxidation state when changing between electrolyzer and fuel cell mode. As mentioned above, this is the reason the PEM system uses different oxygen catalysts for fuel cells and electrolyzers. It is possible to apply two catalysts in the same electrode, but if the fuel cell catalyst is corroded in electrolyzer mode, it is a problem. The alkaline system might face similar problems, but with so many metal oxide based choices, it cannot be ruled out that some catalysts are stable in a large enough potential range to work in both modes.

With the solid oxide cells, it is more likely that regenerative cells have a future. All reactants and products are gasses so the hydrophilicity/hydrophobicity is not a problem. Moreover, the electrode polarization (the overvoltage) is smaller, which makes it easier to find materials stable in both modes.



Actually, same solid oxide cells (SOC, the term used when referring to both fuel cells and electrolyzer cells) do in many cases work well in both modes. See the combined polarization curves in **Figure 13**.



**Figure 13.** Polarization curve of a solid oxide cell (SOC) operated in both electrolyzer mode (left) and fuel cell mode (right). (DTU)

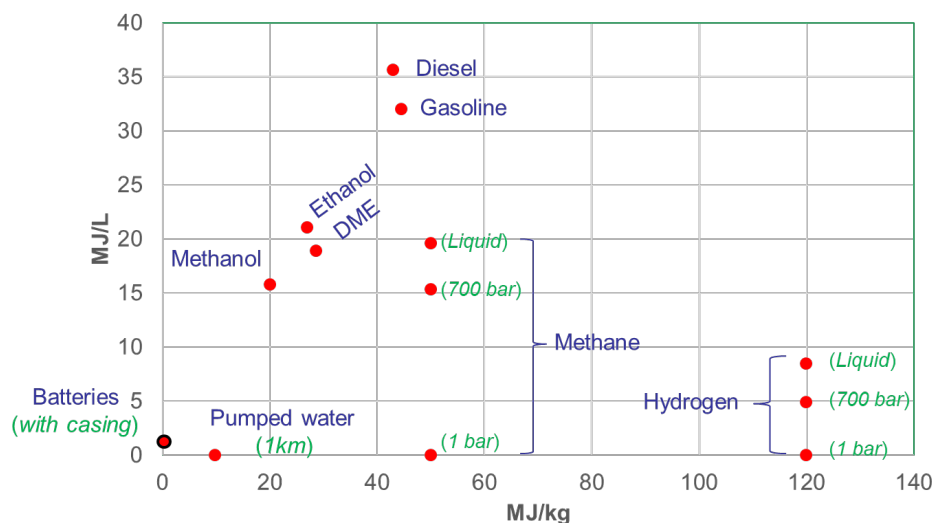
## Synthetic fuels

The term “*synthetic fuel*” or just “*synfuel*” means fuel that is made synthetically as compared to fuels extracted from natural reserves e.g., in oil and gas fields or coal mines. It can be questioned if cracked and refined petrochemical products are less synthetic, but the term synthetic fuel is well established and used for the variety of fuels that can be built from simple starting materials, which can be hydrogen and CO or CO<sub>2</sub>. Today, the hydrogen is often expected to stem from electrolysis driven by renewable electricity generated from wind or solar, but hydrogen from gasification of coal is also considered. Then it is not part of the green transition, but just a possible business case or a necessity in an isolated economy with limited oil reserves. Examples of the latter are Germany during WW2 where fuel for the war machine was synthesized from coal. A similar solution was adopted in South Africa during the apartheid embargo. Synfuels in which the energy comes from electricity are also termed “*electrofuels*” and at time even “*liquid electricity*”, perhaps with a smile. Hydrogen formally falls within the definition of a synthetic fuel, but in many contexts it is carbonaceous fuels that are referred to.

When hydrogen is processed further to methane, methanol or gasoline by reaction with CO or CO<sub>2</sub>, some energy is lost in the synthesis process and the final fuel contains a little less energy than the original hydrogen. This can make it look silly to make the effort, and strictly energetically, it doesn't make sense. However, the benefit is a fuel that is easier to store, transport and fill. The energy density is higher than of hydrogen regardless of the way hydrogen is stored. This is important for energy intense mobile applications like heavy transport and aviation. Moreover, and in contrast to hydrogen, many synfuels fit into the existing fuel infrastructure, perhaps with minor modifications. These advantages might be decisive, but for applications where hydrogen can be used, this is clearly the most energy efficient solution. The energy density (energy pr. volume) and the specific energy (energy pr. mass) of

some common fuels are plotted in **Figure 14**. Hydrogen, batteries and pumped hydro are added for comparison. Pumped hydro is water elevated to a high level, typically a mountain reservoir, storing the energy as potential energy, which can be reclaimed with high efficiency via a turbine.

