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EU harmonised terminology for low-temperature water electrolysis for energy-storage applications

Tsotridis G., Pilenga A.

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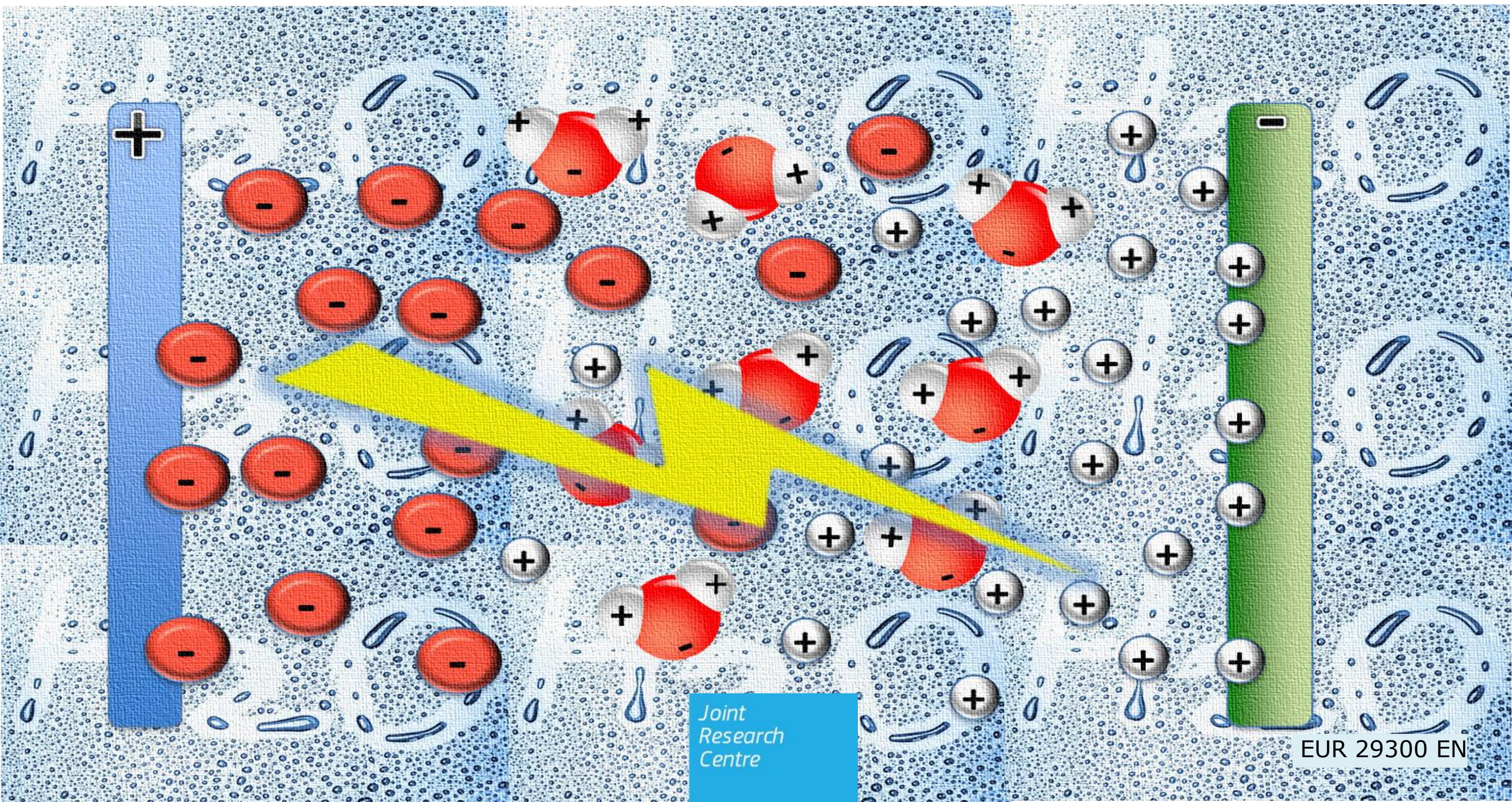

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FOREWORD

This report on *EU harmonised terminology for low-temperature water electrolysis for energy-storage applications* was carried out under the framework contract between the Joint Research Centre and the Fuel Cells and Hydrogen 2 Joint Undertaking (FCH2JU), 2017 rolling plan deliverable B.2.3 ‘Harmonised electrolysis testing’.

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The authors would like to thank the International Electrotechnical Commission (IEC) for permission to reproduce information from its international standards. All such extracts are the copyright of IEC, Geneva, Switzerland. All rights reserved (1).

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1. INTRODUCTION

The energy transition towards low-carbon technologies is a key political objective for the European Union, which has defined a strategy to progressively decrease CO_2-equivalent content throughout all relevant power generation and distribution, industrial, transport and buildings sectors, with the ultimate goal of decreasing greenhouse gas emissions to 80 % below 1990 levels by 2050, with intermediate steps of 20 % by 2020 and 40 % by 2030.

In this context, hydrogen could play an important role as it has significant potential benefits to enable this transition to low-carbon energy systems. Hydrogen, in fact, is not only considered as the ultimate cleaner-energy carrier as it has no CO_2 emissions when burned, but is very versatile and therefore could be used in a number of industrial applications, from feedstock in many industries (ammonia, refineries, etc.) to the fuel transportation sector.

Hydrogen production is still largely based on steam reforming of natural gas. Such a type of production cannot be classified as renewable as it is linked to a fossil fuel as feedstock. Water would be a better source of hydrogen, but although the water electrolysis process has been known for more than a century, today only 4 % of hydrogen is produced by this process due to the higher cost of production. However, recently water electrolysis has been receiving new industrial attention as a possible relevant player in the emerging sustainable energy storage field, because electrolysers can operate when electricity generation is available at very low prices or when there is an excess of demand due to the introduction of renewable energy sources.

This report on *EU harmonised terminology for low-temperature water electrolysis for energy-storage applications* was produced under the framework contract between the Joint Research Centre and the Fuel Cells and Hydrogen 2 Joint Undertaking, 2017 rolling plan.

This document is the result of a collaborative effort between industry partners, research organisations and academia participating in several Fuel Cells and Hydrogen 2 Joint Undertaking-funded projects in low-temperature water electrolysis applications.

The objective of the report is to present to those involved in research and development a comprehensive and harmonised compendium of various terminology terms which are encountered in low-temperature water electrolysis for energy storage applications.

It provides clear definitions of module and system boundaries for the three low-water electrolysis technologies, namely alkaline water electrolysis (AWE), anion exchange membrane water electrolysis (AEMWE) and proton exchange membrane water electrolysis (PEMWE). In addition, the report provides, in alphabetical order, a comprehensive list of appropriate terminology expressions used in various electrolysis applications, such as various ‘electrochemical expressions’. It also presents a set of expressions frequently used within the ‘renewable energy-storage sector’ with ‘power distribution grid balancing’ terminology expressions, where electrolysis technology could play an important role.

In this respect, the document also makes reference to terminology expressions derived from other international standards drafting organisations, such as the IEC, and from relevant European initiatives such as the European Network of Transmission System Operators for Electricity and the Fuel Cells and Standardisation Network.

In addition, the document provides an extensive account of science-based industry-endorsed definitions of key performance indicators, such as definitions of various ‘efficiency’ terms currently in use by research, academia and industry, and provides a detailed methodology of the derivation of the relevant efficiency equations.

2. LOW-TEMPERATURE WATER ELECTROLYSIS TECHNOLOGIES

Three different types of low-temperature water electrolysis technologies are currently available as commercial products, namely PEMWE, which uses an acidic polymer electrolyte (and for this reason is sometimes also called polymer electrolyte membrane), AWE (liquid electrolyte electrolysis) and, most recently, AEMWE.

The relevant differences between the three aforementioned technologies are summarised in Table 1 below.

Table 1: State-of-the art low-temperature water electrolysis technologies

Type	AEMWE	AWE	PEMWE
Charge carrier	OH^-	OH^-	H^+
Reactant	Water	Water	Water
Electrolyte	Anion exchange membrane	KOH 20-40 wt. %/water	Proton exchange membrane
Electrode	Ni, NiO, Co-based catalyst	Raney Ni, Fe, Co, Mn	Pt/C, IrO_2
Current density	0.2-0.8 A/cm^2	0.2-0.5 A/cm^2	0.2-3.0 A/cm^2
Temperature	40-50 °C	40-90 °C	20-80 °C (*)
Pressure H_2 out	$10^5 - 30 \cdot 10^5$ Pa	$10^5 - 30 \cdot 10^5$ Pa	$10^5 - 30 \cdot 10^5$ Pa
Cathode reaction (hydrogen evolution reaction) (**)	$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2\,HO^-(aq)$	$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2\,HO^-(l)$	$2H^+(aq) + 2e^- \rightarrow H_2(g)$
Anode reaction (oxygen evolution reaction) (**)	$2\,HO^-(aq) \rightarrow H_2O(l) + 1/2\,O_2(g) + 2e^-$	$2\,HO^-(aq) \rightarrow H_2O(l) + 1/2\,O_2(g) + 2e^-$	$H_2O(l) \rightarrow 1/2\,O_2(g) + 2H^+(aq) + 2e^-$

(*) Research efforts are targeting temperatures up to 120 °C.

(**) (aq), (l) and (g) refer to aqueous, liquid and gaseous states.

Each type of electrolyser is a combination and assembly of various parts that can be grouped in ascending order of complexity per individual technology as follows:

- single cell (electrolysis cell),
- stack (electrolysis stack),
- electrolysis component or string,
- electrolysis system.

2.1. ALKALINE WATER ELECTROLYSIS CELL

An electrolysis set-up consisting of three functional elements: a cathode, a microporous diaphragm or membrane and an anode, which are embedded in an alkaline solution for hydrogen-and-oxygen production with the provision of electrical energy.

2.2. ANION EXCHANGE MEMBRANE WATER ELECTROLYSIS CELL

An electrolysis cell consisting of three functional elements: a cathode, a solid hydroxyl exchange polymer membrane as an electrolyte for the transport of hydroxides and an anode for hydrogen-and-oxygen production with the provision of external electrical energy as the driving force in an electrochemical process.

2.3. PROTON EXCHANGE MEMBRANE WATER ELECTROLYSIS CELL

An electrolysis cell consisting of three functional elements: a cathode, a solid proton exchange polymer and an anode, which is able to produce hydrogen and oxygen from electrochemical water splitting by providing external electrical energy.

2.4. ELECTROLYSIS STACK

An electrolysis stack is an assembly of more than one electrolysis cell, mostly in a filter press arrangement and connected electrically either in parallel (diagram (a), monopolar assembly), in full series (diagram (b), bipolar assembly) or in series with a central anode (diagram (c)) and hydraulically in parallel. In addition to these cells, an electrolysis stack consists of further components such as separators, cooling plates, manifolds and a supporting structure.

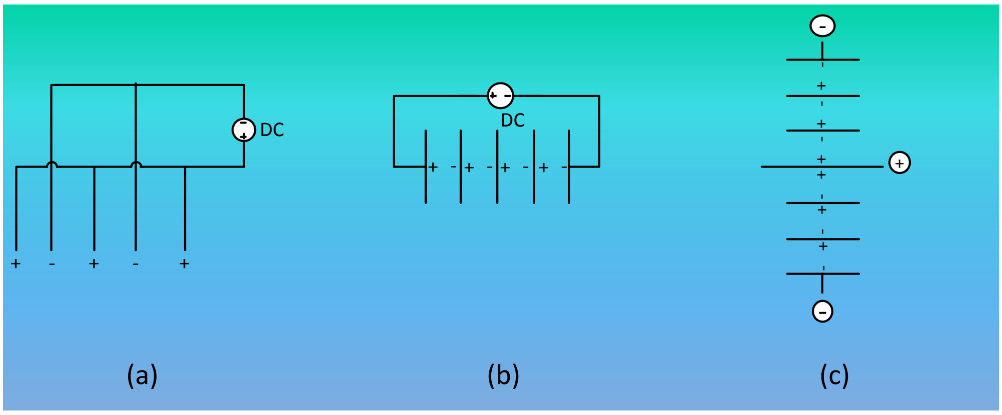


Figure 1: Schematic diagram showing various cell interconnection modes

The typical components of an electrolysis stack are:

- membrane or diaphragm;
- electrodes (anode and cathode);
- porous transport layers or liquid gas diffusion layer;
- bipolar plate as a separator plate between two adjacent electrolysis cells, sometimes with additional flow fields for an easier fluid distribution;
- cell frames and/or gaskets and/or sealing;
- current distributor;
- end plates for mechanical compression;
- electrical terminals;
- remaining components of the stack such as tie bolts, etc.

2.5. PROTON EXCHANGE MEMBRANE WATER ELECTROLYSIS SYSTEM

A **PEMWE system**, a typical diagram of which is depicted in Figure 2, is an assembly incorporating various components designed to operate the electrochemical conversion units (also called stacks) under the intended operating conditions (temperature, pressure, water, etc).

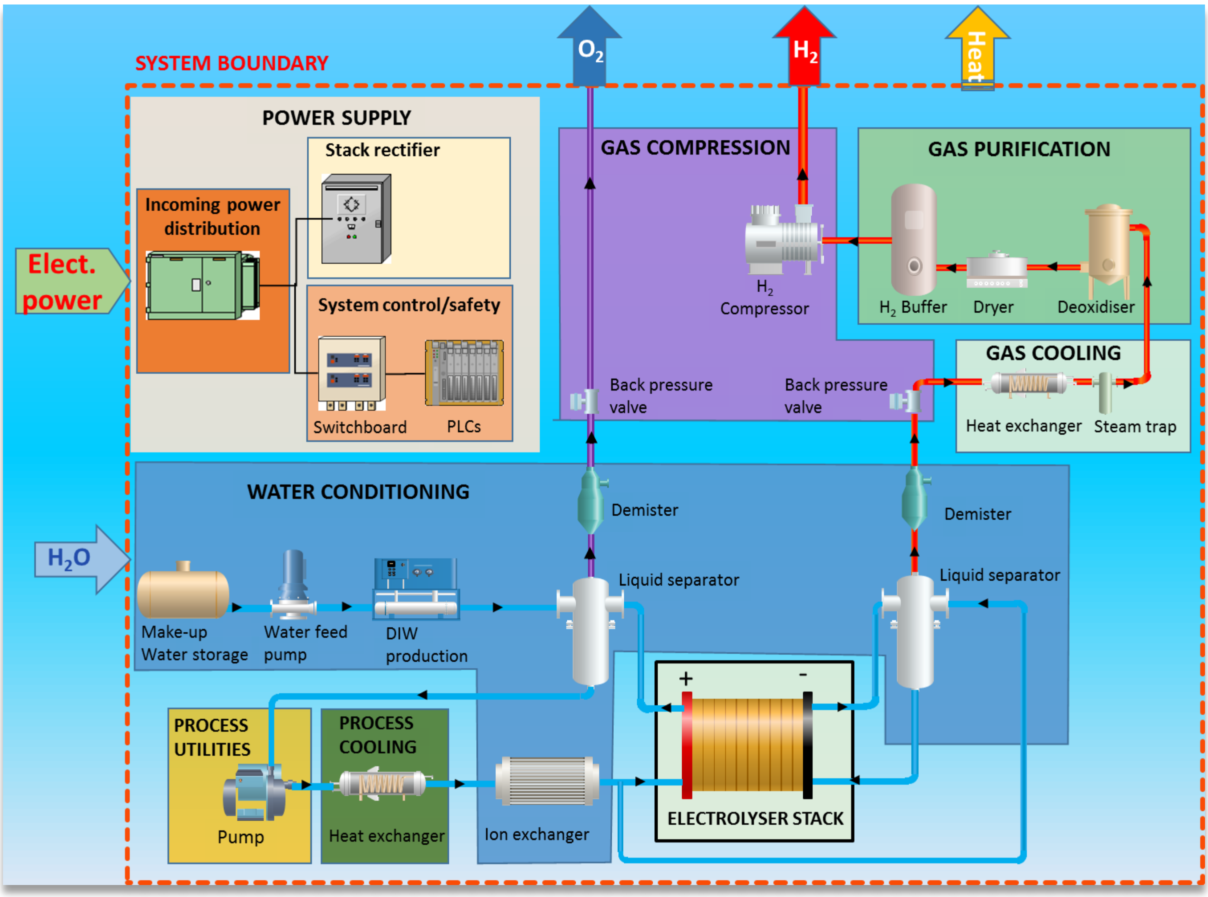


Figure 2: Schematic representation of the components of a PEMWE system

2.5.1. PROTON EXCHANGE MEMBRANE WATER ELECTROLYSIS COMPONENTS

The typical **components** of a **PEMWE** system are as follows.

- **Power supply,** which includes the following parts.
  - **Incoming power distribution,** which consists of the grid connection and transformer to adjust the electricity from the transportation or distribution network to the operational requirements.
  - **Rectifier for stack operation**.
  - **System control board** for other auxiliary components of the electrolysis system, including an automatic control system to operate the system according to the manufacturer's specifications. It includes safety sensors, process parameter measuring devices, piping and valves, programmable logic controller (PLC), data input/output (data I/O), personal computer (PC).
- **Water conditioning** for the necessary treatment of the water supplied and recovered, composed of the following.

    - Make-up water tank.
    - Water feed pump.
    - Deionised water production unit.
    - Anodic circulation loop consisting of:
        - water purification unit — mostly an ion-exchange resin bed — used to keep the water quality at the desired level, to minimise the risk of chemical contamination of the stack;
        - oxygen/water separator vessel used for a first separation of residual liquid water in the gas outlet stream;
        - demisters used for further removal of small liquid-water droplets from the gas outlet stream.
    - Cathodic circulation loop consisting at least of a hydrogen/water separator vessel and subsequent demister, and sometimes an additional circulation pump for defined thermal management of the cathode side.
- **Electrolyser stack,** which is the core of the system where water is electrochemically converted into hydrogen and oxygen by means of a DC current. It comprises one or more PEMWE stack(s) connected either in series or parallel mode.
- **Process utilities** consisting of the elements using power for the operation, such as the water recirculation pump enabling a continuous flow of water into the stack for the electrochemical reaction itself and for the thermal management of the stack; process-value-measuring devices (i.e. pressure sensor, flow meter, gas sensors).
- **Process cooling** consisting of heat exchangers for the thermal management of the pumped water to remove heat from the circulation loop and to keep the stack at the proper temperature range.
- **Gas cooling** consisting of heat exchangers for the thermal management of the gases produced during the electrolysis process.
- **Gas purification** to clean the hydrogen product stream to the desired level of quality consisting of the following.
    - A de-oxidation stage, to recombine catalytically residual traces of oxygen that could be present due to crossover effects.
    - A gas dryer to remove residual moisture down to the parts per million (ppm) level.
    - A buffer tank for compensation of variable hydrogen production.
- **Gas compression** composed of the following.
    - A pressure control valve for hydrogen and oxygen to operate the electrolyzer system at the desired pressure level (either pressure balanced or differential pressure).
    - A compressor, to bring the gas pressure to the specified value.
    - High-pressure storage tanks for the final storage of the gas produced by the electrolyser.

2.6. ALKALINE WATER ELECTROLYSIS SYSTEM

The principle layout of an **AWE system** is shown in Figure 3. The most noticeable difference compared to PEMWE systems is that in this case the electrolyte is an aqueous alkaline solution called lye, formed by KOH with a concentration of approximately 20-30 % in deionised water. The anode and cathode electrodes are immersed in this solution and separated by a diaphragm. This solution is caustic and this should be taken into consideration for the selection of the proper material for the components that are or may be in contact with a lye solution.

