Efficiency – Electrolysis

White paper

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Electrolysis

In 1800, the two English scientists William Nicholson and Anthony Carlisle discovered direct current electrolysis, thereby establishing electrochemistry as a new scientific field. For a long time, electrolysis was the dominant technology for the industrial generation of hydrogen. However, the increasing use of natural gas largely displaced this technology with the more cost-effective steam reforming. Now, over 200 years later, the splitting of water with electrical current is experiencing a renaissance. This is because this technology provides the possibility of converting and storing regenerative electric power in the form of hydrogen as a chemical energy source. In this process, traditional alkaline electrolysis is supplemented by the modern technology of polymer electrolyte membrane (PEM) electrolysis.

This is based on a publication by Russell et al. in 1973.[1] The high reaction rate and the high power density make PEM electrolysis interesting with the use of fluctuating renewable energy.

The efficiency of the electrolysis systems is critical both technically and economically for electrochemical hydrogen generation using renewable energy.[2]

Hydrogen generation costs are primarily dominated by the relatively high power costs in addition to operating hours and amortization of the plant. From a technical standpoint, these costs can only be reduced by increasing overall efficiency.

The following document is intended to illustrate for the reader what has to be taken into account when specifying or comparing efficiency levels for electrolysis systems.

Efficiency is not just efficiency

The efficiency of two processes can only be compared if all of the reference points are specified, if necessary also including standard conditions or system boundaries.

Summary

The efficiency of an electrolysis plant is one of its key parameters. It is largely determining for power consumption and therefore the bulk of operating costs. On the other hand, efficiency is interrelated with all of the peripheral parameters that also influence hydrogen generation costs, such as operating mode (operating hours) service life and investment costs. For that reason alone, the definition, calculation and interpretation of efficiency in electrolysis technology merit a closer look.

Stack, system and plant efficiency are often referred to in actual use of this technology. All three of these represent the products of various sub-efficiencies and are therefore not clearly defined. Stack efficiency, which is sometimes also known as DC efficiency, is itself the product of Faraday efficiency (also known as current efficiency) and the voltage efficiency, which is often used as a characteristic curve for an electrolysis process due to the dominating losses. In an ideal cell, voltage defines the efficiency over the range of current densities.
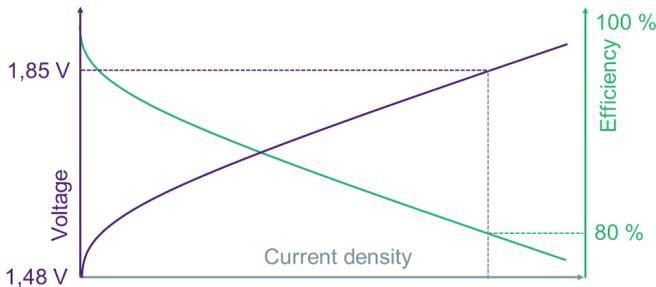
Figure 1: Schematic representation of a U/I characteristic and its indirectly proportional effect on efficiency.

The so-called U/I characteristic is therefore also the most important graph in the evaluation of electrolysis technology. In addition to the dominating losses in the cell, various auxiliary loads must be accounted for in determining the efficiency of a system or plant. The greatest challenge in this regard is to clearly define the boundaries of the system or balance. This affects not only the individual packages and their power consumption, but also the condition and quality of all parameters at the balance interfaces, such as water quality, waste heat, the quality of the electrical power and gas quality and pressure level.

$$\varepsilon_{Sys} = \frac{\dot{V}_{H_2, interface\ customer} \cdot H_o}{P_{el,AC,interface\ grid}}$$

$$\varepsilon_C = 1 - \frac{T_u}{T}$$

$$\varepsilon_V = \frac{E_{th}}{E_{cell}(i,T)}$$

$$\varepsilon_F = \frac{\dot{m}_{re\ H_2}}{\dot{m}_{id\ H_2}}$$

$$\varepsilon = \frac{E_{useful}}{E_{expended}} = \frac{P_{useful}}{P_{expended}}$$