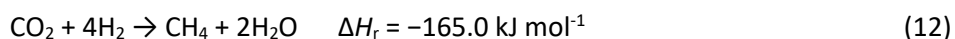
Basically, what it takes to make synthetic fuels is a carbon source and hydrogen. If the carbon source is itself a fuel (coal, heavy oil or other fossil fuels that are not easily serving a given fuel purpose) then the chemical energy is already there. If the carbon source is CO<sub>2</sub>, then the energy of the fuel that is the desired outcome of the process, must be provided by other sources, typically hydrogen and perhaps to some extent heat.



**Figure 14.** Energy density (energy pr. volume) and specific energy (energy pr. mass) of selected fuels.

### *The Sabatier process for methane*

The Sabatier process (*Paul Sabatier*) is a process for the synthesis of methane from hydrogen and carbon dioxide



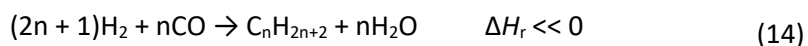
It is carried out at 300-400 °C over a nickel catalyst. The product is often referred to as “*synthetic natural gas*” (SNG) although it is just methane. One obvious use of the process is for the methanation of the CO<sub>2</sub> of biogas. Biogas is made by fermentation of organic substances like farming waste of all kinds. The microorganisms consume some of the chemical energy and produce CO<sub>2</sub>. Additional CO<sub>2</sub> is formed by the oxygen already present in starch, cellulose and other biological substances. Up to about 50 % of biogas can be CO<sub>2</sub>, so upgrading to CH<sub>4</sub> represents a significant boost of the energy content. The CO<sub>2</sub> is moreover a high concentration source of CO<sub>2</sub> for synthetic fuels. A nice feature of synthetic natural gas is that it can be handled by the natural gas infrastructure that is already present in many countries, especially natural gas grids and pipelines.

### *Fischer-Tropsch synthesis for longer hydrocarbons*

When it comes to larger hydrocarbons for liquid fuels like synthetic gasoline and jet fuel, the way is to build the chains up carbon by carbon. The technology was originally developed by *Franz Fischer* and *Hans Tropsch* in 1925 and is named after the inventors. The building blocks are then CO and H<sub>2</sub>. A mixture of CO and H<sub>2</sub> is called *syngas* (synthesis gas) and by tuning the ratio of the two components and the process condition and with a proper choice of catalyst, a variety of substance can be synthesized. If the carbon source is CO<sub>2</sub> it is first converted to CO by the *reverse water gas shift reaction* or by electrolytic reduction of CO<sub>2</sub>



Then follows the Fischer–Tropsch process:



The product is a mix of many different hydrocarbons and it might be necessary to crack the largest molecules into the right size for the desired fuel. This was the technology used in Germany during World War II and in South Africa during the international embargo in the apartheid days.

### *Methanol*

Methanol is another fuel (or chemical) that can be produced from syngas. The reaction takes place over a copper based catalyst at 200-220 °C and moderate pressure after



or



### *Ammonia*

Ammonia production is the largest application of hydrogen today and most of the ammonia is used as the nitrogen source in synthetic fertilizers. However, ammonia can also be regarded as a fuel. Ammonia is a gas at standard conditions, but the vapour pressure is only around 10 bar at room temperature so at that pressure it is liquefied and easily stored as such.

Ammonia is produced in large plants by the Haber-Bosch process (after *Fritz Haber* and *Carl Bosch*) which is a direct reaction between hydrogen and nitrogen after



at 100 – 250 bar and 400 - 500 °C over an iron based catalyst. Since the number of gas molecules decline in the reaction, high pressure favours the product. High temperature favours the reaction rate, but it also shifts the reaction equilibrium towards the reactants (negative reaction enthalpy). Consequently, temperature is a compromise between reaction rate and equilibrium.