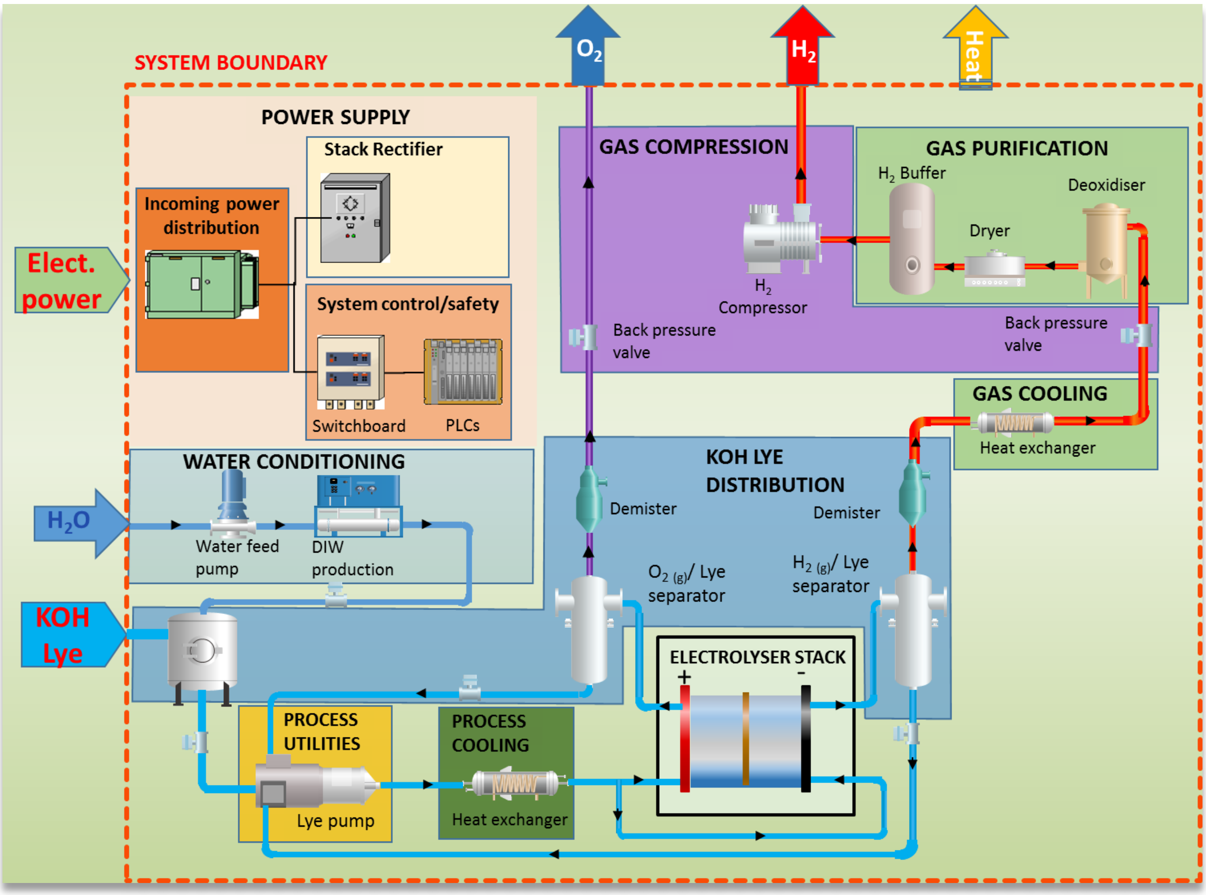


Figure 3: Schematic representation of the components of an AWE system

2.6.1. ALKALINE WATER ELECTROLYSIS COMPONENTS

The typical **AWE components** include the following items.

- **Power supply,** see Section 2.5.1.
- **Water conditioning as follows.**
  - Alkaline electrolysis stack.
  - A lye supply/recirculation system is used to provide a continuous electrolyte flow into the stack for the electrochemical reaction and thermal management. The main components are:
    - lye recirculation pump;
    - lye heat exchanger.
  - Gas/lye separator, used for the first separation of a residual liquid in the gas outlet stream produced.
  - Demisters and scrubbers are devices used for the further removal of water and lye aerosols from the gas outlet stream.
- **Electrolyser stack,** see Section 2.5.1.
- **Process utilities,** see Section 2.5.1.
- **Process cooling,** see Section 2.5.1.

- **Gas cooling,** see Section 2.5.1.
- **Gas purification,** see Section 2.5.1.
- **Gas compression,** see Section 2.5.1.

2.7. ANION EXCHANGE MEMBRANE WATER ELECTROLYSIS SYSTEM

An **AEMWE system** is an assembly essentially similar to a PEMWE system but the type of stack technology used is based on the anion exchange membrane instead of the ion exchange membrane.

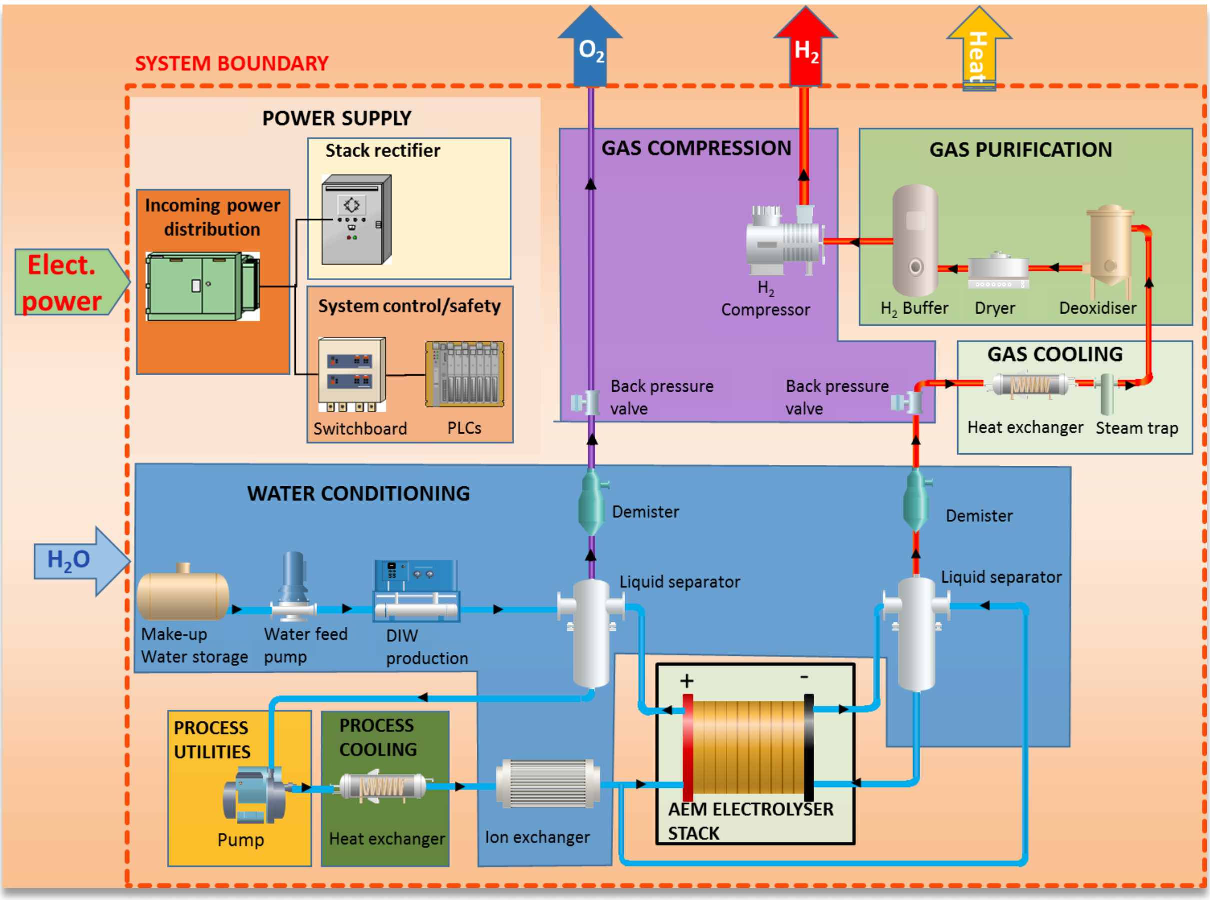


Figure 4: Schematic representation of the components of an AEMWE system

2.7.1. ANION EXCHANGE MEMBRANE WATER ELECTROLYSIS COMPONENTS

As mentioned above, the components are equivalent to the ones described for the PEMWE system in Section 2.5.1, with the only difference being related to the stack technology.

3. TERMINOLOGY

3.1. Area

3.1.1. Active area

Geometric area of the electrode, which is perpendicular to the direction of the current flow and is available for an electrochemical reaction (2).

Note 1 to entry: it is expressed in m².

[*Source:* Modified from IEC TS 62282-1:2013, *Fuel cell technologies — Part 1*]

3.1.2. Cell area

Geometric area of the bipolar plate perpendicular to the direction of the current flow (1).

[*Source:* IEC TS 62282-1:2013, *Fuel cell technologies — Part 1*]

3.1.3. Geometric electrode area

Geometric electrode area is the largest area of the electrode projected on a plane.

Note 1 to entry: it is expressed in m².

3.1.4. Effective area

See active area.

3.1.5. Electrochemical surface area

Electrochemical surface area (ECSA) is the actual surface area of an electrocatalyst accessible to an electrochemical process due to its open porous structure.

Note 1 to entry: it is presented as ECSA per unit mass (or volume) of the catalyst or per geometric electrode area.

Note 2 to entry: it is expressed in m^2/g, m^2/m^3, m²/m².

3.1.6. Specific surface area

Electrochemical surface area per unit mass (or volume) of the catalyst.

Note 1 to entry: the specific surface area corresponds to the area of an electrocatalyst accessible to reactants due to its open porous structure, per unit mass (or volume, or electrode geometric area) of the catalyst (1).

Note 2 to entry: it is expressed in m^2/g, m^2/m^3.

[*Source:* IEC TS 62282-1:2013, *Fuel cell technologies — Part 1*]

3.2. Axial load

Compressive load applied to the end plates of an electrolysis cell or stack to ensure contact and/or gas tightness (2).

Note 1 to entry: it is expressed in Pa.

[*Source:* Modified from IEC TS 62282-1:2013, *Fuel cell technologies — Part 1*]

3.3. Cell components

3.3.1. Bipolar plate

Electrical conductive and gas-tight plate separating individual cells in a single cell or stack, acting as a reagent flow distributor and current distributor and providing mechanical support for the electrodes or membrane electrode assembly (2).

[*Source:* Modified from IEC TS 62282-1:2013, *Fuel cell technologies — Part 1*]

3.3.2. Catalyst

Substance that increases the rate of a reaction without being consumed itself. The catalyst lowers the activation energy of the reaction, allowing for an increase in the reaction rate, or allowing it to proceed at a lower temperature or overpotential. A catalyst that promotes an electrochemical reaction is termed an ‘electrocatalyst’ (2).

[*Source:* Modified from IEC TS 62282-1:2013, *Fuel cell technologies — Part 1*]

3.3.3. Catalyst-coated membrane

Specific configuration of a membrane electrode assembly (for PEMWE and AEMWE cells) where catalyst layers are coated directly onto the membrane as electrodes.

3.3.3.1. Catalyst layer

Layer adjacent to the membrane on either side of the membrane comprising electrocatalyst particles and ionomers with co-existing ionic and electronic conductivity. This layer comprises the spatial region where electrochemical reactions take place (4).

3.3.3.2. Catalyst loading

Amount of catalyst incorporated per unit of electrode geometric area, specified either separately per anode or cathode, or as combined anode and cathode loading (2).

Note 1 to entry: it is expressed in g/cm^2.

[*Source:* Modified from IEC TS 62282-1:2013, *Fuel cell technologies — Part 1*]

3.3.3.3. Catalyst poisoning

Inhibition of the catalyst properties by adsorbate substances (poisons) (2).

[*Source:* Modified from IEC TS 62282-1:2013, *Fuel cell technologies — Part 1*]

3.3.3.4. Electrocatalyst

Catalyst that participates in and accelerates/catalyses an electrochemical reaction.

For low-temperature water electrolysis, the electrocatalyst can be built up as a porous bulk catalyst or it can consist of a catalyst dispersed on support particles, such as carbon powder or titanium sub-oxides, which increase the ECSA of the catalyst.

3.3.3.5. Electrocatalyst support

Component of an electrode that supports the electrocatalyst and serves as a porous and electrically conductive medium. It also leads to a higher ECSA of the catalyst and reduced loading of the electrocatalyst in the electrode (2).

[*Source:* Modified from IEC TS 62282-1:2013, *Fuel cell technologies — Part 1*]

3.3.4. Clamping plate

See end plate, Section 3.3.8.

3.3.5. Compression end plate

See end plate, Section 3.3.8.

[*Source:* Modified from IEC TS 62282-1:2013, *Fuel cell technologies — Part 1*]

3.3.6. Electrode

Electronic conductor through which an electric current enters or leaves the electrochemical cell as the result of an electrochemical reaction (1).

[*Source:* IEC TS 62282-1:2013, *Fuel cell technologies — Part 1*]

3.3.6.1. Anode

Electrode at which the water oxidation reaction (electron loss) occurs, leading to an oxygen evolution reaction.

3.3.6.2. Cathode

Electrode at which the water reduction reaction (electron gain) occurs, leading to a hydrogen evolution reaction reduction.

3.3.6.3. Electrode potential

Difference between the internal electric potential of the electrode (electronic conductor) and the electrolyte (ionic conductor).

3.3.7. Electrolyte

Medium for charge transfer between the electrodes in an electrochemical cell.

It is an ionic conductor (e.g. solution, solid, molten salt or gas) in which the electric current is carried by ionic species (cations and anions). The respective transference number characterises the fraction of the current carried either by cations or anions. In an electrochemical cell the charge transfer reactions (e.g. oxygen evolution reaction or hydrogen evolution reaction) take place at the interface between the electrode and the electrolyte.

The nature of the electrolyte is the main distinctive feature of the different fuel cell technologies and determines the useful operating temperature range (4).

3.3.7.1. Electrolyte molar conductivity

Specific conductivity of an electrolyte solution that depends on the electrical conductivity and concentration of the gas-free electrolyte solution.

Note 1 to entry: it is expressed in m2 Ω^{-1}mol^{-1}.

3.3.7.2. Liquid electrolyte leakage

Undesired escape of liquid electrolyte from a cell/stack (2).

[*Source:* Modified from IEC TS 62282-1:2013, *Fuel cell technologies — Part 1*]

3.3.7.3. Electrolyte loss

Any decrease with respect to the initial electrolyte content in an electrolysers system (2).

[*Source:* Modified from IEC TS 62282-1:2013, *Fuel cell technologies — Part 1*]

3.3.7.4. Electrolyte matrix

Insulating gas-tight cell component with a properly tailored pore structure that retains the liquid electrolyte (1).

[*Source:* IEC TS 62282-1:2013, *Fuel cell technologies — Part 1*]

3.3.7.5. Electrolyte migration

Ion transport mechanism resulting from electric potential gradients affecting the local electrolyte local concentration.

3.3.7.6. Electrolyte reservoir

Component of a liquid electrolyte module. A proper amount of liquid electrolyte is stored therein with the purpose of replenishing electrolyte losses over the life of the cell (2).

[*Source:* Modified from IEC TS 62282-1:2013, *Fuel cell technologies — Part 1*]

3.3.8. End plate

Component located on either end of the electrolysis cell or stack to transmit the required compression to the stacked cells to allow proper electrical contact and to avoid fluid leaks. The end plate may comprise ports, ducts or manifolds for the conveyance of fluids (reactants, coolant, cable wiring) to/from the cell or stack (2).

[*Source:* Modified from IEC TS 62282-1:2013, *Fuel cell technologies — Part 1*]

3.3.9. Gasket

Component that prevents the exchange of fluids between two or more compartments of a device or the leakage of fluids from a device to the outside (4).

3.3.10. Ionomer solution

Dispersion of ion-conductive polymers in water, or in water and low-aliphatic alcohols. It is used in the manufacturing of electrocatalytic layers to increase the electrode-electrolyte interface area by ensuring better contact between the electrocatalyst particles and the ion-conducting polymer membrane.

3.3.11. Liquid-/gas-diffusion layer

Porous diffusion layer facilitating the mass transport of reactants and the removal of reaction products. It is made of a porous medium or a combination of different porous media forming adjacent layers or a composite layer.

3.3.12. Membrane

Separating layer that acts as an electrolyte (ion exchanger) as well as a barrier film separating H_2/O_2 gases and electronic conducting materials of the anode and cathode compartments of the AEM or proton exchange membrane (PEM) electrolyser (4).

3.3.12.1. Anion exchange membrane

Polymer-based membrane with **anion** conductivity, which acts as an electrolyte and a separator between the anode and the cathode.

3.3.12.2. Proton exchange membrane

Polymer-based membrane with **proton** conductivity, which acts as an electrolyte and a separator between the anode and the cathode.

3.3.13. Membrane electrode assembly

Catalyst-coated membrane assembly with thin porous transport layers and edge-reinforcement membranes. Its geometric area includes active (see Section 3.1.1) and non-active areas.

3.3.14. Porous transport layer

See liquid-/gas-diffusion layer, Section 3.3.11.

3.3.15. Separator plate

See equivalent definition of bipolar plate.

[*Source:* IEC TS 62282-1:2013, *Fuel cell technologies — Part 1*]

3.3.16. Single electrolysis cell

Basic unit of an electrolysis device composed of three functional elements, namely a cathode, an electrolyte and an anode, which are capable of breaking up chemical compounds by means of applied electrical energy to produce reduced and oxidised compounds. In a water electrolysis cell, hydrogen and oxygen are generated by the electrochemical splitting of deionised water or water in alkaline aqueous solutions by providing external electrical energy.

3.3.17. Spacer

Electrically insulating component that separates two opposite electrodes and provides space for the flow of electrolytes between the electrodes.

3.3.17.1. Gap

Space between electrodes or an electrode separator.

3.3.17.2. Zero-gap design

Electrolyser cell where electrodes are separated only by the gas separator.

3.3.18. Water separator

Device that condenses and separates water vapour from the gas discharged from the cell/system (2).

[*Source:* Modified from IEC TS 62282-1:2013, *Fuel cell technologies — Part 1*]

3.4. Coolant

Fuid used to control heat transfer between various media and components (4). Heat dissipated into the atmosphere through the cooling circuit of the system, typically by an air-to-liquid heat exchanger (4).

3.5. Current

3.5.1. Current density

Vector-point function describing the magnitude and direction of the charge flow, i.e. the current intensity per unit area (4).

Note 1 to entry: it is expressed in A/m^2 or A/cm^2.

3.5.2. Current ramp rate

Rate at which the amount of electric current changes over time.

Note 1 to entry: it is expressed in A/s.

3.5.3. Leakage current

Electric current on an unwanted conductive path other than a short circuit (1)

Note 1 to entry: it is expressed in A.

[*Source:* IEC TS 62282-1:2013, *Fuel cell technologies — Part 1*]

3.5.4. Nominal current

Electric current value associated with the nominal design point as specified by the manufacturer.

Note 1 to entry: it is expressed in A.

3.5.5. Overload current

See rated current.

3.5.6. Rated current

Maximum continuous electric current, as specified by the manufacturer, at which the electrolysers system has been designed to operate (2).

Note 1 to entry: it is expressed in A.

[*Source:* Modified from IEC TS 62282-1:2013, *Fuel cell technologies — Part 1*]

3.5.7. Specific current density

Current per unit of electrochemical surface area at a given cell voltage.

Note 1 to entry: it is expressed in A/m^2.

3.5.8. Volumetric current density

Vector-point function describing the magnitude and direction of the charge flow, i.e. the current-intensity-per-unit volume.

Note 1 to entry: it is expressed in A/m^3.

3.6. Degradation

3.6.1. Degradation rate

Rate of change of a measurable quantity over time.

Note 1 to entry: the degradation rate can be used to measure both reversible (non-permanent) and irreversible (permanent) losses in cell performance. The degradation rate mainly refers to the cell voltage (2).