$$\varepsilon_{LHV} = \frac{\dot{V}_{H_2} \cdot H_u}{P_{el}}$$

$$\varepsilon_{HHV} = \frac{\dot{V}_{H_2} \cdot H_o}{P_{el}}$$

$$\varepsilon_{id} = \frac{\Delta G_m}{\Delta H_m} = 1 - \frac{T\Delta S_m}{\Delta H_m}$$

$$\dot{n}_{id\ H_2} = \frac{I}{zF}$$

$$\varepsilon_{DC} = \frac{\dot{V}_{H_2} \cdot H_o}{P_{el,DC}}$$

$$\varepsilon = \frac{useful}{expended}$$

Electrolysis efficiency

Definitions of efficiency

A systematic examination of the efficiency of an electrolysis plant for hydrogen generation yields many specifications for a wide range of system boundaries. The most frequently used parameters are presented below.

Faraday efficiency
Faraday efficiency is the ratio of the actually produced and technically usable volume of hydrogen production and the theoretical maximum production volume. For example, it accounts for H_2 diffusion losses through the membrane, electrical current losses or hydrogen losses through the conversion of oxygen contamination in the downstream hydrogen purification system. Mass losses due to sampling or other losses can also be included in the calculation.

$$\varepsilon_F = \frac{\dot{m}_{re\,H_2}}{\dot{m}_{id\,H_2}} \tag{8}$$

$\dot{m}_{re\,H_2}$ is defined as the actual production volume of usable hydrogen and $\dot{m}_{id\,H_2}$ as the maximum possible hydrogen production volume under ideal conditions.

Voltage efficiency
Voltage efficiency is often confused with DC efficiency. Voltage efficiency is defined as the quotient of thermoneutral voltage E_{th} and the measured cell voltage $E_{cell}(i, T)$. Thermoneutral voltage comprises the heat energy bound by the change in entropy and is 1.48 V under standard conditions. This is not to be confused with the reversible cell voltage (E_{rev} = 1.23 V) that must be applied as a minimum to split water into its components of H_2 and O_2. The cell voltage, however, also includes all of the catalytic and electrical losses within the DC-powered electrochemical cell.

$$\varepsilon_v = \frac{E_{th}}{E_{cell}(i, T)} \tag{9}$$

DC efficiency
DC efficiency comprises the efficiency of the stack or of a module. Ultimately, it represents the ratio of the energy input to the stack in the form of DC current and the energy content of the technically usable hydrogen at the stack output. Specification of the higher or lower heating value is relevant here.

$$\varepsilon_F = \frac{\dot{V}_{H_2} \cdot H_O}{P_{el, DC}} \tag{10}$$

The product with voltage efficiency can also be used depending on the definition of the system boundaries for Faraday efficiency.

$$\varepsilon_{DC} = \varepsilon_v \cdot \varepsilon_F \tag{11}$$
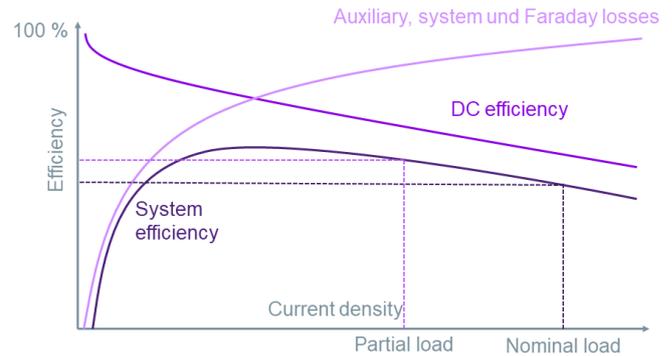

Figure 2: System efficiency and its schematic shape

System/plant efficiency
While the hydrogen community is somewhat in agreement regarding the above efficiency definitions, with the exception of the nomenclature, the system boundaries for system or plant efficiency are defined arbitrarily. Depending on the scope of supply, losses may also be included from AC/DC conversion and transformation from medium voltage, water treatment, the cooling systems, the provision of electrical energy for buildings and auxiliary packages or compression and hydrogen purification.
The respective system boundaries must be investigated in corresponding detail to enable the comparison of efficiency data.