The obvious disadvantage of ammonia is the strong and unpleasant smell and the fact that it is harmful and even lethal at certain concentrations in the air. The very attractive feature is that it does not contain carbon. Thus it doesn't emit CO<sub>2</sub> and extraction of N<sub>2</sub> from air is so much easier than of CO<sub>2</sub> because four out of five molecules in the air is N<sub>2</sub>. If ammonia is to be produced from renewable hydrogen, there is no dependence on point source with CO<sub>2</sub> at practical concentrations, like cement factories and traditional coal fired power plants.

Ammonia can be combusted as is with oxygen after



It can also be easily converted directly in a solid oxide fuel cell, but before use in a PEM fuel cell it has to be converted back to hydrogen first by cracking, which is the reverse of the formation process above. This requires a temperature of at least 300 °C both for kinetic reasons and for the equilibrium composition to be in favour of H<sub>2</sub> and N<sub>2</sub>. Ammonia is considered as a future fuel for certain large scale uses, like in ships. For commuter vehicles and smaller scale applications it is questionable whether the safety issues can be handled satisfactory.

## Carbon capture

Carbonaceous synfuels require a carbon source, and CO<sub>2</sub> which would otherwise be emitted, is normally considered carbon neutral. This is based on the simple assumption that it just makes another fuel cycle before it is emitted. This makes sense, but energy used for collecting the CO<sub>2</sub>, for the handling and for the synthesis processes has to be carbon neutral as well for the assumption to hold completely.

Carbon capture is easiest and least energy consuming when done from point sources. These are sources with high large amounts at high concentration or partial pressure. Common examples are cement factories, biogas facilities and conventional power plants. As long as such sources are not fully utilised they are the first choice. On the longer term, they will not suffice and capturing from the ambient air may be necessary. This is called *direct air capture* (DAC) although it is not the air that is captured.

In the literature, distinction is made between *pre-combustion* and *post combustion* capture, but the caption process is in principle the same. Pre-combustion relates to CO<sub>2</sub> from a combustion process, but in a setup where CO<sub>2</sub> is separated after a reforming process where the fuel reacts with water, forming hydrogen and CO<sub>2</sub> prior to the combustion process (combustion of the formed hydrogen). Then CO<sub>2</sub> is not diluted with nitrogen as it is after combustion with air. Another process leading to high CO<sub>2</sub>

concentration is the *oxy-fuel process* in which the fuel is combusted with pure oxygen. The oxygen can be the product of electrolysis.

Capturing can be performed by *absorption*, *adsorption* or *filtration*. The difference between absorption and adsorption is that adsorption occurs at a surface while absorption occurs in the bulk of a liquid, a solution or a solid. A common term for both processes is *sorption*. Separation via sorption can be *pressure swing* or *temperature swing* in which either temperature or pressure (or both) is changed to shift from sorption mode to desorption mode. In some techniques where water is involved in the sorption process, sorption and release can be driven by *moisture swing*. The Swiss company Climeworks develop direct air capture plants with large CO<sub>2</sub> collectors.

## Absorption

The state of art CO<sub>2</sub> adsorbing medium is amines like monoethanolamine, NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH (MEA), diethanolamine, NH(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub> (DEA), and methyldiethanolamine, CH<sub>3</sub>N(C<sub>2</sub>H<sub>5</sub>OH)<sub>2</sub> (MDEA). These are liquids and CO<sub>2</sub> binds as shown in Figure 15. The binding process is exothermic and CO<sub>2</sub> is later released by heat at higher temperature.

The lower the concentration of CO<sub>2</sub>, the stronger bonding is needed for effective absorption. Stronger absorbents are hydroxides, e.g., Ca(OH)<sub>2</sub> and NaOH. Solutions of these inorganic salts readily absorb CO<sub>2</sub> from air, but the downside of the strong bonding is that it also takes more energy to release the absorbed CO<sub>2</sub>.