[*Source:* Modified from IEC TS 62282-1:2013, *Fuel cell technologies — Part 1*]

3.6.2. Cell-voltage degradation rate

Increase in cell voltage due to material degradation processes inside an electrolysis cell.

Note 1 to entry: the cell-voltage evolution rate is the expression used most often to describe the degradation rate of an electrolysis cell and is defined as an average cell-voltage increase per time unit.

Note 2 to entry: it is expressed in µV/h or µV/1,000 h.

3.6.2.1. Initial cell-voltage degradation rate

Voltage rate of change during the initial part of a test or operation phase when this time is excluded from the operational cell-voltage degradation time.

It is expressed as the absolute voltage difference divided by the initial test time.

$$\Delta U_{in} = (|U_{t\_start} - U_{t\_0}|)/\ (t_{\_start}\text{-}t_{\_0})$$

Where $t_{\_start}$ is the start time of a degradation measurement and $t_{\_0}$ is the start time of the test/operation.

3.6.2.2. Operational cell-voltage degradation rate

Voltage rate of change during a defined experiment time.

It is expressed as the absolute voltage difference divided by the operation time.

$$\Delta U_{op} = (|U_{t\_end} - U_{t\_start}|)/\ (t_{\_end}\text{-}t_{\_start})$$

Where $t_{\_start}$ is the start time of a degradation measurement and $t_{\_end}$ is the time of the end of the test.

3.6.3. Durability

Ability to withstand wear, pressure or damage within the defined operational settings.

3.6.4. Efficiency degradation rate

Decrease in overall efficiency over time with reference to the initial efficiency level and expressed in percentage per unit of time.

Note 1 to entry: it is expressed in %/h.

3.6.5. Performance degradation rate

Decrease in hydrogen productivity over time with reference to initial productivity under constant operating conditions of load, temperature and pressure, expressed in percentage per unit of time.

Note 1 to entry: it is expressed in %/h.

3.6.5.1. Cell lifetime

Length of time under operating conditions between first start-up and the time at which the cell voltage, under the defined conditions, exceeds the maximum acceptable voltage specified (2).

Note 1 to entry: it is expressed in h.

[*Source:* Modified from IEC TS 62282-1:2013, *Fuel cell technologies — Part 1*]

3.6.5.2. Stack lifetime

Lifespan of the stack when the process-relevant (i.e. hydrogen production rate or hydrogen production efficiency) performance loss over time has reached 20 % compared with its initial performance (beginning of life) or when the average cell potential has reached the cut-off voltage defined by the manufacturer. This condition is indicated as end of life.

Note 1 to entry: it is expressed in operating hours (h) at nominal load. This relates to steady-state operation at the nominal operating point.

3.6.6. Stability factor

Parameter used to assess the stability characteristics defined as the reciprocal of the product of the voltage increase rate (operational cell-voltage degradation) and the initial cell overvoltage versus the thermoneutral potential (~ 1.47 V at 80 °C).

Stability factor $\mathbf{= 1 / [\Delta U_{op} \cdot (U_{cell}-U_{tn})_{t\_start}]}$

Note 1 to entry: it is expressed in $h{\cdot}V^{-2}$.

3.7. Efficiency

3.7.1. General comments on efficiency

A critical review of the different definitions of the efficiency of the water electrolysis reactions (at cell, stack, component and system level) found in the literature is provided in this section. The discussion is applicable to near-ambient-temperature technologies such as PEM, alkaline and anion membranes only.

From a thermodynamic viewpoint, the water electrolysis cells, stacks and systems can be seen as energy-conversion devices. The energy efficiency of such devices is defined as the ratio between the useful chemical energy output (the hydrogen/oxygen energy content) and the energy input (electricity and heat). The efficiency factors or descriptors thus obtained offer a common and practical way to characterise such conversion devices, assess the quality of the conversion process and compare the results.

The following Figure 5 provides a schematic overview of mass and energy flows across the boundaries of the system under consideration and the environment.

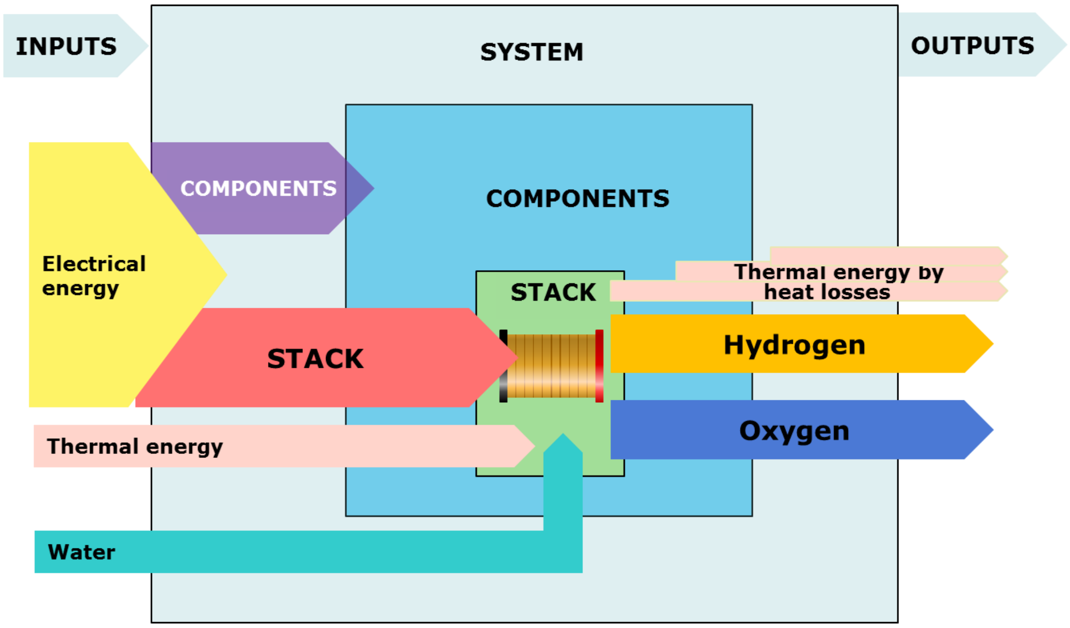


Figure 5: Schematic diagram of typical input/output mass flows and energy of an electrolyser system

The approach used in this document reviews the definitions, starting from the fundamental thermodynamics of the electrolysis processes, and in turn applies them at single cell, stack, component and finally system level. To facilitate the comparison of water electrolysis technologies (at cell, stack or system level), quantitative descriptors must be used. In this document, the term ‘energy efficiency coefficient’ (the symbol for which is ε) will be the descriptor used for this purpose. ε is a real number such as: $0 \leq \varepsilon \leq 1$. To express the energy efficiency coefficient as a percentage, it is necessary to multiply ε by 100. It should be noted here that in the literature, the term ‘efficiency’ is sometimes used instead of ‘energy efficiency coefficient’. In some cases, this might lead to confusion (e.g. it is necessary to differentiate between energy, current and overall efficiencies), which needs to be avoided by using the appropriate terms (in this document, the descriptor used for current and overall efficiency is labelled using the symbol η). It should also be noted here that there are several methods to define the ‘energy efficiency coefficient’ of water electrolysis. The objective of this document is to review the various definitions and explain their differences and the corresponding simplifying assumptions.

There are basically **three main approaches** to defining and calculating the water electrolysis efficiency coefficient to facilitate comparison of results.

The **first approach** is mostly used by the academic/scientific research community. It is based on thermodynamic considerations. The focus is on the water electrolysis reaction only, under constant temperature and pressure (T,p) conditions. The electrolysis cell is placed in a thermostat (this could be air when electrolysis takes place at ambient temperature, but in most laboratory experiments it is a thermostatic device which is used to perform electrolysis at temperatures other than ambient temperature). The energy efficiency coefficient is defined as the ratio of the minimum amount of energy required to split one mole of water at T,p (when the current is zero) to the actual amount of energy required to split one mole of water at T,p (when the current is not zero). The difference is due to the second principle of thermodynamics: the transport of electric charges across the cell induces irreversible energy degradation (dissipation). Therefore, the denominator is larger than the numerator and $\varepsilon \leq 1$, except at equilibrium where $\varepsilon = 1$.

$$\varepsilon_{cell} = \frac{energy\ requirement\ in\ reversible\ conditions}{energy\ requirement\ in\ irreversible\ conditions} = \frac{W_t\ (J.mol^{-1})}{W_r\ (J.mol^{-1})} \qquad [A]$$

It should be noted here that despite the simplicity of this definition, **three different cases (quantitative expressions)** of ε could be found in literature for this first approach. The difference arises from the different thermodynamic simplifying assumptions that are applied in the evaluation of the energy flows between the electrolysis cell and the environment. These assumptions impact both the numerator and the denominator of equation $[A]$.

In **case 1**, the enthalpy change of the reaction (reversible electrical work + reversible heat) is taken as reference at the numerator and the total electrical work plus a constant additional reversible heat input is provided at the denominator.

In **case 2**, the Gibbs free energy of the reaction (reversible electrical work) is taken as reference at the numerator and only the total electrical work is provided at the denominator.

In **case 3,** the enthalpy change of the reaction (reversible electrical work + reversible heat) is taken as reference at the numerator (as for case 1) and the total electrical work plus a variable additional heat input (depending on U_{Cell} to differentiate between an endothermal and exothermal mode of operation) is provided at the denominator.

Case 4 is a more general approach than case 3, where it is assumed that the heat input into the cell is provided in full by an external source.

These four cases will be presented and discussed in detail in Section 3.7.3.

The **second approach** is a more practical one and is mainly used by the industry sector. Compared with the definitions of the first approach, there are two main differences: (i) all parasitic losses (those of the electrolysis unit, such as energy and current losses, heat losses, etc., but also those of auxiliary subsystems such as heaters, pumps, etc.) are taken into account at the denominator of the definition of $\boldsymbol{\eta}$, in order to define the overall performance of the complete electrolyser system; (ii) the energy of reference (the numerator in the definition of ε) is different.

This is the ratio of the energy content of the products obtained at the output of the device (cell, stack, system plant) to the total energy that is provided to the system.

$$\eta_{cell} = \frac{energy\, content\, of\, products}{total\, energy\, requirements} = \frac{W_t\ (J.mol^{-1})}{W_r\ (J.mol^{-1})} \qquad [B]$$

The **third approach** acknowledges the fact that the efficiency definitions of the first and second approaches provide insights into the conservation of energy only (first principle of thermodynamics). Environmental conditions and energy degradation are not considered quantitatively. However, ensuring meaningful comparisons between different technologies (e.g. electrolysis plant, photovoltaic system, wind turbine generator) and eventually ranking them is not a straightforward task. In order to do that, there is a need to define the best theoretical performance of a device. The best approach is to perform a detailed **exergy** analysis, i.e. to take into account the exergy (energy quality) of various input/output energy flows to calculate the efficiency. The analysis of the exergy losses (magnitude and location within the device) will provide a more detailed picture of the strengths and weaknesses of any energy-conversion device and it will help in identifying improvements in various components of the device. However, this approach will not be taken in this document.

3.7.2. Electrolysis thermodynamics fundamentals

3.7.2.1. Thermodynamics of the water dissociation reaction

The energetics of the water electrolysis reaction performed under reversible conditions (current intensity I = 0) under **standard ambient temperature and pressure conditions (SATP) (International Union of Pure and Applied Chemistry, IUAPC) T° = 25 °C (298.15 K) and p° = 10^5 Pa = 1 bar(a)** are summarised in equation [1]:

$H_2O(l)$ + 48.6 kJ mol^{-1} heat + 237.2 kJ mol^{-1} electrical energy → H_2 (g)+ ½ O_2 (g) [1]

The total energy required by the electrolysis process $\Delta H_{cell}(T°,p°)$ = 285.8 kJmol^{-1} is the sum of the thermal energy needs $\Delta Q_{rev}(T°,p°)$ and the electrical energy needs $\Delta G_{cell}(T°,p°)$, also known as the Gibbs free energy change of the reaction. All of these quantities are connected by means of the Gibbs-Helmholtz equation:

$$\Delta H_{cell}(T,p) = \Delta Q_{rev}(T,p) + \Delta G_{cell}(T,p) \qquad [2]$$

where T is the absolute temperature (in K) of the electrolysis cell.

Under reversible conditions (I = 0) the thermal energy change is related to the entropy change ΔS(T) of the water-splitting reaction, i.e. $\Delta Q_{rev}(T,p) = T\,\Delta S(T,p)$.

The entropy change ΔS(T°,p°) for one mole of water at standard conditions, based on:

$S^0_{H2} = 130.7\ \mathrm{J\ (mol \cdot K)^{-1}}, S^0_{O2} = 205.1\ \mathrm{J(mol \cdot K)^{-1}}$ and $S^0_{H2O} = 69.9\ \mathrm{J(mol \cdot K)^{-1}}$ is:

$\Delta S(298) = 130.7 + 0.5 \times 205.1 - 69.9 = 163.3\ \mathrm{J\ (mol \cdot K)^{-1}}$,

leading to $\Delta Q_{rev}(298) = 298 \times 163.3 = 48.6$ kJ mol^{-1}.

3.7.2.2. Cell voltage of the water electrolysis reaction

From the thermodynamic viewpoint, the minimum but necessary cell voltage required for the onset of the water electrolysis reaction under reversible conditions, U_{rev}^{0} , **under standard ambient temperature and pressure conditions**, is defined as (²):

$$U_{rev}^{0} = \Delta G^{0}/(n\ F) \qquad [3]$$

where n is the number of electrons transferred (n = 2 in the case of water electrolysis) and F is the Faraday constant (i.e. the product of the elementary electric charge by the Avogadro number, F = 96485.3329 ≈ 96485 C mol^{-1}).

Hence, under standard conditions ΔG^0 = 237.22 kJ mol^{-1}, then U_{rev}^{0} **= 1.2293 V.**

The following remarks should be taken into account.

- This is only valid when the heat corresponding to $T\Delta S$ (48.6 kJ mol^{-1}) can be entirely transferred from the surrounding environment to the process, for example by supplying preheated water to the cell when the process is in an endothermic state.
- Hydrogen generation cannot take place when the cell voltage is $U_{Cell} < U_{rev}^{0}$.
- The electrolysis cell can operate adiabatically (with a zero heat balance between thermal energy transferred to the cell and produced by the cell) at the so-called **thermoneutral potential**, E_{tn}, or the **thermoneutral voltage,** U_{tn}, which is defined, under SATP conditions, by:

$$U_{tn}^{0} = \Delta H^{0}/(n\ F) \qquad [4]$$

In equation [4], under SATP conditions, **ΔH^0 = HHV = 285.84 kJ mol^{-1}** **(U_{tn} = 1.4813 V**). Under different physical conditions, namely when water is in a gaseous state, **ΔH^0 = LHV = 241.8 kJ mol^{-1}** **(U_{tn} = 1.253 V**). It should be noted that U_{tn}^{0}, equation [4], is larger than U_{rev}^{0} , equation [3], as it contains the heat associated with the entropy change ΔQ_{rev}.

- **Higher heating value (HHV in J.mol^{-1}),** which includes the heat of water vaporisation, is used as a reference for **liquid water electrolysis.**
- **Lower heating value (LHV)** is used for steam electrolysis, for example solid oxide electrolysis, which is not discussed in this document.
- Under strictly adiabatic conditions (a case of limited interest), the cell is cooling down when $U_{rev} < U_{cell} < U_{tn}$ because the necessary heat required for the entropy change is taken only from the heat stored inside the cell. In such cases, thermal exchange between the cell and the surroundings is not possible.
- When the operating cell voltage is $U_{cell} > U_{tn}$, the heat required by the reaction is provided *in situ* by internal dissipation (overvoltages and ohmic dissipations). In cases in which the dissipated heat is higher than the required heat, this results in an increase in cell temperature.

(²) IUAPC notation should be used here. E or E^{emf} is used for automotive cells ($\Delta G < 0$). Voltage = U is used for electrolysis cells ($\Delta G > 0$).

3.7.2.3. Heat balance (Q_{cell}) of the water electrolysis reaction

Under specific operating conditions (under constant T and p operating conditions), the heat balance, Q_{cell}, can be defined as the difference between **the reversible heat ΔQ_{rev}** associated with the entropy change of the reaction, **$\Delta Q_{rev} = T\Delta S$**, which is spontaneously transferred from the surroundings to the cell when the temperature gradient $T_{cell} < T_{out}$, and the energy loss due to internal dissipation via charge transfer overvoltages ($\Sigma|\eta_i|$) and ohmic dissipation ($R_e I$) associated with the **irreversible heat, Q_{irrev}**, which is spontaneously transferred from the cell to the surroundings when $T_{cell} > T_{out}$:

$$\mathbf{Q_{output}} = \mathbf{Q_{irrev}} \ (\mathrm{J.mol^{-1}}) = n\cdot F\cdot(U_{cell} - U_{rev}) = n\cdot F\cdot\eta_{loss} = n\cdot F(\Sigma|\eta_i| + R_e I) \qquad [5]$$

$$\Leftrightarrow nFQ_{irrev} \sim (U_{cell} - U_{rev}) = \eta_{loss}$$

$$=> Q_{cell} = Q_{input} - Q_{output} = \Delta Qrev - Q_{irrev} = T\Delta S - n\cdot F\cdot(U_{cell} - U_{rev})$$

$$\text{With } \mathbf{Q_{input}} = \mathbf{\Delta Q_{rev}} = T\Delta S = \Delta H_{rev} - \Delta G_{rev} = n\cdot F\cdot(U_{tn} - U_{rev}) \qquad [6]$$

This leads to the expression of the **Q_{cell} heat balance** as follows:

$$\mathbf{Q_{cell}} = n\cdot F\cdot(U_{tn} - U_{rev}) - n\cdot F\cdot(U_{cell} - U_{rev}) = n\cdot F\cdot(U_{tn} - U_{cell}) \qquad [7]$$

Under SATP conditions: $\Delta Q°_{rev} = nF\ (1.48 - 1.23) = 285.8 - 237.2 = 48.6\ \mathrm{kJ\ mol^{-1}}$ and $\Delta Q_{rev}/2F \sim 0.25$ volts.

This expression describes the total heat exchange between the surroundings and the electrolysis cell according to the value of U_{cell} compared with the value of U_{tn}. Under all operating conditions, the Q_{cell} heat balance depends on the reversible heat ($\Delta Q_{rev} = T\Delta S$) exchanged with the outside area and the irreversible heat ($n\cdot F\ \eta_{loss}$) resulting from overvoltages and the joule effect. It is not possible to distinguish between these two sources of heat, but if $U_{cell} < U_{tn}$ the system needs an external heat input (via the thermostat), and if $U_{cell} > U_{tn}$ excess heat is released to the environment (via the thermostat or by radiation, conduction or convection). However, the direction of the heat flow can be known: towards the system or towards the surroundings.

In the scientific community there are two opposing points of view with regard to cell level.

- One suggesting that it is **possible** to distinguish between reversible (i.e. provided by the surroundings or the thermostat (called **Q_{input}**)) and irreversible (i.e. heat released to the surroundings) sources.
- One suggesting that it is **not possible** to distinguish between the two.

The consequence of this disagreement explains (at least partly) the different definitions of the efficiency cases described below.

The algebraic sign for Q_{cell} shows the direction of the net heat flow.

- $Q_{cell} = 0$ (when $U_{cell} = U_{tn}$), i.e. the cell operates isothermally without a net exchange of heat between the cell and the surroundings.
- $Q_{cell} > 0$ (when $U_{cell} < U_{tn}$), heat is absorbed by the cell at low current intensity to keep T constant.

- $Q_{cell} < 0$ (when $U_{cell} > U_{tn}$), the excess heat produced at high current intensity is released from the cell and some external cooling may be needed to keep T constant.