$$\varepsilon_{Sys} = \frac{\dot{V}_{H_2, interface\,customer} \cdot H_O}{P_{el,\,AC, interface\,grid}} \tag{12}$$
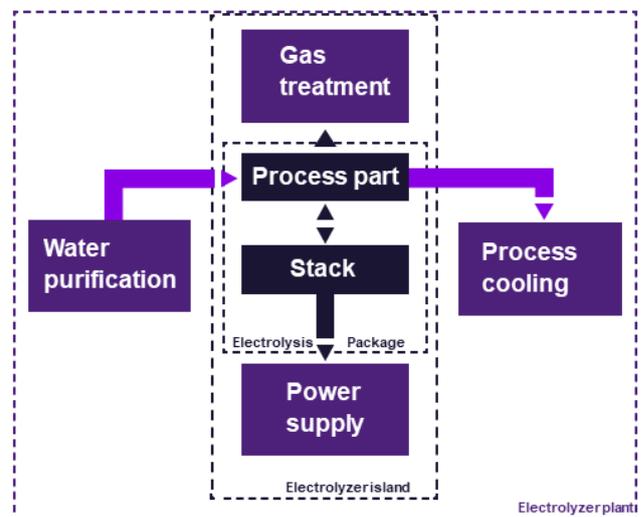

Figure 3: : Examples of system boundaries

U/I characteristic

As for most technical equipment, efficiency also depends on the operating point. The delightful aspect of electro-chemistry is that the efficiency of the electrochemical reaction, i.e. voltage efficiency, increases at part load. Temperature also has a significant effect on efficiency, as does pressure to a lesser extent.

Operating parameter I – current density

An electrolysis power curve is typically represented as a U/I characteristic.
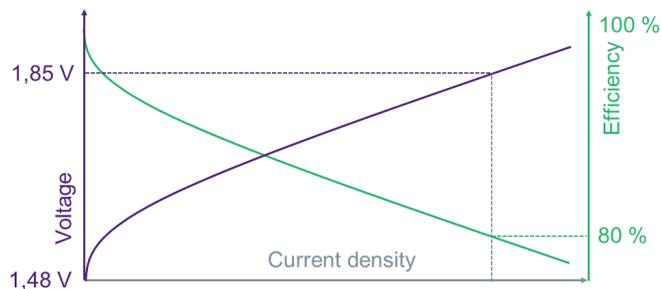
Figure 4: Schematic representation of a U/I characteristic

Because the current density is directly proportional to the rate of hydrogen generation (see formula 13), a higher current density defines a higher hydrogen production rate.

$$\dot{n}_{id\,H_2} = \frac{I}{zF} \qquad (13)$$

Where z represents the number of electrons participating in the reaction and F represents the Faraday constant. Cell voltage also increases with increasing current density, thereby reducing voltage efficiency in accordance with Equation 8.

Why not simply operate at low current densities?

The higher the current density, the higher the rate of hydrogen produc-tion. This means that the specific costs for an electrolyzer increase significantly at lower current density. The correct current density should always be optimized with the objective of minimizing hydrogen production costs, i.e. the optimum between high-efficiency and low specific CAPEX.

Operating parameter II – temperature

Temperature has a further significant effect on efficiency. Both the catalytic reaction rate as well as specific resistance are heavily dependent on temperature. The higher the temperature, the higher the efficiency.
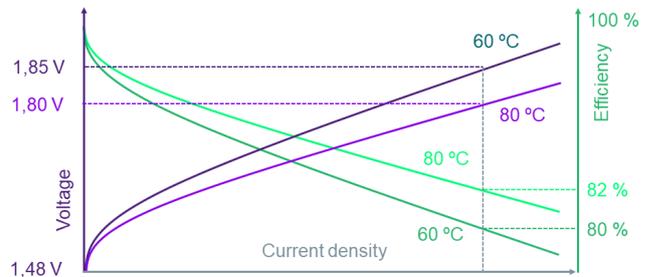
Figure 5: Schematic showing the effect of temperature on efficiency

Higher pressure has only a slight negative effect on effi-ciency, which is in part compensated by improved fluid dynamic properties in the cell, i.e. smaller gas bubbles.

Why not simply operate at higher temperatures?

Temperature has a significant effect on ageing and thus also on the longevity of an electrolyzer. The higher the temperature, the lower the service life. The correct oper-ating temperature should always be optimized with the objective of minimizing hydrogen production costs. The objective is to obtain an optimum balance between high efficiency and service life.