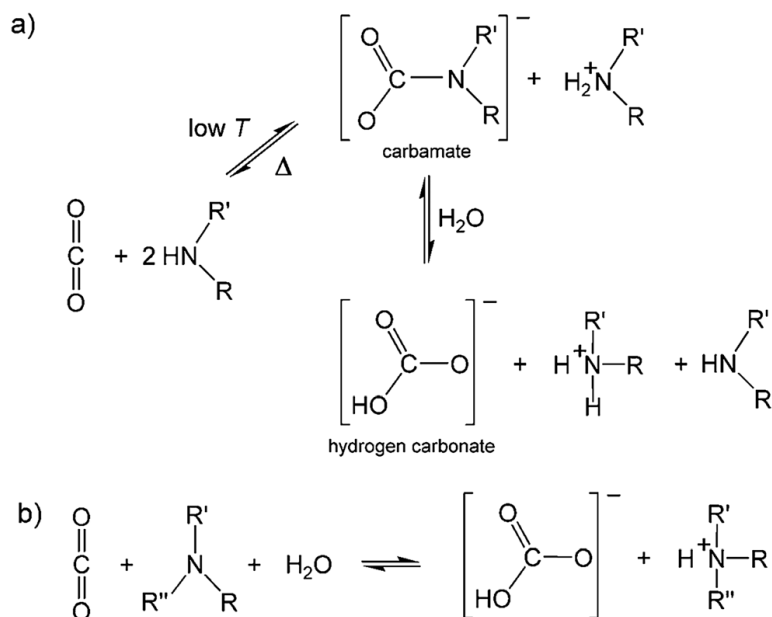
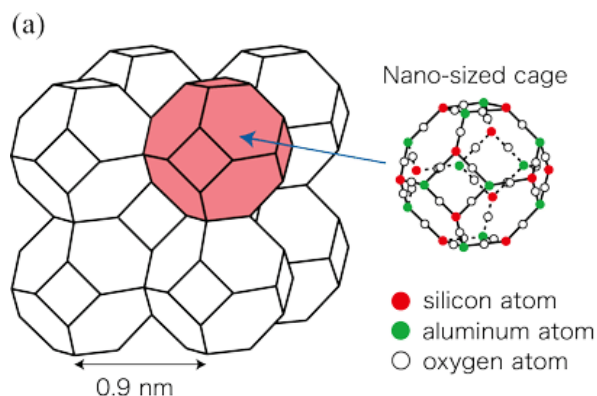


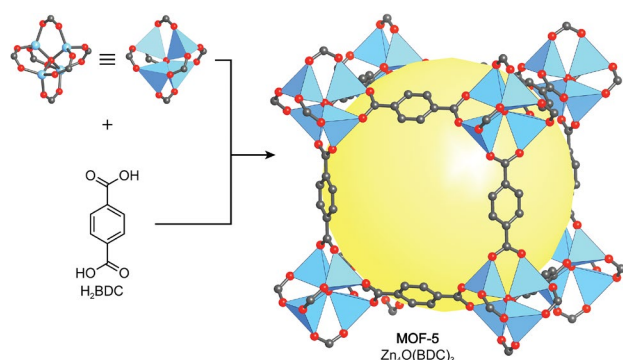
Figure 15. The binding and release of CO<sub>2</sub> by amines. R, R' and R'' are hydrogen, methyl groups or radicals of ethanol.

## Adsorption

Adsorption requires a material with a high surface area. Common classes of high surface area materials are various carbon materials (active carbon, carbon nanotubes etc.), zeolites and metal-organic frameworks (MOF). Zeolites and MOFs are inorganic and organic/inorganic structures, respectively, with very well-defined pore sizes. See Figure 16 and Figure 17. They can be tailored to selective adsorption of CO<sub>2</sub>. Regeneration, i.e., CO<sub>2</sub> release is done by pressure or temperature swing.



**Figure 16.** An example of a zeolite. Specific structures are formed by the mixed oxides of cations of different charge and size. The pore shapes and sizes are well-defined and given by the choice of positive ions and their ratio. The shown structure continues in all directions.



**Figure 17.** An example of a metal-organic framework (MOF). The blue tetrahedral arrangements are zinc ions coordinated with four oxygen ions. The inorganic corner structures (nodes) made around metal ions are connected by organic bridges. The shown structure continues in all directions.

## Membrane filtration

Semi-permeable membranes can be used to separate CO<sub>2</sub> from a gas mixture. The selectivity is caused by a combination of pore sizes and affinity to specific molecules in the membrane. The driving force for the passage through the membrane is the partial pressure difference across. Therefore, membrane filtration of CO<sub>2</sub> for direct air capture requires a very high total pressure in order to make the partial pressure of CO<sub>2</sub> high enough and then the partial pressure of more abundant gasses becomes even higher and the CO<sub>2</sub> selectivity has to be very significant.