3.7.3. Energy efficiency definition: first approach

As mentioned above, in the simplest case of a single electrolysis cell, the energy efficiency $\boldsymbol{\varepsilon_{cell}}$ of the electrolysis cell can be defined as the ratio between the theoretical amount of total energy $\mathbf{W_t}$ (J/mol) required to split one mole of water (i.e. the opposite of its enthalpy of formation ΔH_f) and the actual amount of energy $\mathbf{W_r}$ (J/mol) used in the process. When liquid water is electrolysed (as in the case of PEM, alkaline and anionic membrane technologies), the reference energy consumption is that of liquid water (absolute value of the HHV of hydrogen combustion in oxygen).

$$\varepsilon_{cell} = \frac{energy\ requirement\ in\ reversible\ conditions}{energy\ requirement\ in\ irreversible\ conditions} = \frac{W_t\ (J.mol^{-1})}{W_r\ (J.mol^{-1})} \qquad [8]$$

Hereafter, **four different cases** are presented **as being state of the art** with regard to the definition of energy efficiency, performed on the basis of different thermodynamic assumptions.

3.7.3.1. Energy efficiency — case 1 (constant reversible heat input based)

The definition is as follows.

In this first case, which takes into account all the energies (electrical and thermal) involved, the numerator of equation [8] (the energy requirement in reversible conditions) is defined as the necessary electrical work + the necessary heat flow ($\Delta Q_{rev} = T \cdot \Delta S$ $J.mol^{-1}$) associated with the entropy change. Therefore:

$$W_t = \Delta G_{rev} + \Delta Q_{rev} = \Delta H_{rev} \Leftrightarrow W_t = n \cdot F \cdot U_{rev}\ \textit{(electrical work)} + n \cdot F \cdot (U_{tn} - U_{rev})\ (\textit{reversible } Q)$$

$$W_t = n \cdot F \cdot U_{tn}\ \text{(J/mole)}\ (\textit{total energy})$$

The denominator of equation [8], the energy requirement in irreversible conditions, is defined as the actual electrical energy consumption (the necessary electrical work + the extra amount of electrical work which is dissipated internally into heat) + the necessary heat associated with the entropy increase. Therefore:

$$W_r = \Delta G_{rev} + \Delta Q_{rev} + nF\eta_{loss}$$

$$W_r = n \cdot F \cdot U_{rev}\ \textit{(electrical work)} + n \cdot F \cdot (U_{tn} - U_{rev})\ \textit{(reversible Q)} + n \cdot F \cdot (U_{cell} - U_{rev})\ (\textit{irreversible } Q)$$

$$W_r = n \cdot F \cdot (U_{tn} + U_{cell} - U_{rev})\ \text{(J/mole)}\ (\textit{total energy}).$$

Therefore, the 'energy efficiency coefficient' in case 1 is given as:

$$\varepsilon_{cell,case1} = \frac{\Delta H_{rev}}{\Delta H_{rev} + nF\eta_{loss}} = \frac{\Delta G_{rev} + \Delta Q_{rev}}{nFU_{cell} + \Delta Q_{rev}} = \frac{U_{tn}}{U_{tn} + U_{cell} - U_{rev}} \qquad [9]$$

Under SATP conditions:

$$\varepsilon^0_{cell,case1} = \frac{U^0_{tn}}{U^0_{tn}+U_{cell}(SATP)-U^0_{rev}} = 1 \qquad [10]$$

as $U_{cell}(SATP) = U^0_{rev}$.

Under any T,p conditions:

$$\varepsilon_{cell,case1} = \frac{U_{tn}(T,p)}{U_{tn}(T,p)+U_{cell}(T,p)-U_{rev}(T,p)} < 1 \qquad [11]$$

The graphical analysis is as follows.

Figure 6 shows the plot of equation [9], the energy efficiency coefficient ε_{cell} compared with U_{cell} up to 2.0 V under SATP conditions (U^0_{tn} = 1.48 V and U^0_{rev} = 1.23 V). Starting at $U_{cell} = U^0_{rev}$, this is a continuous decreasing function of U_{cell}. The plot is similar to the plot obtained for case 2 but the rate at which ε_{cell} decreases with U_{cell} is slower (see the quantitative comparison of cases 1, 2 and 3 in Figure 12 below).

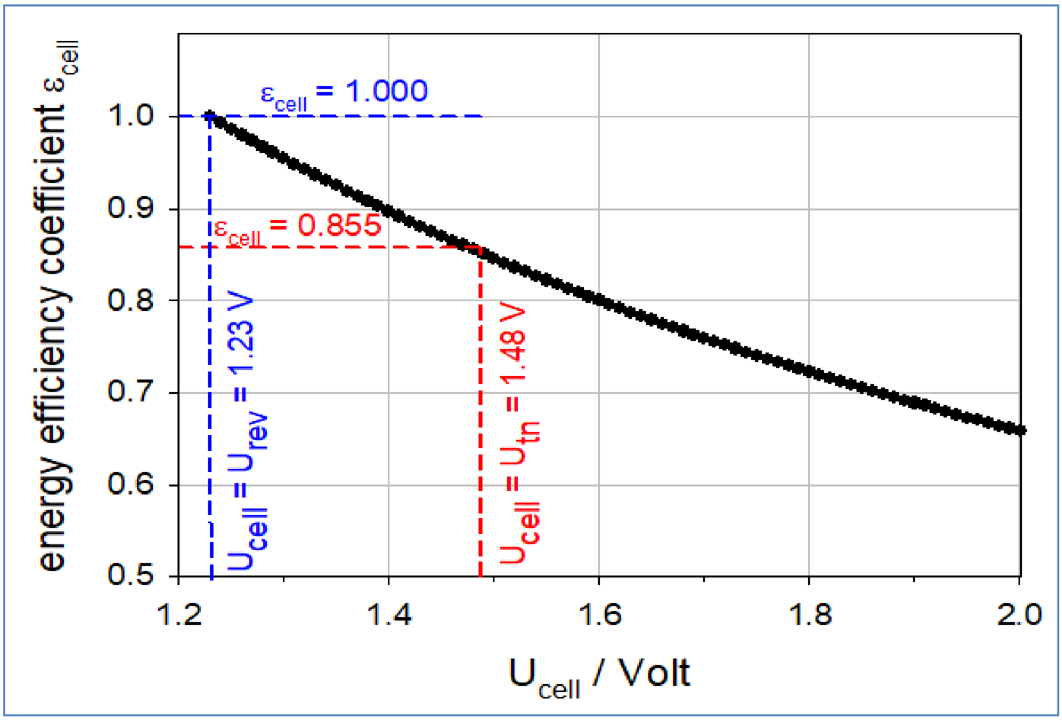


Figure 6: Thermodynamic efficiency plot (case 1)

Discussion

Arguments in favour

- The necessary fixed thermodynamic quantity ΔQ_{rev} (the reversible heat needed for the entropy increase of the water dissociation reaction) is provided **only** by an external heat source (air or thermostat) and **not** by internal dissipation of electrical work. The possibility that heat can be partly (when $U_{rev} < U_{cell} < U_{tn}$) or totally (when $U_{cell} \geq U_{tn}$) produced *in situ* by internal dissipation and thus can vary with U_{cell} (according to the exothermic or endothermic operating conditions) is disregarded. There is a constant external input of reversible heat to the cell under all operating conditions (exothermic and endothermic) and this is the only heat that is provided by the surroundings to the cell.

Arguments against

- W_r contains a constant heat input from an external source equal to ΔQ_{rev} under all operating conditions (any U_{cell}) including operation under strong exothermic conditions ($U_{cell} > U_{tn}$) where excess heat is produced by the cell and not absorbed by an external source.
- The heat balance in case 1 is **not** fully consistent with the temperature gradient between the cell and the surroundings and is therefore **not** consistent with non-equilibrium thermodynamics.
- It is not possible to differentiate between the heat arising from the thermostat and the heat arising from internal dissipation. Only the temperature gradient (non-equilibrium thermodynamics) determines the direction of ΔQ_{rev} (where ΔQ_{rev} heat comes from).
- All the dissipated heat generated by additional electrical work inside the cell due to the irreversible process is reverted to the external temperature-control device and is **not** used inside the cell for the entropy increase. Therefore, none of the heat produced inside the cell by the dissipation of electrical work is used for the entropy increase of the reaction.
- The energy input for a system is equivalent to the electricity input for the stack plus the electricity input for the auxiliaries (denominator). Thus, if ΔQrev is added at the denominator of the stack efficiency calculation, and stack and system efficiencies are compared, the power consumption of the auxiliaries will be lower than what can be effectively measured.
- In addition, in case 1, the energy input is in part calculated instead of being simply measured, as usually occurs with the conversion efficiency of any process.

3.7.3.2. Energy efficiency — case 2 (free energy variation based)

Definition

In this second case, the numerator of equation [8] (the energy requirement under reversible conditions) is defined as the necessary electrical work **only**. The necessary heat flow ($\Delta Q_{rev} = T.\Delta S\ J.mol^{-1}$) associated with the entropy change (and that is transferred from the thermostat to the cell) is not taken into account. Therefore:

$$W_t = \Delta G_{rev} = n \cdot F \cdot U_{rev} \textit{ (electrical work)}$$

The denominator of equation [8], the energy requirement under irreversible conditions, is defined as the actual electrical energy consumption. This is the necessary electrical work + the extra amount of electrical work which is dissipated internally into heat. Therefore:

$$W_r = \Delta G_{rev} + nF\eta_{loss}$$

$$W_r = n \cdot F \cdot U_{rev} \textit{ (reversible electrical work)} + n \cdot F \cdot (U_{cell} - U_{rev}) \textit{ (irreversible Q)}$$

$$W_r = n \cdot F \cdot (U_{cell}) \text{ (J/mole) } (\textit{total energy = total electrical work})$$

Therefore, the 'energy efficiency coefficient' in case 2 (in the literature, in case 2 the $\boldsymbol{\varepsilon}_{\mathbf{cell}}$ definition is sometimes called the **thermodynamic voltage efficiency**) is given by:

$$\varepsilon_{cell,case2} = \frac{\Delta G_{rev}}{nFU_{cell}} = \frac{nFU_{rev}}{nFU_{cell}} = \frac{U_{rev}}{U_{cell}} \qquad [12]$$

Under SATP conditions:

$$\varepsilon^{0}_{cell,case2} = \frac{U^{0}_{rev}}{U_{cell}(SATP)} = 1 \qquad [13]$$

since $U_{cell}(SATP) = U^{0}_{rev}$

Under any T,p conditions:

$$\varepsilon_{cell,case2}(T,p) = \frac{U_{rev}(T,p)}{U_{cell}(T,p)} \qquad [14]$$

Graphical analysis

Figure 7 shows the plot of equation [12], the thermodynamic voltage efficiency as a function of U_{cell} **under SATP conditions**. Starting at $U_{cell} = U_{rev}$, this is a continuous decreasing function of U_{cell}. It can be seen that ε_{cell} is **100 %** when U_{cell} is equal to U_{rev} = 1.23 V. When the cell voltage is equal to the thermoneutral voltage ($U_{cell} = U_{tn}$ = 1.48 V under SATP conditions), the energy efficiency coefficient expressed in percentage is equal to 83.1 %. Regarding the heat balance, it should be noted here that when $U_{rev} < U_{cell} < U_{tn}$ (i.e. the cell voltage is less than the thermoneutral voltage), there is a heat flux from the thermostat to the cell: this range of U_{cell} is called the endothermal mode of operation. When $U_{cell} = U_{tn}$ (i.e. the cell voltage is equal to the thermoneutral voltage), the heat flow between the thermostat and the cell is zero because all the necessary heat is produced *in situ*, inside the cell, by degradation of electrical work (second principle, dissipation associated with the transport of charged species). When $U_{cell} > U_{tn}$ (i.e. the cell voltage is higher than the thermoneutral voltage), there is a heat flux in the opposite direction, from the cell to the thermostat, because the amount of heat produced *in situ* by dissipation exceeds the cell requirements: this is the exothermal mode of operation. The sign for the temperature gradient (T_{in}-T_{out}) is negative in the endothermal domain, equal to zero at the thermoneutral point and positive in the exothermal domain.

Under endothermic operations, $U_{rev} < U_{cell} < U_{tn}$, of relatively large thermally isolated cells where the water flow rate is relatively low, the outlet water temperature, T_{out}, is lower than the inlet water temperature, T_{in}. Under exothermic conditions $U_{cell} > U_{tn}$ T_{out} will be higher than T_{in}.

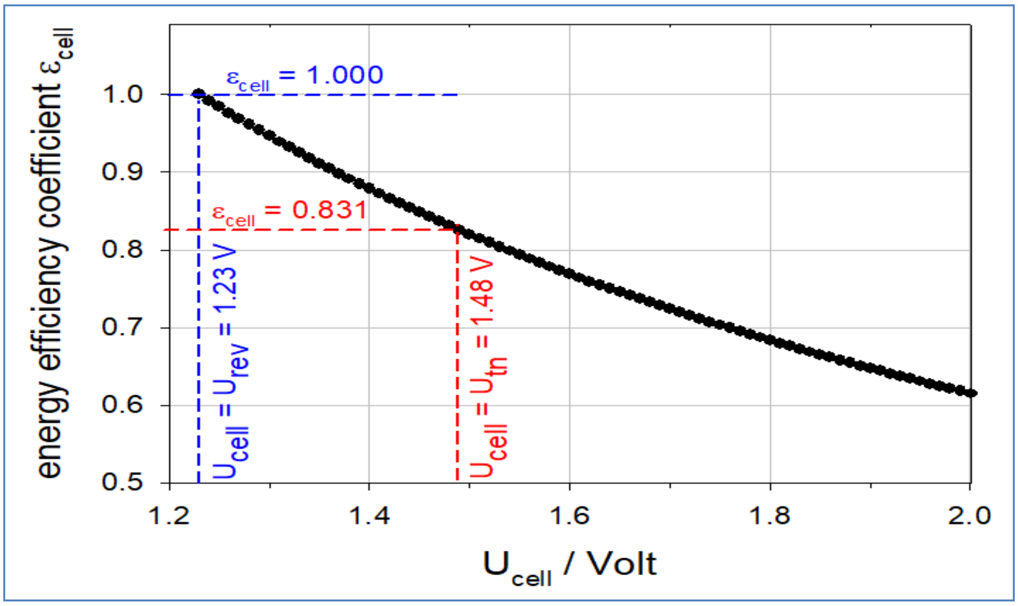


Figure 7: Thermodynamic efficiency plot (case 2)

Discussion

Arguments in favour

- Equation [12] is homogeneous because only the electrical work is taken into account at the numerator and the denominator.
- Heat flows are disregarded: this is acceptable for near-ambient-temperature electrolysis (PEM and alkaline) because the lack of reversibility at the anode makes the endothermal range very narrow (the thermoneutral point is reached at very low current densities such as 10-20 mAcm^{-2}).
- Corrections for operating conditions other than SATP conditions can be easily implemented.

Arguments against

- Equation [12] does not reflect the actual conditions and is not rigorous because it considers only the electrical work as useful energy output and not the total energy output.
- In transient operation, with periodic cycles, the time spent in the endothermal domain may increase, and in such cases the heat flow should be taken into account.

3.7.3.3. Energy efficiency — case 3 (enthalpy based)

Definition

In this third case, the numerator of equation [8] (the energy requirement under reversible conditions) is defined as ΔH_{rev}, as for case 1. Therefore:

$$W_t = \Delta G_{rev} + \Delta Q_{rev} = \Delta H_{rev} \Leftrightarrow W_t = n \cdot F \cdot U_{rev} \text{ (electrical work)} + n \cdot F \cdot (U_{tn} - U_{rev}) \text{ (reversible Q)}$$

$$W_t = n \cdot F \cdot U_{tn} \text{ (J/mole) (total energy)}$$

The denominator of equation [8], the energy requirement under irreversible conditions, takes into account the detailed heat balance. Therefore, the expression of the denominator depends on the value of U_{cell}. There are three situations: (i) $U_{rev} < U_{cell} < U_{tn}$; (ii) $U_{cell} = U_{tn}$; (iii) $U_{cell} > U_{tn}$. Therefore the following applies.

When $U_{rev} < U_{cell} < U_{tn}$: endothermal range of operation

W_r = electrical work from DC source + heat from DC source resulting from electricity dissipation + complementary heat from the thermostat to keep cell temperature constant. Therefore:

$W_r = n \cdot F \cdot U_{rev}$ (electrical work) + $n \cdot F\ (U_{cell}-U_{rev})$ (internal heat dissipation) + $n \cdot F \cdot\ (U_{tn}-U_{cell})$

where $n \cdot F\ (U_{tn}-U_{cell}) = Q_{cell}$. This is the net heat input (**Q_{input}**) since part of the heat is already supplied via the irreversible reaction (internal heat dissipation).

The following equation:

$W_r = n \cdot F \cdot U_{rev} + n \cdot F \cdot \eta_{loss} + (\Delta Q_{rev} — n \cdot F \cdot \eta_{loss})$

can be modified to:

$W_r = n \cdot F \cdot U_{rev} + \Delta Q_{rev} = n \cdot F \cdot U_{rev} + nF\ (U_{tn}-U_{rev})$

$W_r = n \cdot F \cdot U_{tn}$

Therefore, if the heat input is an exact match for $n \cdot F\ (U_{tn}-U_{cell}) = Q_{cell}$, the 'energy efficiency coefficient' in case 3 when $U_{rev} < U_{cell} < U_{tn}$ is given by:

$$\varepsilon_{cell,case3} = \frac{W_t}{W_r} = \frac{n \cdot F \cdot U_{tn}}{n \cdot F \cdot U_{tn}} = 1\ for\ U_{rev} < U_{cell} < U_{tn} \quad [15]$$

When $U_{cell} = U_{tn}$: thermoneutral point of operation

W_r = electrical work from DC sources only. Therefore:

$$W_r = n \cdot F \cdot U_{rev} + n \cdot F \cdot\ (U_{tn}-U_{rev}) = n \cdot F \cdot U_{tn}$$

Then the 'energy efficiency coefficient' in case 3 when $U_{cell} = U_{tn}$ is given by:

$$\varepsilon_{cell,case3} = \frac{W_t}{W_r} = \frac{n \cdot F \cdot U_{tn}}{n \cdot F \cdot U_{tn}} = 1\ for\ U_{cell} = U_{tn} \quad [16]$$

This applies if there is no external heat input to the cell. Using a thermostat means that there is an external heat input hence case 4 for the condition of $U_{cell} = U_{tn}$ must be used.

When $U_{cell} > U_{tn}$: exothermal range of operation

This is the usual mode of operation of PEM and alkaline technology. In this field the process is exothermic, thus no heat is supplied from the surroundings to the cell. As a result, $Q_{input} \sim 0$; and based on these other assumptions:

- the cell is thermally insulated;
- the energy needed for cooling the water in order to keep the temperature constant (balance of plant) is disregarded.

W_r = electrical work from power source only (zero heat from thermostat).

$W_r = n \cdot F \cdot U_{rev} + n \cdot F\ \eta_{loss=} = n \cdot F \cdot U_{cell}$

with $n \cdot F\ \eta_{loss} > \Delta Q_{rev}$

which means the heat produced internally in the exothermic process is **greater** than the required reversible heat associated with the entropy variation of the process and thus no external heat is absorbed by the cell (therefore cooling may be needed).