Increasing voltage efficiency

The slope of the U/I characteristic is thus a true indicator for efficiency improvement. A smaller slope can be achieved with more effective catalysts or lower resistances in the cell.
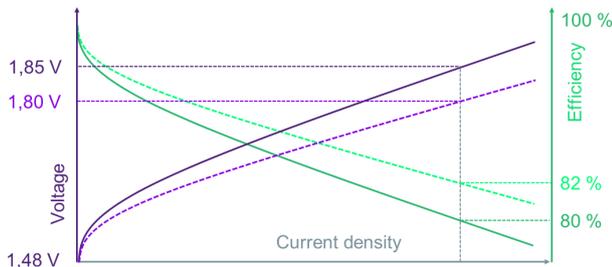

Figure 6: Schematic showing the effect of lower resistance on efficiency

The distance between the two electrodes has a large effect on the slope of the U/I characteristic. The shorter the distance the charge carriers have to traverse between the anode and the cathode, the smaller the voltage drop is, with correspondingly higher efficiency.

Why not just move the electrodes closer together?

For safety reasons alone, the oxygen generated at the anode shall not be allowed to mix with the hydrogen generated at the cathode. The smaller the distance, the higher the diffusion rate of contaminant gases from one side to the other if the material remains the same. This results in higher Faraday losses and to higher contamination of the product gases.

PEM and alkaline electrolysis – specific differences

There are currently two commercially relevant electrolysis technologies on the market that are implemented for production in the MW range: PEM and alkaline electrolysis. Both technologies differ primarily in the ionic charge carrier that electrically closes the electrochemical process, as well as in the actual electrolytes.

Polymer electrolyte membrane (PEM) or proton exchange membrane technology, as the name indicates, includes a solid electrolyte that electronically isolates the anode from the cathode but electrically closes the electric circuit through its selective conductivity for cations. This nearly gas-tight solid electrolyte offers several specific advantages. On the one hand, it serves as a physical divider between the anode (oxygen side) and the cathode (hydrogen side) and prevents mixing of the generated gases. This enables operation with a differential pressure. Unintentional pressure differentials that could result in mixing of the gases and thus to a safety hazard can therefore be more easily handled. On the other hand, the membrane also ensures a high gas product purity in dynamic operation or during more extended part-load operation where the contaminant gas concentration in both electrolysis technologies increases specifically as a function of the gas production rate due to diffusion.
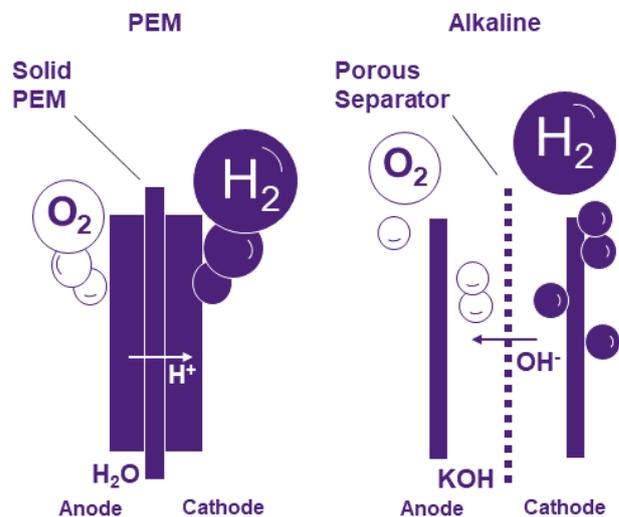

Figure 7: Schematic of PEM and alkaline electrolyzers

Alkaline electrolyzer have a porous separator to physically separate the hydrogen and oxygen gases while still enabling transport of the liquid electrolyte. This porous separator increases the requirements for alkaline electrolyzers in dynamic operation. Differential pressures that can result in hazardous mixing of oxygen and hydrogen absolutely must be prevented in the alkaline electrolyzer due to its porous separator.