With $W_t = n \cdot F \cdot U_{tn}$

the 'energy efficiency coefficient' in case 3 when $U_{cell} > U_{tn}$ (sometimes called the enthalpy efficiency in the literature) is given by:

$$\varepsilon_{cell,case3} = \frac{W_t}{W_r} = \frac{n \cdot F \cdot U_{tn}}{n \cdot F \cdot U_{cell}} = \frac{U_{tn}}{U_{cell}} < 1 \quad [17]$$

Summary

The 'energy efficiency coefficient' in case 3 is given by the following two sets of equations:

$$\begin{cases} when\ U_{rev} < U_{cell} \leq U_{tn}: \varepsilon_{cell,case3} = 1 \\ when\ U_{cell} > U_{tn}: \varepsilon_{cell,case3} = \frac{U_{tn}}{U_{cell}} < 1 \end{cases} \quad [18]$$

Under SATP conditions:

$$\begin{cases} when\ U_{rev}^0 < U_{cell}(SATP) \leq U_{tn}^0: \varepsilon_{cell,case3} = 1 \\ when\ U_{cell}(SATP) > U_{tn}^0: \varepsilon_{cell,case3}^0 = \frac{U_{tn}}{U_{cell}} < 1 \end{cases} \quad [19]$$

Under any T,p conditions:

$$\begin{cases} when\ U_{rev}\ (T,p) < U_{cell}(T,p) \leq U_{tn}(T,p): \varepsilon_{cell,case3} = 1 \\ when\ U_{cell}(T,p) > U_{tn}\ (T,p): \varepsilon_{cell,case3} = \frac{U_{tn}\ (T,p)}{U_{cell}\ (T,p)} < 1 \end{cases} \quad [20]$$

Graphical analysis

Figure 8 shows the plot of the energy efficiency ε_{cell} versus U_{cell} calculated up to 2.0 V in case 3 (using equations 15, 16 and 17).

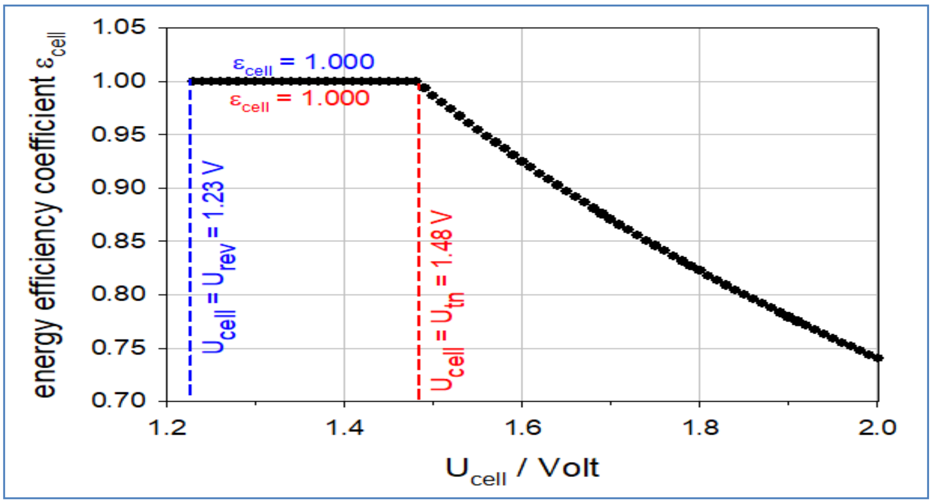


Figure 8: Thermodynamic efficiency plot (case 3)

Discussion

Arguments in favour

- Case 3 is close to physical reality: when $\mathbf{U_{cell} < U_{tn}}$, the heat associated with the entropy increase is provided by the external temperature-control device **and** by internal dissipation. This is the reason why the efficiency is conventionally assumed constant for $\mathbf{U_{rev} < U_{cell} < U_{tn}}$, since only the exact amount of heat needed is provided by external + internal sources. When $\mathbf{U_{cell} > U_{tn}}$, the cell does not receive any heat from the thermostat ($Q_{input} = 0$); Q_{cell} becomes < 0 because the excess heat produced by internal irreversibility is released outside the cell. Each mole of water inside the cell receives from outside exactly the amount of heat needed (from internal dissipation + a fraction from the thermostat).
- The heat balance in case 3 is consistent with the temperature gradient between the cell and the surroundings and is therefore consistent with non-equilibrium thermodynamics.
- Case 3 definition of cell and stack efficiency is perfectly homogeneous with the system efficiency definition. This is the equation reported in almost all publications.

Arguments against

- Equation [17] is not valid when $U_{cell} < U_{tn}$, because it gives $\varepsilon_{cell} > 1$. However, assuming that the correct definition is given by the sum of equations [15], [16] and [17], then $\varepsilon_{cell} \leq 1$ regardless of the U_{cell}.
- The definition of $\Delta Q_{rev} = 0$, implies that either $T = 0$ or $\Delta S = 0$, which is impossible above zero Kelvin. A differentiation has to be made between ΔQ_{rev}, which is the necessary heat required by the reaction, and the origin of that heat. In case 3, the origin of the necessary heat ΔQ_{rev} depends on the temperature gradient (non-equilibrium thermodynamics): it can originate partly from the thermostat and partly from internal dissipation when $(T_{cell} - T_{out}) < 0$ (in the endothermal mode $\cong U_{cell} < U_{tn}$) or only from internal dissipation (in the exothermal mode $\cong U_{cell} > U_{tn}$).
- With this definition it is not possible to distinguish between the part of the heat arising from the reversible heat (i.e. from the surroundings or the thermostat) and that coming from irreversible losses (i.e. heat released to the surroundings) in the total balance.

3.7.3.4. Energy efficiency — case 4 (electricity and heat input based)

In a more general approach when the **heat is supplied by an external source**, this heat source should be taken into account in the efficiency equation.

In this case, $\mathbf{Q_{cell} = Q_{input} > 0}$. Consequently Q_{input} must be measured and reported in the efficiency equation:

$$\varepsilon_{cell,case4,general} = \frac{\Delta H_{rev}}{nFU_{cell}+Q_{input}} = \frac{n\cdot F\cdot U_{tn}}{nFU_{cell}+Q_{input}} \qquad [21]$$

This equation is largely applicable in cases where ΔT is measurable with adequate accuracy such as in large single cells, short stacks and stacks.

If the external heat is supplied by heating the water at the inlet, for example to bring the temperature of the water to the desired operating temperature, Q_{input} can be determined as follows:

$Q_{input=}$thermal power·time=$P_{thermal}$ (J/s)·t (s).

$P_{thermal}$ = water flow · water thermal capacity·ΔT.

$$P_{thermal} = \dot{m}_{H_2O} \cdot \mathrm{Cp} \cdot \Delta \mathrm{t}$$

$\dot{m}_{H_2O}$ is provided in (g/s).

Water heat capacity under standard conditions Cp = 4.186 J/(g·K).

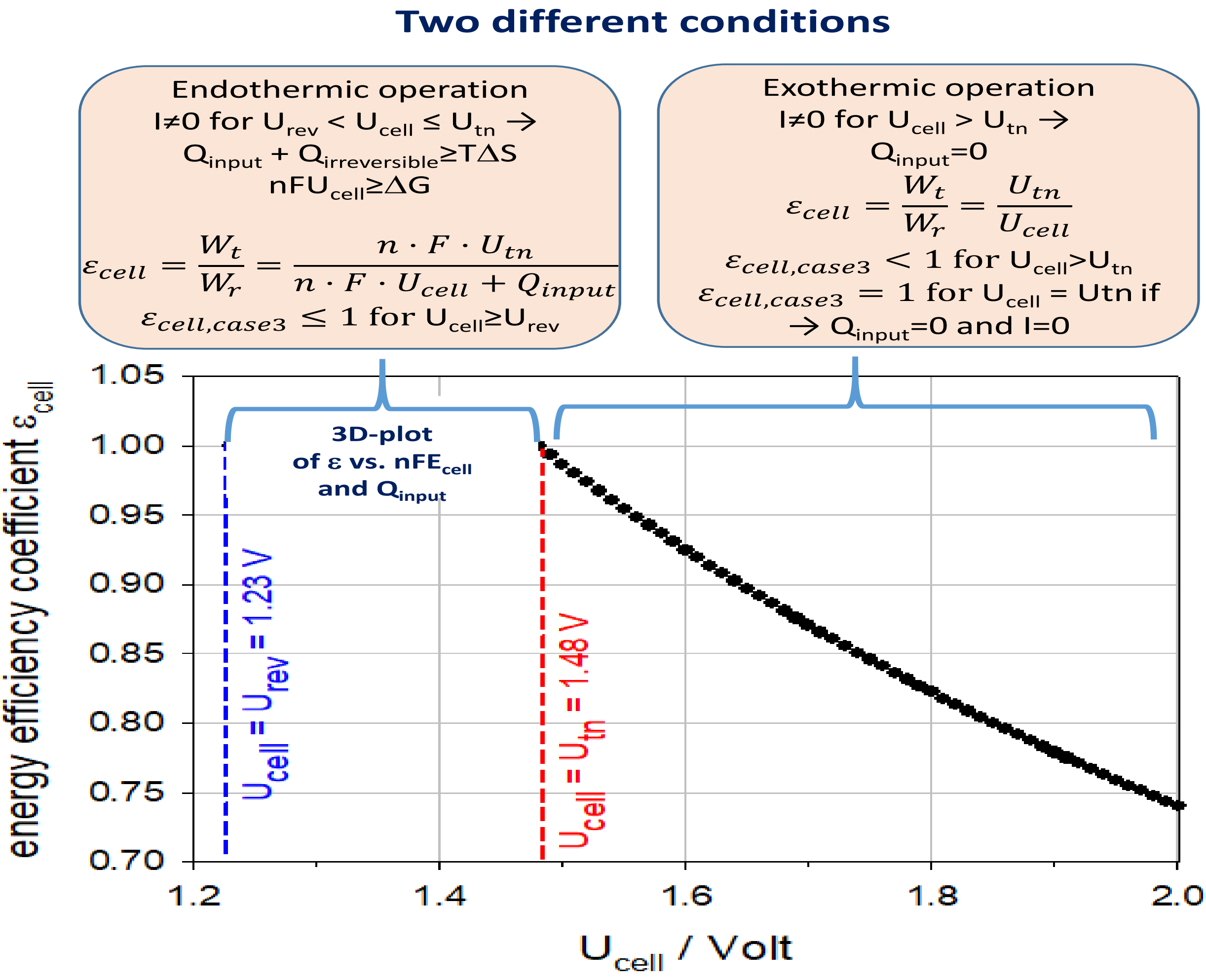
$\Delta T = T_{out,\ cell} - T_{in,cell}$ (K).

T_{in} = water temperature at the inlet of the cell.

T_{out} = water temperature at the outlet of the cell.

This approach can give information on the effective heat exchange between the cell and the surroundings. If $\Delta T < 0$ the reaction inside the cell is endothermic and the heat provided to the cell must be considered in the efficiency equation. Thus, when the effective heat supplied to the process is properly taken into account for $U_{rev} < U_{cell} < U_{tn}$, the resulting efficiency is below 100 %.

Graphical analysis



Two different conditions

Endothermic operation
I≠0 for $U_{rev} < U_{cell} \le U_{tn}$ →
$Q_{input} + Q_{irreversible} \ge T\Delta S$
$nFU_{cell} \ge \Delta G$

$$\varepsilon_{cell} = \frac{W_t}{W_r} = \frac{n \cdot F \cdot U_{tn}}{n \cdot F \cdot U_{cell} + Q_{input}}$$

$\varepsilon_{cell,case3} \le 1$ for $U_{cell} \ge U_{rev}$

Exothermic operation
I≠0 for $U_{cell} > U_{tn}$ →
$Q_{input}=0$

$$\varepsilon_{cell} = \frac{W_t}{W_r} = \frac{U_{tn}}{U_{cell}}$$

$\varepsilon_{cell,case3} < 1$ for $U_{cell} > U_{tn}$
$\varepsilon_{cell,case3} = 1$ for U_{cell} = Utn if
→ Q_{input}=0 and I=0

Figure 9: Thermodynamic efficiency plot (case 4)

A reaction can only occur if n·F·U_{cell} ≥ ∆G and Q_{input} + Q_{irr} ≥ T∆S and the efficiency is a function of both electrical and thermal energy input as per equation [21]:

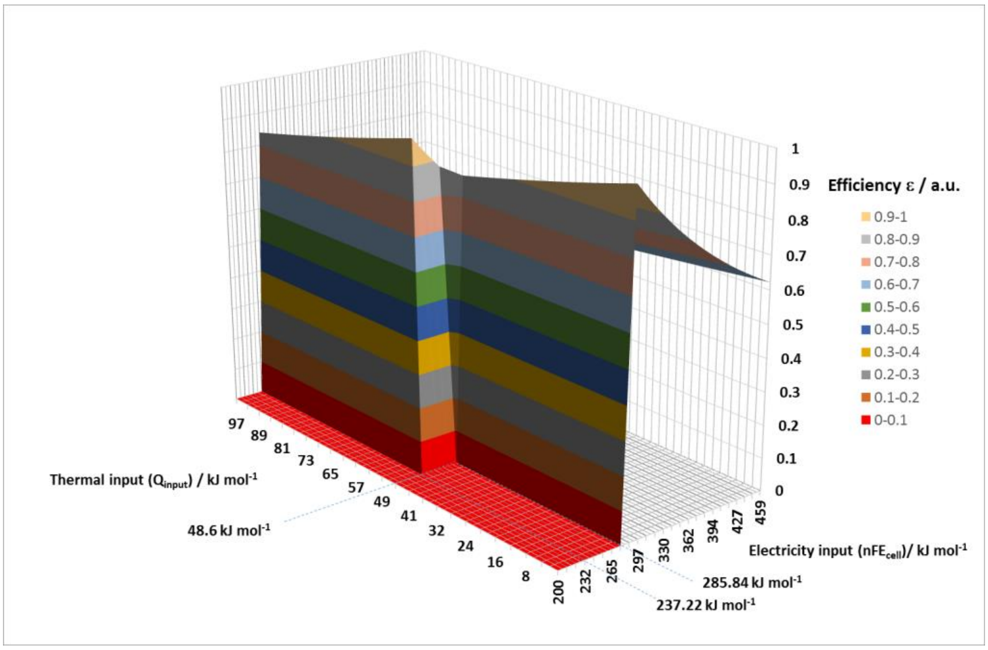


Figure 10: Thermodynamic efficiency plot (case 4)

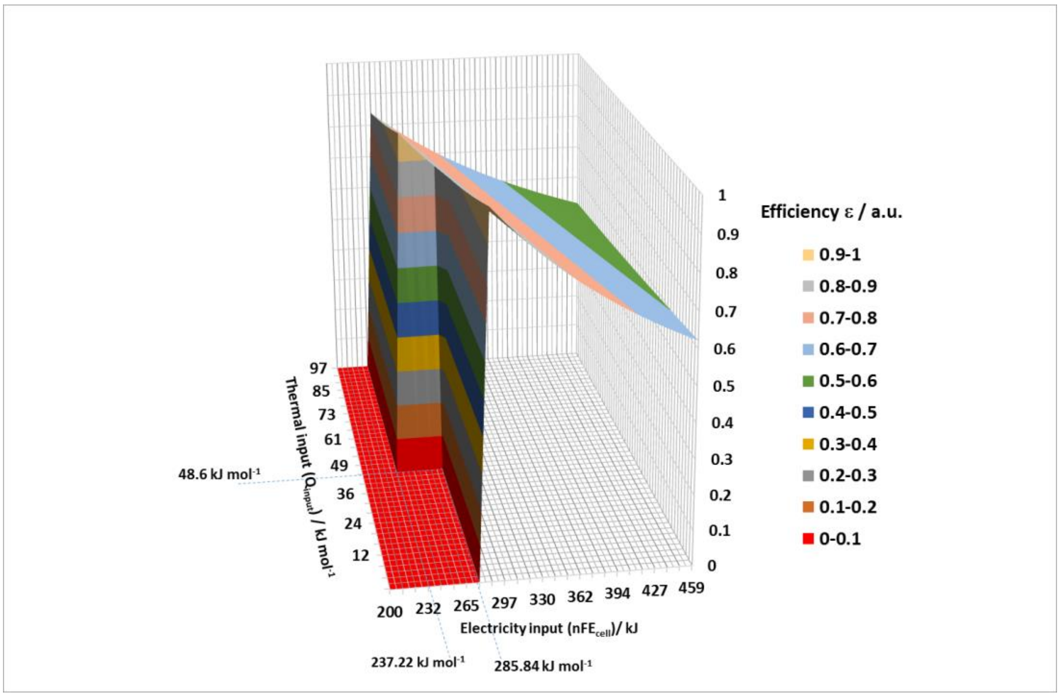


Figure 11: Thermodynamic efficiency plot (case 4)

When Q_{input} is zero, the bi-dimensional plot is equal to that reported above for case 3, see Figure 8.

The efficiency is 1 when total energy input (heat and electricity) is 285.84 KJ mol^{-1}. This minimum energy requirement can be supplied as electricity + heat or electricity only.

3.7.3.5. Water electrolysis efficiency case comparison

A comparison of the energy efficiencies for cases 1, 2 and 3 presented above is shown in Figure 12. For any given U_{cell}, it is evident that case 3 provides a higher efficiency value compared to cases 1 and 2, with a difference of around 15-17 %, while between case 1 and case 2, the difference of efficiency ranges from 0 % at U_{rev} to 5 % at 2.0 V.

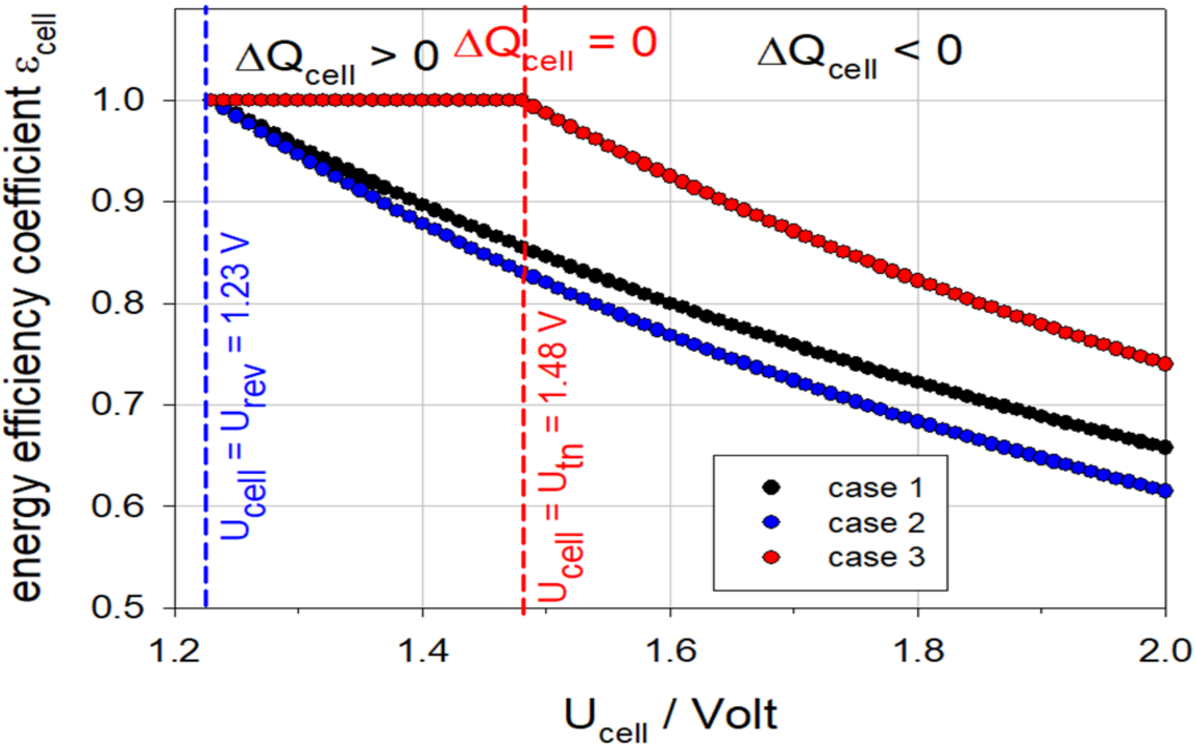


Figure 12: Plots of the energy efficiency versus U_{cell} for cases 1, 2 and 3

3.7.4. Energy efficiency as a function of operating temperature

Absolute temperature (T) and pressure (p) are the two main physical variables used to define the state of the electrolysis cell. All thermodynamic functions of interest used to define the energy efficiency coefficient are functions of (T,p). Therefore, it is necessary to provide an expression of these thermodynamic functions under any (T,p) operating conditions of interest in order to be able to calculate the efficiency of the electrolyser (cell, stack or system level) under such conditions.

Simplified expression of the efficiency versus T at p = 1 bar (10^5Pa)

For PEM and alkaline electrolysis, in a first approximation, the enthalpy change of the water-splitting reaction **ΔH(T,p) can be considered as constant over the limited temperature range of interest** (0-100 °C). This is shown in Figure 13. ΔH(T,p) is equal to the standard enthalpy change $\Delta H^0 = nF\, U_{tn}^0$. Hence, the energy efficiency coefficient ε_{cell} of a water electrolysis cell or stack can be approximated over this temperature range by using the SATP reference values for U:

$$U_{rev}^0 = 1.23 \text{ V and } U_{tn}^0 = 1.48 \text{ V}$$

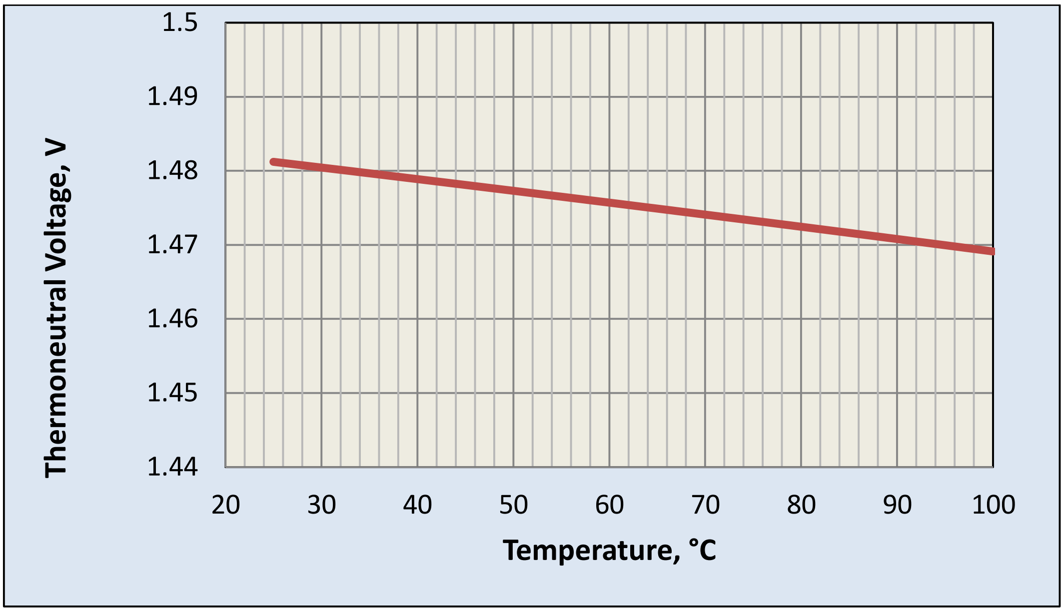


Figure 13: Thermoneutral voltage evolution versus liquid water temperature

Expression of the efficiency versus T at p = 1 bar without simplifying assumption

For a more accurate energy efficiency calculation, it is necessary to take into account the effect of the operating temperature. Empirical polynomial expressions for the calculation of the thermodynamic voltage U_{rev}(T,p), based on Gibbs free energy change, and the thermoneutral voltage U_{tn} have been reported in the literature (9). For liquid water conditions, in the 0 to 100 °C range and p =1.013 10^5 Pa = 1.013 10^5 bar and up to 200 °C with p = 1.824·10^5 Pa = 1.824 bar, the expressions are:

$$U_{rev}(T,1atm) = \Delta G(T)/2F = 1.5184 - 1.5421 \cdot 10^{-3} \cdot T + 9.523 \cdot 10^{-5} \cdot T \cdot Ln(T) + 9.84 \cdot 10^{-8} T^2 \quad [22]$$

$$U_{tn}(T,1atm) = \Delta H(T)/2F = 1.485 - 1.49 \cdot 10^{-4} \cdot (T - T^0) - 9.84 \cdot 10^{-8} \cdot (T - T^0)^2 \quad [23]$$

where T is expressed in Kelvin in both cases and T^0 = 273.15 K. It should be noted here that these two equations are valid for p = 1 atm, and not p = 1 bar. The difference in pressure is 1 %. Therefore, equations [22] and [23] can be used when the pressure is 1 bar.

The example of the corrected thermoneutral voltage value, U_{tn}, as a function of the reaction temperature, at atmospheric pressure, is described in Figure 13 (water in the liquid state). Its value changes from 1.481 V at 25 °C to 1.469 V at 100 °C (a variation of only 0.82 % that confirms the above assumption that temperature effect can be neglected in a first approximation). A similar linear behaviour applies to the variation of the cell voltage under reversible conditions, U_{rev}, but with a relatively larger change of around 5 % being U_{rev} 1.229 V at 25 °C and 1.167 V at 100 °C.

3.7.5. Energy efficiency as a function of operating pressure

Dry and ideal gas conditions

It should first be noted that only the Gibbs free energy change of the water dissociation reaction (ΔG) changes with pressure. The enthalpy change (ΔH) is constant because the effect of pressure on the free energy and the entropy changes cancel each other out. Therefore, there is a need to provide a definition of the role of pressure in the reference case (the numerator of equation [8]) only for case 2 (ΔH is used at the numerator for cases 1 and 3).

Assuming that the product streams (H_2 and O_2) at the exhaust of the electrolyser are dry and ideal gases, the minimal electrical energy required to evolve 1 mole of hydrogen W_t = ΔG_{rev}(T,p,I=0) (in J/mol_{H2}) can be determined by introducing the variation ΔU_{cell} of the cell voltage with the pressure of the reacting species (p_{H_2O}) and products (p_{H_2} and p_{O_2}), as follows:

$$nF\ U_{rev}(T,p)\ =\ \Delta G_{rev}(T,p^{\theta}) + RT\ \ln\left[(\frac{p_{O_2}}{p^{\theta}})^{\frac{1}{2}}\left(\frac{p_{H_2}}{p^{\theta}}\right)/\left(\frac{p_{H_2O}}{p^{\theta}}\right)\right]\ =\ nF\ (U_{rev}(T,p^{\theta}) + \Delta U_{cell}) \quad [24]$$

with:

$$\Delta U_{cell}\ =\ U_{rev}(T,p) -\ U_{rev}(T,p^{\theta})\ =\ \frac{RT}{2F}\ln\left[(\frac{p_{O_2}}{p^{\theta}})^{\frac{1}{2}}\left(\frac{p_{H_2}}{p^{\theta}}\right)/\left(\frac{p_{H_2O}}{p^{\theta}}\right)\right] \quad [25]$$

The different pressures (expressed in bar) in equations [24] and [25] have the following meanings:

- p_{O_2} = oxygen partial pressure,
- $p_{H_2O}/p^{\theta} = a_{H2O} = 1$ for PEM and AWE (where a_{H2O} is the water activity),
- p_{H_2} = hydrogen partial pressure,
- p^{θ} = reference pressure at the working temperature.

In each cell compartment, the total pressure p is the sum of partial pressures:

- $p\ =\ \sum p_i\ =\ p_{O_2} + p_{H_2} + p_{H_2O}$,
- p^A = pressure of the anodic compartment = p, including the presence of some H_2 (hydrogen leakage through the separator) and water vapour,
- p^C = pressure of the cathodic compartment = p + Δp, assuming a differential pressure Δp between the two compartments.

Water saturated and ideal gases

Since gases produced during electrolysis are usually saturated with water vapour, equations [24] and [25] need corrections.

For ideal wet gases:

$$nFU_{rev}(T,p^{\theta})\ =\ \Delta G_{rev}(T,p^{\theta}) + RT\ \ln\left[(\frac{p^A - p^{sat}_{H_2O}}{p^{\theta}})^{\frac{1}{2}}\left(\frac{p^C - p^{sat}_{H_2O}}{p^{\theta}}\right)/\left(\frac{p^{sat}_{H_2O}}{p^{\theta}}\right)\right] = 2F(U_{rev}(T,p^{\theta}) + \Delta U_{cell}) \quad [26]$$

$$\Delta U_{cell}\ = \frac{RT}{2F}\ \ln\left[(\frac{p^A - p^{sat}_{H_2O}}{p^{\theta}}))^{\frac{1}{2}}\left(\frac{p^C - p^{sat}_{H_2O}}{p^{\theta}}\right)/\left(\frac{p^{sat}_{H_2O}}{p^{\theta}}\right)\right] \quad [27]$$

where $U_{rev}(T,p^{\theta})$ is the cell voltage at reference pressure p^{θ} and temperature T, and $p^{sat}_{H2O}(T)$ = water saturation pressure at an operating temperature T.

Equi-pressure operation

For pressure values identical at both electrodes ($p^A = p^C = p = p^{\theta}$), and assuming there are no gas leakages through the separator, it is possible to use a **simplified expression of equation [27]** to take into account the effect of pressure on the cell voltage U_{rev} derived from the Nernst equation. This simplified expression is given by equation [28].

$$\Delta U_{cell} = U_{rev}(T,p) - U_{rev}(T,p^{\theta}) = \frac{RT}{2F}\ln\left[\left(\frac{p-p^{sat}_{H_2O}}{p^{\theta}}\right)^{\frac{1}{2}}\right] \qquad [28]$$

Real and wet gases

Finally, to take into account the fact that real gases are produced instead of ideal gases (large operating pressures above 100 bars), it is necessary to use appropriate state equations that pertain to real gases (not considered here).

3.7.6. Energy efficiency stack

The energy efficiency of a liquid water electrolysis stack operating at temperature T and pressure p is equal to the mean energy efficiency of the individual cells, multiplied by the number *N* of cells in the stack. The energy consumption of auxiliaries (W_{aux}) is **not** taken into account. In other words, a stack is equivalent to a single cell having a mean cell-voltage value of $U_{cell} = U_{stack}/N$. Therefore, all the previous equations used to define the energy efficiency coefficient prevail. The only thing to be done is to replace U_{cell} with U_{stack}/N, whenever necessary, in these equations.

NB: It is also possible to calculate the energy efficiency coefficient of the jth cell in a stack of N cells by setting:

$$U_{cell} = U_{cell}^{j^{th}} \qquad [29]$$

In cases where U_{stack} is used, the corresponding efficiency equations are as follows.

Case 1:

$$\varepsilon_{stack,case1} = \frac{N\cdot U_{tn}(T,p)}{N\cdot U_{tn}(T,p)+U_{stack}(T,p)-N\cdot U_{rev}(T,p)} \qquad [30]$$

Case 2:

$$\varepsilon_{stack,case2} = \frac{N\cdot U_{rev}(T,p)}{U_{stack}(T,p)} \qquad [31]$$

Case 3:

when $U_{cell} > U_{tn}$ $$\varepsilon_{stack,case3} = \frac{N\cdot U_{tn}}{U_{stack}} \qquad [32]$$

when $U_{rev} < U_{cell} \leq U_{tn}$ $$\varepsilon_{stack,case\ 3} = \frac{N\cdot n\cdot F\cdot U_{tn}}{N\cdot n\cdot F\cdot U_{tn}} = 1 \qquad [33]$$

Case 4:

$$\varepsilon_{stack,case\ 4} = \frac{N\cdot n\cdot F\cdot U_{tn}}{N\cdot n\cdot F\cdot U_{tn}+Q_{input}} = 1 \qquad [34]$$

With $U_{stack} = N \cdot [U_{cell}(T,p^{\theta},I) + \Delta U_{cell}]$ and Q_{stack} the heat balance at stack level as derived from equation[7], i.e.:

$$Q_{stack} = N\cdot n\cdot F\cdot (U_{tn} - U_{cell}) = n\cdot F\cdot (N\cdot U_{tn} - U_{stack}) \qquad [35]$$

3.7.7. Energy efficiency system

At system level, the energy consumption of **all** the necessary ancillary equipment (e.g. AC/DC conversion, water purification, water preheating, pumps for water circulation, hydrogen purification, hydrogen drying, process monitoring, etc.) used to operate the electrolyser are added to the denominator of the equations used for the definition of the energy efficiency coefficient. This term (W_{aux} for auxiliary equipment in $J.mol^{-1}$) is added to the energy requirement under irreversible ($I \neq 0$) conditions.

The efficiency equation for the system is the following:

$$\frac{N \cdot U_{tn}(T,p)}{U_{stack} + W_{aux}/(nF)} \qquad [36]$$

The heat balance equation for the system is the following:

$$Q_{system} = n \cdot F \cdot (N \cdot U_{tn} - U_{stack}) + W_{aux} \qquad [37]$$

3.7.8. Current efficiency

3.7.8.1. Current efficiency losses

In an ideal water electrolysis cell where membranes/separators are assumed to be impermeable to gases, the current efficiency $\boldsymbol{\varepsilon}_I$ is equal to 100 %. However, the materials (polymer electrolyte for PEM or diaphragm for alkaline) are not fully impermeable. Mass transport of hydrogen and/or oxygen across the cell separator, especially when the cell is operated under pressure, is an issue that raises both safety and current-efficiency problems. Depending on the characteristics of the materials used in the cells, a fraction of the gases transported across the cell separator can react chemically or electrochemically. In conclusion, in a water electrolysis cell, the current efficiency is less than 100 % due to gas crossover or permeation effects.

It is usually difficult to measure the gas flow rates accurately (in moles per second) for gases permeated through the membrane separator, $\dot{n}_{H_2\_loss}$ and $\dot{n}_{O_2\_loss}$, because the hydrogen flow rates could be relatively small (in single cell and short-stack laboratory tests), containing water vapour residues, and as already mentioned, due to the crossover and permeation effects, some hydrogen and oxygen can react together and produce water before the measurement procedure.

3.7.8.2. Current efficiency — single cell

Fraction of the electric current passing through an electrochemical cell which accomplishes the desired chemical reaction. For a set of cell components and for a given cell design, the current efficiency $\boldsymbol{\eta}_I$ is mainly a function of the operating temperature T, operating pressure p and operating current density.

$$\eta_I(T,p,I) = 1 - \frac{2 \cdot F}{I_{DC}} \cdot \left[\dot{n}_{H_2\_loss}(T,p,I) + 2\dot{n}_{O_2\_loss}(T,p,I)\right] \qquad [38]$$

where $\dot{n}_i$ is the molar flow of component (i) permeated through the membrane separator in moles per second, 2 is the number of Faraday per mole of H_2 and 4 per mole of O_2, and I_{DC} the direct current provided, expressed in amperes.
In an ideal water electrolysis cell, $\dot{n}_{H_2\_loss} = \dot{n}_{O_2\_loss} = 0$ and $\eta_I(T,p,I) = 1$, independently of the operating conditions (T,p,I).
In a real water electrolysis cell, $\dot{n}_{H_2\_loss} \neq \dot{n}_{O_2\_loss} \neq 0$ and $\eta_I(T,p,I) < 1$.

Under practical conditions, it is easier and more accurate to measure the hydrogen or the oxygen flow rates at the exhaust of the electrolyser instead of measuring H_2 and O_2 cross-permeating flows, which are in many cases extremely small. Equation [39] (for hydrogen production) or equation [40] (for oxygen production) will then apply:

$$\eta_I^{H_2} = \frac{measured\ H_2\ flow\ rate}{theoretical\ H_2\ flow\ rate} = \frac{2 \cdot F \cdot \dot{n}_{H_2\ measured}}{I_{DC}} \qquad [39]$$

$$\eta_I^{O_2} = \frac{measured\ O_2\ flow\ rate}{theoretical\ O_2\ flow\ rate} = \frac{4 \cdot F \cdot \dot{n}_{O_2\ measured}}{I_{DC}} \qquad [40]$$

The measurement of the relevant outlet gas, hydrogen or oxygen should be performed using a properly dimensioned and highly accurate mass flow meter located after the water-removal steps designed to remove more than 99.9 % of gas water content. The concentration of hydrogen in oxygen should be measured by gas chromatographic analysis or via other analytical techniques with a similar detection limit after a gas-drying step. The molar fraction of the components in the outlet gases should be also measured, but under normal conditions it is assumed that traces of oxygen and water vapour in hydrogen or hydrogen and water vapour in oxygen are minor and thus usually negligible. In the event of high differential pressures and thin membranes (50 to 90 μm), current efficiency of about 98 % or even lower can instead be observed. Nevertheless, safety sensors to monitor the oxygen level in the hydrogen outlet or the hydrogen level in the oxygen outlet are strongly recommended to detect dangerous situations due to gas crossover of the separator.

3.7.8.3. Current efficiency — stack

Stack current efficiency at the operating temperature and pressure that is defined as the ratio between the flow rate of the hydrogen produced, $\dot{n}_{H_2}$, expressed in moles per second multiplied by the Faraday constant, and the direct current provided, I_{DC}, expressed in amperes multiplied by the number of cells, *N*. It is expressed as follows:

$$\eta_{I\ stack}^{H_2} = \frac{measured\ H_2\ flow\ rate}{theoretical\ H_2\ flow\ rate} = \frac{2 \cdot F \cdot \dot{n}_{H_2\ measured}}{N\ I_{DC}} \qquad [41]$$

$$\eta_{I\ stack}^{O_2} = \frac{measured\ O_2\ flow\ rate}{theoretical\ O_2\ flow\ rate} = \frac{4 \cdot F \cdot \dot{n}_{O_2\ measured}}{N\ I_{DC}} \qquad [42]$$

3.7.8.4. Coulombic and faradic efficiencies

These expressions have the same meaning as current efficiency.

3.7.9. Total efficiency — single cell and stack

Total efficiency, η_ω, that is defined as the product of energy efficiency and current efficiency values. It can be applied at single cell or stack level:

$$\eta_\omega^{cell} = \varepsilon_{cell} \cdot \eta_I^{cell} \qquad [43]$$

$$\eta_\omega^{stack} = \varepsilon_{stack} \cdot \eta_I^{stack} \qquad [44]$$

3.7.10. Energy efficiency definition: industry viewpoint

3.7.10.1. Energy efficiency coefficient

As already discussed earlier in this document (Section 3.7.1), the reference energy state used by the industry sector to define the energy efficiency coefficient of a water electrolysis cell, stack or system is different from the reference case used by the academic community. The general definition is:

$$\eta_{cell} = \frac{energy\ content\ of\ products}{total\ energy\ requirements} = \frac{W_t\ (J.mol^{-1})}{W_r\ (J.mol^{-1})} \qquad [B]$$

The energy content of products used at the numerator of the equation is usually the hydrogen heating value in oxygen (not in air), which is by definition the opposite of the standard enthalpy of the formation of one mole of water having HHV = **ΔH^0 = 285.8 kJ mol^{-1}**. There are potentially different practices that will inevitably lead to different values of the energy efficiency coefficient. In order to facilitate comparison, it is necessary to list these different practices, as follows.

- Some authors use the heating value of hydrogen combustion in air instead of oxygen.
- Some authors use the HHV of hydrogen combustion in oxygen/air (leading to the formation of liquid water) and others use the LHV of hydrogen combustion in oxygen/air (leading to the formation of gaseous water).
- Authors use different (T,p) conditions to calculate the energy content of their product.
- The usual practice in industry is not to calculate the efficiency coefficient in percentage (as in the academic community) but instead to calculate the specific energy consumption of a system (e.g. in kWh/kg$_{H2}$ or in kWh/Nm$^3_{H2}$).

The reason for such discrepancies is clear: the reference state is not unique but dictated by the applications. Therefore, the same electrolyser, when used for different applications, can have different efficiencies. Hence, there is a need to provide clear specifications to allow comparisons.