Differences in characteristic

The electrodes for alkaline electrolysis are traditionally further apart from each other then those in PEM electrolysis. In addition to different electrode materials, this generally results in a steeper U/I characteristic for alkaline electrolyzers. The conductivity of the electrolytes also plays a significant role.
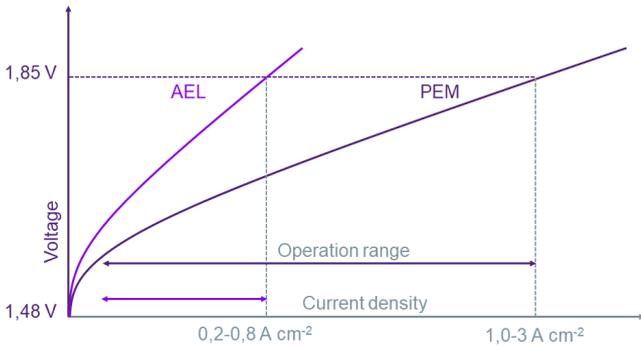

Figure 8: Operating range for alkaline and PEM electrolyzers

In addition to ionic conductivity, a 30% KOH solution also has a considerably higher electrical conductivity than that of deionized water. This results in so-called shunt currents (loss currents), i.e. electrons that do not participate in the electrochemical reaction but rather flow through the electrolyte to the adjacent cell. These must be prevented or assigned to Faraday efficiency.

The question of comparing the efficiency of both technologies is therefore not easy to answer. The fact is that the selection of the operating point and the associated voltage are decisive for efficiency. The generally low overall resistances in PEM technology result in a broader range of operating modes. While PEM electrolysis is operated at between 0 and 3 A cm-2, alkaline electrolyzers permit significantly lower current densities to achieve a comparable voltage and therefore also a comparable efficiency.

Further fundamental principles[2,3]

Efficiency ⬚ is a technical parameter that is generally specified with values of between 0 and 1 or 0% and 100%. In principal, the definition of efficiency is generally applicable and can be described with the following equation:

$$\varepsilon = \frac{Useful}{Expended} \tag{1}$$

The term efficiency is most frequently found in connection with energy flow E. Useful energy is in the numerator and the energy expended is in the denominator. Power P can also be used if no energy is stored within the balance boundaries.

$$\varepsilon = \frac{E_{Useful}}{E_{Expended}} = \frac{P_{Useful}}{P_{Expended}} \tag{2}$$

Efficiency of an ideal galvanic cell

The attractive aspect of electrochemistry is the direct conversion of chemical energy to electrical energy and vice versa. This advantage can be illustrated by a comparison of the maximum theoretical efficiency of a thermal power plant with that of a galvanic cell such as a fuel cell. Instead of converting chemical energy first in to thermal energy, then into mechanical energy and finally into electrical energy, electrochemistry accomplishes this in a single step.
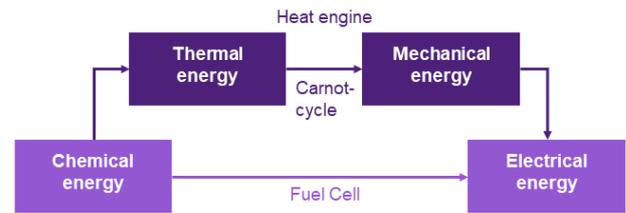

Figure 9: Comparison of the energy conversion chain between heat engine and fuel cell

The description of the classic Carnot cycle defines the maximum theoretical efficiency with the following formula:

$$\varepsilon_C = 1 - \frac{T_u}{T} \tag{3}$$

Where T is the maximum process temperature and T_u the ambient temperature. The higher the temperature of the Carnot cycle, the higher the efficiency of the thermal power plant.

The ideal efficiency ε_{id} of a galvanic cell comprises the quotient of Gibbs free energy ΔG and overall reaction enthalpy ΔH.

$$\varepsilon_{id} = \frac{\Delta G_m}{\Delta H_m} = 1 - \frac{T\Delta S_m}{\Delta H_m} \tag{4}$$