The main issue is to specify the (T,p) conditions under which the reference energy content of hydrogen is calculated. These (T,p) conditions could be considered at the exhaust of the electrolysis cell stack or the (T,p) conditions at the exhaust of the plant, after gas treatment (oxygen removal, drying and possibly compression).

Specifically, the **instantaneous** hydrogen production efficiency (based on the **HHV**) is defined as the ratio between the flow rate of the produced hydrogen, $\dot{n}_{H2}$, expressed in moles per second multiplied by the HHV expressed in joules per mole of hydrogen, and **the total thermal and electric power** provided to the system expressed in watts, i.e.:

$$\eta^{HHV} = \frac{HHV \cdot \dot{n}_{H_2}}{P_{thermal} + P_{electrical}} \qquad [45]$$

Equation [45] provides a practical and general (energy + current) value of the efficiency. An integral form of equation [45] is needed to determine the specific energy consumption in kWh/kg$_{H2}$. When the system is operated under stationary conditions, the expression (over a given time interval Δt) is simply:

$$\eta^{HHV} = \frac{HHV \cdot \dot{n}_{H_2} \cdot \Delta t}{W_e + Q_{cell} + Q_{H2O}} = \frac{HHV \cdot N_{H_2}}{W_e + Q_{cell} + Q_{H2O}} \qquad [46]$$

where:

- $\dot{n}_{H_2}$ is the number of moles of hydrogen produced over time (molar flow rate);
- N_{H_2} is the number of moles of hydrogen produced over the time period Δt in question;
- W_e = nF U_{cell} is the electrical energy input;
- Q_{cell} is the difference between the entropy change (TΔS) and the heat Q_{irrev} associated with irreversible losses due to overvoltages of the electrochemical reactions and the joule effect in the internal resistance;
- Q_{H20} is the thermal energy input of the additional heat exchanger (external to the system) for further water heat-up.

3.7.10.2. Overall component efficiency

Component efficiency for the HHV is defined as the ratio between the flow rate of the hydrogen produced, $\dot{n}_{H_2}$, expressed in moles per second multiplied by the HHV expressed in joules per mole, and the **total thermal and electric power** provided to the component expressed in watts as follows:

$$\eta^{HHV}_{component} = \frac{HHV}{P_{component\ extern}} \cdot \dot{n}_{H_2} \qquad [47]$$

3.7.10.3. Overall system efficiency

At system level (stack + balance of plant), it is necessary to take into account the energy consumption of all the necessary ancillary equipment. System efficiency for the HHV is defined as the ratio between the flow rate of the hydrogen produced, $\dot{n}_{H_2}$, expressed in moles per second multiplied by the HHV expressed in J.mol^{-1}, and the **total thermal and electric power** supplied to the system, for the operation of all ancillary equipment, expressed in watts. It is expressed in percentage as:

$$\eta^{HHV}_{system} = \frac{HHV}{P_{system\ extern}} \cdot \dot{n}_{H_2} \qquad [48]$$

3.7.10.4. Other expressions of practical interest

Some authors also calculate the energy efficiency coefficient of the system by multiplying the stack efficiency (assuming there is a current efficiency of 1) by the AC/DC conversion efficiency (in this case, the reference case is the enthalpy change of the reaction = case 3 of the definition used in the academic community, and the efficiency of gas conditioning is not taken into account):

$$\varepsilon_{system} = \frac{N \cdot U_{tn}(T,p)}{U_{stack}}$$

This definition contains the same equation [32] as in case 3 under exothermal operation, which, multiplied by the AC/DC conversion efficiency, gives:

$$\varepsilon_{system} = \frac{N \cdot U_{tn}(T,p)}{U_{stack}} \left(\frac{\eta_{AC/DC}}{1+\xi}\right) \qquad [49]$$

In equation [49], ξ is the ratio between parasitic power and net power consumed by the electrolyser due to the energy consumption by the auxiliaries.

$\eta_{AC/DC}$ = efficiency of the AC/DC converter, DC/DC voltage regulator or power conditioner.

Another equation of practical interest is obtained from equation [49] by taking into account the hydrogen current efficiency (10):

$$\varepsilon_{system} = \frac{N \cdot U_{tn}(T,p)}{U_{stack}} \cdot \frac{2 \cdot F \cdot \dot{n}_{H_2}}{I_{DC} \cdot N} \cdot \left(\frac{\eta_{AC/DC}}{1+\xi}\right) \qquad [50]$$

3.7.11. Exergy analysis

3.7.11.1. Exergy definition

In general terms exergy can be defined as the maximum work that can be extracted when a system is brought into equilibrium with its surroundings without incurring any losses (11). The efficiency of a process is defined as the exergy outflow used divided by the exergy inflow used. The term **yield** is brought together with **exergy** to replace the term efficiency, to avoid confusion between energy and exergy efficiency descriptors.

Field of application

The water-splitting reaction (chemical reaction) is analysed under constant (T,p,I) conditions only. The transformation takes place in a thermostatic reactor. The heat needed to bring tap water up to the operating temperature of interest is not taken into account in the efficiency calculation and the reaction products (H_2 and O_2) are considered under the same (T,p) conditions.

The water electrolysis cell (device) is also analysed under constant (T,p,I) conditions, but the heat needed to bring tap water up to the operating temperature of interest is taken into account in the efficiency calculation and the (T,p) of product gases may differ from those of the reaction.

The water electrolysis cell, stack and plant are thermodynamically open systems operating under either stationary or non-stationary conditions. The exergy balance can be established in integral form (J) or in power ($J \cdot s^{-1}$) or in specific power ($J \cdot s^{-1} \cdot m^{-2}$). The exergy yield relates the exergy output to the exergy input. Due to internal irreversible degradation (mainly dissipation at cell and stack levels), the exergy output is less than the exergy input and the exergy yield is less than unity. To calculate the exergy yield, it is necessary to take into account the different exergy contributions, as follows.

- The work or work power received from the DC power source (the exergy content of 1 joule of electricity is equal to 1 joule).
- The heat exergy (the heat exergy power or flow rate) associated with heat transfers (the exergy content of 1 joule of heat is modulated by the associated Carnot factor).
- The transformation exergy (the transformation exergy power or flow rate) associated with the chemical reaction. This is the co-enthalpy balance of the water-splitting reaction:

$$\Delta k = \sum_i \nu_i \left[\left(h - h_i^0\right) - T_{env}\left(s_i - s_i^0\right) \right] \qquad [51]$$

where:

ν_i = generalised stoichiometric reaction number;

h = enthalpy under operating conditions;

h_i^0 = enthalpy under reference conditions;

T_{env} = ambient temperature;

s_i = entropy under operating conditions;

s_i^0 = entropy under reference conditions.

The exergy yield can be defined on the basis of the overall efficiency formula used in the industry, equation [45], which takes into account the energy content of the hydrogen production, and the electrical and thermal energy inputs as (7):

$$\zeta^{HHV} = \frac{E^{HHV} \cdot \dot{n}_{H_2}}{\dot{E}_e + \dot{E}_{q,cell}\left(1 - \frac{T_{env}}{T_{cell}}\right) + \dot{E}_{q,H2O}\left(1 - \frac{T_{env}}{T_{cell}}\right)} \qquad [52]$$

where:

ζ^{HHV} is the exergy yield of the water splitting reaction;

E^{HHV} in J/mole is the molar exergy value associated with the hydrogen production under (T_{cell},P_{cell}) conditions (based on the HHV reaction because liquid water is electrolysed in a PEM water electrolysis cell) — the value is very close to the energy content;

$\dot{n}_{H_2}$ in mol/s is the molar hydrogen flow;

$\dot{E}_e$ in J/s is the electricity exergy input from the DC power source;

$\dot{E}_{q,cell}$ in J/s is the exergy input to the PEM cell for the reaction;

T_{env} in K is the environment (ambient) temperature;

T_{cell} in K is the operating temperature of the electrolysis cell;

$\dot{E}_{q,H2O}$ in J/s is the exergy content of input water that is heated up from ambient temperature to operating temperature.

3.7.11.2. Relationship between energy efficiency and exergy yield

Since PEM, AEM and AWE cells operate under near-ambient operating conditions, the exergy content of the heat flows ($\dot{E}_{q,cell}$ and $\dot{E}_{q,H2O}$) is small because $\mathbf{T_{cell} \approx T_{env}}$. Under these conditions, when an electrolyser operates in exothermic mode, the only thermal energy needed is for the heating of water added to the system to replace the one which is converted into hydrogen and oxygen. Therefore, the main type of energy supplied to the system is electrical, and as electricity has 100 % exergy content, the energy efficiency and exergy yield are similar.

Also, the heat produced by a water electrolysis plant operating under near-ambient conditions has a low exergy value and cannot be used for work production. It is considered as a loss and can only be used for heating purposes.

This is why an energy analysis is considered sufficient to determine the characteristics of a water electrolysis cell or stack operating in such near-ambient conditions. The situation is different for a high-temperature water electrolysis cell, but this analysis is not considered in this document. At system level, it is important to evaluate the exergy yield contribution by the different balance of plant components in order to obtain the total exergy yield of the system.

3.7.12. Equation summary tables

The following tables provide a summary of the various efficiency equations presented in this document.

Table 2: Energy efficiency

ENERGY EFFICIENCY — ε		
Single cell	**Note**	**Equation No**
$U^0_{rev} = \Delta G^0/(n\ F)$	1.229 V under SATP	[3]
$U_{rev}(T, 1atm) = 1.5184 - 1.5421 \cdot 10^{-3} \cdot T + 9.523 \cdot 10^{-5} \cdot T \cdot Ln(T) + 9.84 \cdot 10^{-8} T^2$	U_{rev} in the 0-100 °C temperature range	[22]
$U^0_{tn} = \Delta H^0/(n\ F)$	1.481 V under SATP	[4]
$U_{tn}(T, 1atm) = 1.485 - 1.49 \cdot 10^{-4} \cdot (T - T^0) - 9.84 \cdot 10^{-8} \cdot (T - T^0)^2$	U_{tn} in the 0-100 °C temperature range	[23]
$\varepsilon_{cell,case1} = \dfrac{U_{tn}}{U_{tn} + U_{cell} - U_{rev}}$	Case 1 Constant heat input-based definition	[9]
$\varepsilon_{cell,case1} = \dfrac{U_{tn}(T,p)}{U_{tn}(T,p) + U_{cell}(T,p) - U_{rev}(T,p)}$	Case 1 For any T,p conditions	[11]
$\varepsilon_{cell,case2} = \dfrac{U_{rev}}{U_{cell}}$	Case 2 Free energy-based definition	[12]
$\varepsilon_{cell,case2}(T,p) = \dfrac{U_{rev}(T,p)}{U_{cell}(T,p)}$	Case 2 For any T,p conditions	[14]
$\varepsilon_{cell,case3} = \dfrac{n \cdot F \cdot U_{tn}}{n \cdot F \cdot U_{tn}}$	Case 3 $\varepsilon = 1$ When $U_{rev} < U_{cell} \leq U_{tn}$	[15] [16]
$\varepsilon_{cell,case3} = \dfrac{U_{tn}}{U_{cell}}$	Case 3 Enthalpy-based definition when $U_{cell} > U_{tn}$	[17]

$\varepsilon_{cell,case3} = \frac{U_{tn}\,(T,p)}{U_{cell}\,(T,p)}$	Case 3 when $U_{cell} > U_{tn}$ For any T,p conditions	[18]
$\varepsilon_{cell,case4} = \frac{n \cdot F \cdot U_{tn}}{n \cdot F \cdot U_{cell} + Q_{input}}$	Case 4	[21]
$\Delta U_{cell} = \frac{RT}{2F} \ln\left[(\frac{p^{A} - p^{sat}_{H_2O}}{p^{\theta}})^{\frac{1}{2}} \left(\frac{p^{C} - p^{sat}_{H_2O}}{p^{\theta}}\right) / \left(\frac{p^{H_2O}}{p^{\theta}}\right)\right]$	Water saturated and ideal gas pressure correction voltage	[27]
$Q_{cell} = n \cdot F \cdot (U_{tn} - U_{cell})$	Cell heat balance $Q_{cell} < 0$ rejected $Q_{cell} > 0$ absorbed	[7]
Stack		
$\varepsilon_{stack,case1} = \frac{N \cdot U_{tn}(T,p)}{N \cdot U_{tn}(T,p) + U_{stack}(T,p) - N \cdot U_{rev}(T,p)}$	Case 1	[30]
$\varepsilon_{stack,case2} = \frac{N \cdot U_{rev}(T,p)}{U_{stack}(T,p)}$	Case 2	[31]
$\varepsilon_{stack,case\,3} = \frac{N \cdot U_{tn}}{U_{stack}}$	Case 3 when: $U_{cell} > U_{tn}$	[32]
$\varepsilon_{stack,case3} = \frac{N \cdot n \cdot F \cdot U_{tn}}{N \cdot n \cdot F \cdot U_{tn}} = 1$	Case 3 when: $U_{rev} < U_{cell} \leq U_{tn}$	[33]
$\varepsilon_{cell,case4} = \frac{n \cdot F \cdot U_{tn}}{N \cdot n \cdot F \cdot U_{cell} + Q_{input\ stack}}$	Case 4 when: $U_{rev} < U_{cell} < U_{tn}$	[34]
$Q_{stack} = n \cdot F \cdot (N \cdot U_{tn} - U_{stack})$	Stack heat balance: $Q_{stack} < 0$ rejected $Q_{stack} > 0$ absorbed	[35]
System		
$N \frac{U_{tn}(T,p)}{U_{stack} + W_{aux}/(nF)}$	System efficiency	[36]
$Q_{system} = n \cdot F \cdot (N \cdot U_{tn} - U_{stack}) + W_{aux}$	Heat balance	[37]

Table 3: Current efficiency

CURRENT EFFICIENCY — η_I		
Single cell	**Note**	**Equation No**
$\eta_I(T,P,I) = 1 - \frac{2 \cdot F}{I_{DC}} \cdot \left[\dot{n}_{H_2\_loss}(T,p,I) + 2\dot{n}_{O_2\_loss}(T,p,I)\right]$	General formula (academic viewpoint)	[38]
$\eta_I^{H_2} = \frac{2\ F\ \dot{n}_{H_2\ measured}}{I_{DC}}$	Hydrogen production efficiency (industry viewpoint)	[39]
$\eta_I^{O_2} = \frac{4\ F\ \dot{n}_{O_2\ measured}}{I_{DC}}$	Oxygen production efficiency (industry viewpoint)	[40]
Stack		
$\eta_{Istack}^{H2} = \frac{2 \cdot\ F\ \cdot \dot{n}_{H_2}}{I_{DC} \cdot N}$	Hydrogen production efficiency (industry viewpoint)	[41]
$\eta_{Istack}^{O2} = \frac{4 \cdot F\ \cdot \dot{n}_{O_2}}{I_{DC}\ N}$	Oxygen production efficiency (industry viewpoint)	[42]

Table 4: Overall efficiency

OVERALL EFFICIENCY — η_ω		
Single cell	**Note**	**Equation No**
$\eta_\omega^{cell} = \varepsilon_{cell} \cdot \eta_I^{cell}$	Total efficiency (academic viewpoint)	[43]
$\eta^{HHV} = \frac{HHV \cdot}{P_{thermal} + P_{electrical}} \cdot \dot{n}_{H_2}$	Instantaneous cell efficiency (industry viewpoint)	[45]
$\eta^{HHV} = \frac{HHV \cdot \dot{n}_{H_2} \cdot \Delta t}{W_e + Q_{cell} + Q_{H2O}}$	Integral form of cell efficiency (stationary operating conditions)	[46]
Stack		
$\eta_\omega^{stack} = \varepsilon_{stack} \cdot \eta_I^{stack}$	Total efficiency (academic viewpoint)	[44]
Component		
$\eta_{component}^{HHV} = \frac{HHV}{P_{component\ extern}} \dot{n}_{H_2}$	Component efficiency	[47]
System		
$\eta_{system}^{HHV} = \frac{HHV}{P_{system\ extern}} \cdot \dot{n}_{H_2}$	System efficiency (industry viewpoint)	[48]
$\varepsilon_{system} = \frac{N \cdot U_{tn}(T,p)}{U_{stack}} \left(\frac{\eta_{AC/DC}}{1+\xi}\right)$	System efficiency excluding faradic efficiency (industry viewpoint)	[49]
$\varepsilon_{system} = \frac{N \cdot U_{tn}(T,p)}{U_{stack}} \cdot \frac{2 \cdot F \cdot \dot{n}_{H_2}}{I_{DC} \cdot N} \cdot \left(\frac{\eta_{AC/DC}}{1+\xi}\right)$	System efficiency including faradic efficiency (industry viewpoint)	[50]

Table 5: Exergy yield (3)

EXERGY YIELD — ζ^{HHV}		
Single cell	**Note**	**Equation No**
$\zeta^{HHV} = \frac{E^{HHV} \cdot \dot{n}_{H_2}}{\dot{E}_e + \dot{E}_{q,cell}\left(1 - \frac{T_{env}}{T_{cell}}\right) + \dot{E}_{q,H2O}(1 - \frac{T_{env}}{T_{cell}})}$		[52]

3.7.13. Reversible potential (Erev)

Minimum necessary cell voltage needed to start water electrolysis as in equation [3].

Note 1 to entry: under SATP conditions it is expressed as E° and its value is 1.229 V

3.7.14. Reversible voltage (Vrev)

See reversible potential.

3.7.15. Thermoneutral potential (Etn)

Voltage at which an electrolysis cell/stack/system operating at a given temperature can operate without producing excess heat. See equation [4].

Note 1 to entry: under SATP conditions it is expressed as $\mathrm{E}_{\mathrm{tn}}^{0}$ and its value is 1.481 V.

3.7.16. Thermoneutral voltage (vtn)

See thermoneutral potential.

3.8. Electrical power

3.8.1. Cell electrical power density

Input power per cell cross section.

Note 1 to entry: it is expressed in W/m^2.

3.8.2. Electrical power — apparent

Square root of the sum of the squares of the active and reactive powers (4).

3.8.3. Electrical power — reactive

For sinusoidal quantities in a two-wire circuit, the product of the voltage, the current and the sine of the phase angle between them. In a multiphase circuit, the sum of the reactive powers of the phases (4).

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(3) Exergy yield expressions for components and systems are not covered in this report.

3.8.4. Electrical power — real

For sinusoidal quantities in a two-wire circuit, the product of the voltage, the current and the cosine of the phase angle between them. In a multiphase circuit, the sum of the active powers of the individual phases (4).

3.8.5. Electrical power factor

Ratio of the total active power in watts to the total apparent power in volt-amperes (the product of root-mean-square voltage and root-mean-square current).

Leading. A designation of the relative instantaneous direction of the currents to the voltages (angle is 0 to – 90°).

Lagging. A designation of the relative instantaneous direction of the currents to the voltages (angle is 0 to + 90°) (4).

3.8.6. Electrical power input rated or nominal

Maximum continuous electrical power input that a device is designed to achieve under normal operating conditions specified by the manufacturer.

Note 1 to entry: it is expressed in W, kW.

3.8.7. Parasitic load

Power consumed by auxiliary machines and equipment such as balance of plant necessary to operate an electrolyser system (2).

Note 1 to entry: it is expressed in W, kW.

[*Source:* Modified from IEC TS 62282-1:2013, *Fuel cell technologies — Part 1*]

3.8.8. Power system capacity — rated

Maximum capacity of the system, in terms of power, as rated by the manufacturer.

Note 1 to entry: it is expressed in kW or MW.

3.8.9. Power stack capacity — rated

Maximum stack capacity, in terms of electrical DC power, as rated by the manufacturer (kW direct current).

Note 1 to entry: it is expressed in kW or MW.

3.8.10. Power supply range

Functional range of an electrolysis system between its minimum power operating value and 100 % (full-scale) rated power DC charge.