In comparison with the ideal efficiency of a classic thermal power plant, the theoretical efficiency of the galvanic cell is thus significantly higher over a wide temperature range.
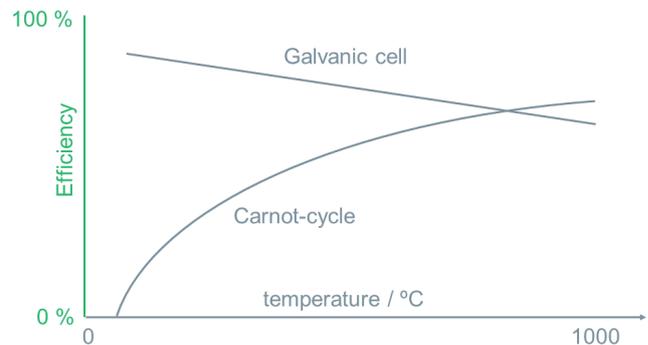

Figure 10: Ideal efficiency curves for a galvanic cell and for the Carnot cycle

Standard	Condition	Density in kg/m$^3_{stp}$	Efficiency in kWh/m$^3_{stp}$	Efficiency in %
DIN 1343	p_n = 1.01325 bar; T_n = 273.15 K	0.0899	4.425	80
Linde/Air Liquide	p_n = 1 bar; T_n = 288.15 K	0.0841	4.1375	80
ISO 2533	p_n = 1.01325 bar; T_n = 288.15 K	0.0852	4.158	80

Table 1: Example calculation for various standard conditions at the same percentage efficiency

Upper or lower heating value

The expenditure associated with a forced cycle such hydrogen electrolysis is the electrical power that must be supplied to the system. Useful output from the electrolysis of water is, however, a matter of definition. If the hydrogen used after generation is reused for energy production after it is generated (conversion to mechanical, electrical or thermal energy), the lower heating value H_u (LHV) must be used under consideration of the entire conversion chain.

$$\varepsilon_{LHV} = \frac{\dot{V}_{H_2} \cdot H_u}{P_{electrical}}$$ (5)

However, if instead of the entire conversion chain, only the hydrogen is regarded as a chemical product for use in the chemical industry or as a technical gas, the fuel value or higher heating value H_o (HHV) can be used for calculating efficiency. The necessary reaction enthalpy for converting the liquid reactant water to gaseous hydrogen corresponds to the higher heating value.

$$\varepsilon_{HHV} = \frac{\dot{V}_{H_2} \cdot H_O}{P_{electrical}}$$ (6)

In general, the higher heating value is used when referring to the electrolysis of water. This is due to the fact that the use to which the hydrogen is put should not be assumed by the manufacturer and the pure percentage value based on the higher heating value suggests a significantly higher efficiency than that based on the lower heating value.

Deviation from specified percentage efficiency
As an alternative to the typical specification of efficiency as a percentage, the efficiency of hydrogen electrolysis can also be communicated in a mixed form between the energy and product stream. The following values are often used here:

$$\frac{kWh}{mstp^3} \quad or \quad \frac{kWh}{kg}$$ (7)

While the representation of efficiency as a percentage requires that the reference value of higher or lower heating value also be indicated, standard conditions must be indicated when communicating energy expenditure per unit volume of gas. There is more than just one definition of the "standard conditions" of a volume, which significantly affects the energy content due to differences in the reference temperature and pressure. The specification of energy expenditure per unit volume is therefore ambiguous without also specifying the standard conditions.

Conclusion

It must be ensured that all relevant reference points are given when evaluating the efficiency of electrolysis systems. This starts with the definition of the system boundaries and standard conditions, affects part-load behavior and dynamic conditions and ends, not least, with degradation. All of these factors ultimately have an effect on efficiency.

A system manufacturer must strike an optimal balance to enable the lowest hydrogen generation costs while providing maximum availability for the customer over the long term.

On the other hand, it is the task of interested parties, be they a customer or the author of a study, to define all of the required reference points to enable an objective comparison.

Sources

1   Russell J. H., Nuttall L. J. & Fickett A. P. Hydrogen Generation by Solid Polymer Electrolyte Water Electrolysis. Am. Chem. Soc. Div. Fuel Chem. Prepr. 18, 24–33 (1973).

2   Lettenmeier P., Dissertation, Development and Integration of new Components for Polymer Electrolyte Membrane (PEM) Electrolyzers, (2018)

3   Georgios Tsotridis, Alberto Pilenga, EU Harmonised terminology for low temperature water electrolysis for energy storage application, (2018)

Index of Abbreviations

PEM   Polymer electrolyte membrane

DC   Direct current

AC   Alternating current

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