3.8.11. Rated power

Value stated on the device’s nameplate. It is the power to be provided at the input terminals of a component or piece of equipment that is operated in compliance with the manufacturer’s performance specifications (4).

3.9. Gas crossover

Gas permeation through the separation membrane leading to the transport of hydrogen to the oxygen side and vice versa, leading to safety and efficiency-reduction issues.

This phenomenon is due to various transport mechanisms: differential pressure, diffusion, electro-osmotic drag and ion flux densities.

3.10. Gas leakage

Sum of all gases leaving the electrolyser module except the intended exhaust gases (2).

[*Source:* Modified from IEC TS 62282-1:2013, *Fuel cell technologies — Part 1*]

3.11. Gas tightness

System characteristic that ensures that no exchange of fluids and gases between two or more compartments of a device occurs, i.e. between anode and cathode or the surrounding space (4).

3.12. Grid or electricity network

Plant and apparatus that are connected for transmitting or distributing electricity (3).

3.12.1. Balance regulation

Balance regulation refers to the regulation actions taken in order to maintain the frequency and time deviation of the electricity grid in accordance with the established quality requirements. Regulation is also carried out for network reasons.

3.12.2. Connection point

Interface at which the power-generating module, demand facility and distribution system are connected to a transmission system, offshore network and distribution system, including closed distribution systems, as identified in the connection agreement between the relevant system operator and either the power-generating or demand facility owner (3).

3.12.3. Control area

Coherent part of the interconnected system operated by a single system operator and including any connected physical loads and/or generation units (5).

[*Source:* ENTSO-E glossary]

3.12.4. Control reserve

Energy stock to be used to control the frequency of the power supply network in case of unpredictable variations in energy injection and withdrawal.

The reserve can be either positive, in order to balance deficits of the network, or negative, in case of surplus balance.

3.12.5. Distribution system

Transport of electricity on high-voltage, medium-voltage and low-voltage distribution systems with a view to delivering it to customers, but does not include supply (5).

[*Source:* ENTSO-E glossary]

3.12.6. Distribution network

Electrical network, including closed distribution networks, for the distribution of electrical power from and to third parties connected to it, a transmission or another distribution network (5).

[*Source:* ENTSO-E glossary]

3.12.7. Distribution network operator

Either a distribution system operator (DSO) or a closed distribution system operator (5).

[*Source:* ENTSO-E glossary]

3.12.8. Disturbance

Unplanned event that may cause the transmission system to divert from its normal state (5).

[*Source:* ENTSO-E glossary]

3.12.9. Energy from renewable sources

Energy from renewable non-fossil sources, namely wind, solar, aerothermal, geothermal, hydrothermal and ocean energy, hydropower, biomass, landfill gas, sewage treatment plant gas and biogases (5).

[*Source:* ENTSO-E glossary]

3.12.10. Energy-storage device

Device being used for the storage of electrical energy and that can be used to balance the system (5).

[*Source:* ENTSO-E glossary]

3.12.11. Electrical time deviation

Time discrepancy between synchronous time and coordinated universal time (5).

[*Source:* ENTSO-E glossary]

3.12.12. Electrical system frequency

Electrical frequency of the system expressed in hertz that can be measured in all parts of the synchronous area under the assumption of a consistent value for the system within a time frame of seconds, with only minor differences between different measurement locations. Its nominal European value is 50 Hz (5).

[*Source:* ENTSO-E glossary]

3.12.13. Frequency control

Capability of a power-generating module or high-voltage DC system to adjust its active power output in response to a measured deviation of system frequency from a set point, in order to maintain stable system frequency (3,5).

3.12.13.1. Load-frequency control area

Part of a synchronous area or an entire synchronous area, physically demarcated by points of measurement at interconnectors to other load-frequency control (LFC) areas, operated by one or more transmission system operators (TSOs) fulfilling the obligations of LFC (5).

[*Source:* ENTSO-E glossary]

3.12.14. Frequency-controlled normal operation reserve

Momentarily available active power for frequency regulation in the range of 49.9-50.1 Hz and which is activated automatically by the system frequency.

3.12.15. Frequency containment reserves

Active power reserves available to contain system frequency after the occurrence of an imbalance (5).

[*Source:* ENTSO-E glossary]

3.12.15.1. Frequency containment reserve full activation frequency deviation

Rated value of frequency deviation at which the frequency containment reserve in a synchronous area is fully activated (5).

[*Source:* ENTSO-E glossary]

3.12.16. Frequency response deadband

Interval used intentionally to make the frequency control unresponsive (5).

[*Source:* ENTSO-E glossary]

3.12.17. Frequency deviation

Difference, which can be negative or positive, between the actual and nominal frequency of the synchronous area (5).

[*Source:* ENTSO-E glossary]

3.12.17.1. Instantaneous frequency deviation

Set of data measurements of the overall system frequency deviations for the synchronous area with a measurement period equal to or shorter than 1 second used for system frequency quality evaluation purposes (5).

[*Source:* ENTSO-E glossary]

3.12.17.2. Maximum instantaneous frequency deviation

Maximum expected absolute value of an instantaneous frequency deviation after the occurrence of an imbalance equal to or less than the reference incident, beyond which emergency measures are activated (5).

[*Source:* ENTSO-E glossary]

3.12.17.3. Maximum steady-state frequency deviation

Maximum expected frequency deviation after the occurrence of an imbalance equal to or less than the reference incident at which the system frequency is designed to be stabilised (5).

[*Source:* ENTSO-E glossary]

3.12.17.4. Steady-state frequency deviation

Absolute value of the frequency deviation after the occurrence of an imbalance, once the system frequency has been stabilised (5).

[*Source:* ENTSO-E glossary]

3.12.18. Frequency restoration control error

Control error for the Frequency Restoration Process (FRP) which is equal to the Area Control Error (ACE) of a Load Frequency Control (LFC) area or equal to the frequency deviation where the LFC area geographically corresponds to the synchronous area (5).

[*Source:* ENTSO-E glossary]

3.12.19. Frequency restoration process

Process that aims at restoring the frequency to nominal and, for synchronous areas consisting of more than one LFC area, a process that aims at restoring the power balance to the scheduled value (5).

[*Source:* ENTSO-E glossary]

3.12.19.1. Frequency restoration reserves

Active power reserves available to restore the system frequency to nominal, and for synchronous areas consisting of more than one LFC area, to restore the power balance to the scheduled value (5).

[*Source:* ENTSO-E glossary]

3.12.19.2. Automatic frequency restoration reserves

Frequency restoration reserves that can be activated by an automatic control device (5).

[*Source:* ENTSO-E glossary]

3.12.19.3. Automatic frequency restoration reserve full activation time

Time period between the setting of a new set-point value by the frequency restoration controller and the corresponding activation or deactivation of automatic frequency restoration reserves (FRR) (5).

[*Source:* ENTSO-E glossary]

3.12.19.4. Manual frequency restoration reserves

Frequency restoration reserves that can be activated manually.

3.12.19.5. Manual frequency restoration reserve full activation time

Time period between the set-point change and the corresponding activation or deactivation of manual FRR (5).

[*Source:* ENTSO-E glossary]

3.12.20. Frequency restoration range

System frequency range to which the system frequency is expected to return in the Great Britain, Ireland/Northern Ireland and Nordic synchronous areas, after the occurrence of an imbalance equal to or less than the reference incident within the time to restore frequency (5).

[*Source:* ENTSO-E glossary]

3.12.21. Frequency set-point

Frequency target value used in the FRP, defined as the sum of the nominal system frequency and an offset value needed to reduce an electrical time deviation (5).

[*Source:* ENTSO-E glossary]

3.12.22. Full activation time

Time period between the activation request by the TSO and the corresponding full activation of the product concerned (5).

[*Source:* ENTSO-E glossary]

3.12.23. Grid-connected operation

Mode in which the system is operated while connected to a utility grid.

3.12.24. Grid control

In the event of a major load fluctuation such as a power station outage or other unpredictable variations in energy injection and withdrawal in the grid, a set of different control reserves, primary, secondary and tertiary, can be activated at different ramp rates and time steps, as described in Figure 14 below.

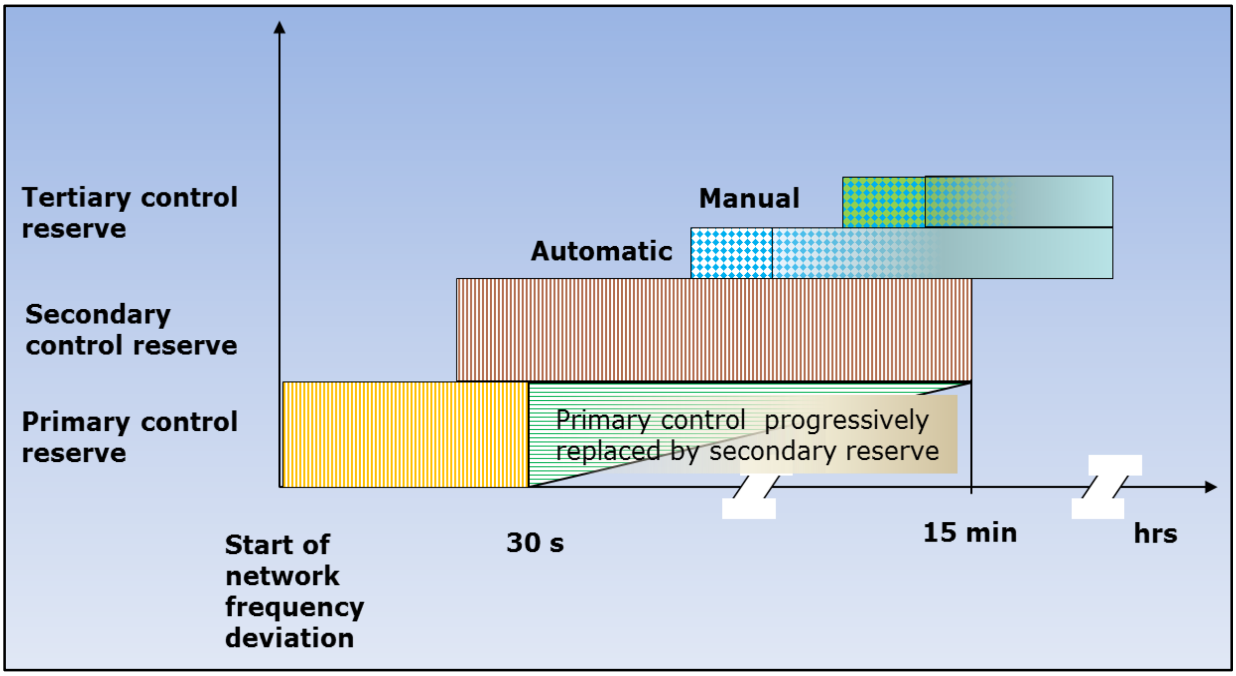

Figure 14: Grid control sequence of activation

3.12.24.1. Replacement reserves

Active power reserves available to restore or support the required level of FRR to be prepared for additional system imbalances, including operating reserves (5).

[*Source:* ENTSO-E glossary]

3.12.24.1. Reserve replacement process

Process to restore the activated FRR and, additionally for Great Britain and Ireland/Northern Ireland, to restore the activated frequency containment reserve (5).

[*Source:* ENTSO-E glossary]

3.12.24.2. Primary control reserve

This is the first and fastest control stock reserve to be used in the event of grid frequency disturbance. It is deployed automatically with a proportional regulation for the re-establishment of the network frequency balance between energy production and consumption as quickly as possible. The complete deployment time of primary control reserve depends on the country. It is usually around 15-30 seconds (6).

[*Source:* ENTSO-E, *Supporting document for the network code on load-frequency control and reserves*, 28 June 2013]

3.12.24.3. Primary reserve

Reserve performing primary control by automatically changing the working points regulated by the frequency (6).

Note 1 to entry: obsolete term replaced by frequency containment reserves.

[*Source:* ENTSO-E, *Supporting document for the network code on load-frequency control and reserves*, 28 June 2013]

3.12.24.4. Secondary control reserve

Stock which is deployed automatically in a selective manner in those control areas where network imbalance occurs for the re-establishment of the frequency setting of 50 Hz between energy production and consumption.

It is started within 30 seconds of the imbalance and can last up to 15 minutes (6).

Note 1 to entry: obsolete term replaced by FRR.

[*Source:* ENTSO-E, *Supporting document for the network code on load-frequency control and reserves*, 28 June 2013]

3.12.24.5. Secondary control

Secondary control is a centralised automatic function to regulate the generation in a control area based on secondary control reserves in order: to maintain its interchange power flow at the control program with all other control areas (and to correct the loss of capacity in a control area affected by a loss of production); and, at the same time (in the event of a major frequency deviation originating from the control area, particularly after the loss of a large generation unit), to restore the frequency in the event of a frequency deviation originating from the control area to its set value in order to free the capacity engaged by the primary control (and to restore the primary control reserves). In order to fulfil these functions, secondary control operates by the network characteristic method. Secondary control is applied to selected generator sets in the power plants comprising this control loop. Secondary control operates for periods of several minutes and is therefore dissociated from primary control (6).

[*Source:* ENTSO-E, *Supporting document for the network code on load-frequency control and reserves*, 28 June 2013]

3.12.24.6. Tertiary control reserve

Power which can be connected (automatically or manually) under tertiary control in order to provide an adequate secondary control reserve is known as the tertiary control reserve or minute reserve. This reserve must be used in such a way that it will contribute to the restoration of the secondary control range when required. The restoration of an adequate secondary control range may take, for example, up to 15 minutes, whereas tertiary control for the optimisation of the network and generating system will not necessarily be complete after this time (6).

Note 1 to entry: obsolete term replaced by replacement reserves.

[*Source:* ENTSO-E, *Supporting document for the network code on load-frequency control and reserves*, 28 June 2013]

3.12.25. Grid current

Rate at which the electric charge flows, measured by the root-mean-square value of the positive sequence of the phase current at fundamental frequency (5).

[*Source:* ENTSO-E glossary]

3.12.26. Grid standard frequency range

Defined symmetrical interval around the nominal frequency within which the system frequency of a synchronous area is supposed to be operated (5).

[*Source:* ENTSO-E glossary]

3.12.27. Grid voltage

Difference in electrical potential between two points measured as the root-mean-square value of the positive sequence phase-to-phase voltages at fundamental frequency (5).

[*Source:* ENTSO-E glossary]

3.12.28. Grid voltage control

Manual or automatic control actions at the generation node, at the end nodes of the AC lines or high-voltage DC systems, on transformers, or other means, designed to maintain the set voltage level or the set value of reactive power (5).

[*Source:* ENTSO-E glossary]

3.12.29. Grid voltage stability

Ability of a transmission system to maintain acceptable voltages at all nodes in the transmission system in the N-situation and after being subjected to a disturbance (5).

[*Source:* ENTSO-E glossary]

3.12.30. Grid time to recover frequency

Maximum expected time after the occurrence of an imbalance less than or equal to the reference incident in which the system frequency returns to the maximum steady-state frequency deviation. This parameter is used in Great Britain and Ireland only (in larger synchronous areas it is not necessary to require power-generating modules to operate continuously within higher system frequency ranges) (5).

[*Source:* ENTSO-E glossary]

3.12.31. Grid frequency recovery range

System frequency range to which the system frequency is expected to return after the occurrence of an imbalance equal to or less than the reference incident within the time to recover frequency (5).

[*Source:* ENTSO-E glossary]

3.12.32. Time to restore frequency

Maximum expected time after the occurrence of an instantaneous power imbalance less than or equal to the reference incident in which the system frequency returns to the frequency restoration range for synchronous areas with only one LFC area; and in the case of synchronous areas with more than one LFC area, the maximum expected time after the occurrence of an instantaneous power imbalance of an LFC area within which the imbalance is compensated for (5).

[*Source:* ENTSO-E glossary]

3.12.33. Grid frequency restoration range

Range to which the system frequency should be restored after the time to restore frequency since the occurrence of a reference incident has elapsed (5).

[*Source:* ENTSO-E glossary]

Figure 15: Frequency quality parameters

3.12.34. Grid-independent or isolated operation

See island operation.

3.12.35. Island operation

Independent operation of a whole network or part of a network that is isolated after being disconnected from the interconnected system, having at least one power-generating module or high-voltage DC system supplying power to this network and controlling the frequency and voltage (3,5).

[*Source:* ENTSO-E glossary]

3.12.36. Metering grid area

Physical area where consumption, production and exchange can be metered. It is delimited by the placement of meters for period measurement for input to and withdrawal from the area. It can be used to establish the sum of consumption and production with no period measurement and network losses (5).

[*Source:* ENTSO-E glossary]

3.12.37. Metering point

Entity where energy products are measured or computed (5).

[*Source:* ENTSO-E glossary]

3.12.38. Network frequency

See electrical system frequency.

3.12.39. Offshore grid connection system

Complete interconnection between an offshore connection point and the onshore system at the onshore grid interconnection point (5).

[*Source:* ENTSO-E glossary]

3.12.40. Offshore power park module

Power park module located offshore with an offshore connection point (5).

[*Source:* ENTSO-E glossary]

3.12.41. Power-generating facility

Facility that converts primary energy into electrical energy and which consists of one or more power-generating modules connected to a network at one or more connection points (3).

3.12.42. Power-generating module

This means either a synchronous power-generating module or a power park module (3).

3.12.43. Renewable energy sources

Renewable non-fossil energy sources (wind, solar, geothermal, wave, tidal, hydropower, biomass, landfill gas, sewage treatment plant gas and biogases) (5).

[*Source:* ENTSO-E glossary]

3.12.44. Tertiary control

Tertiary control is a change in the set-points of participating generations or loads, in order to guarantee the provision of secondary control reserves at the right time and distribute the secondary control power to the various generations in the best possible way (6).

[*Source:* ENTSO-E, *Supporting document for the network code on load-frequency control and reserves*, 28 June 2013]

3.12.45. Reserve provider

Legal entity with a legal or contractual obligation to supply frequency containment reserves, FRR or replacement reserves from at least one reserve-providing unit or reserve-providing group (5).

[*Source:* ENTSO-E glossary]

3.12.46. Transmission system operator

Natural or legal person responsible for operating, ensuring the maintenance of and, if necessary, developing the transmission system in a given area and, where applicable, its interconnections with other systems, and for ensuring the long-term ability of the system to meet reasonable demands for the transmission of electricity (5).

[*Source:* ENTSO-E glossary]

3.13. Heating value

Value of the heat of combustion of a fuel defined by the heat supplied to a thermal system by the entire reaction enthalpy of the exothermal combustion reaction under standard conditions (25 °C, 10^5 Pa)

Note 1 to entry: it is expressed in kJ mol^{-1}.

Note 2 to entry: the heating value is thus the negative reaction enthalpy of the combustion reaction.

3.13.1. Lower heating value

Value of the heat of combustion of a fuel as measured by allowing all products of combustion to remain in the gaseous state. This method of measurement does not take into account the heat energy put into the vaporisation of water (heat of vaporisation).

3.13.2. Higher heating value

Value of the heat of combustion of a fuel as measured by reducing all of the products of combustion back to their original temperature and condensing all water vapour formed by combustion. This value takes into account the heat of vaporisation of water (4).

3.14. Hydrogen

Chemical element with atomic number 1, naturally available as diatomic molecule H_2, in highly flammable, colourless, odourless gaseous form.

3.14.1. Hydrogen production rate

Amount of H_2 produced by an electrolysis cell/stack/system during a specified time interval at a rated power with a defined purity.

Note 1 to entry: it is expressed in kg/h or kg/day.

3.14.1.1. Nominal hydrogen weight capacity

Nominal daily hydrogen production rate by weight.

Note 1 to entry: it is expressed in kg/day.

3.14.1.2. Nominal hydrogen volume capacity

Nominal hourly hydrogen production rate by volume.

Note 1 to entry: it is expressed in Nm^3/h.

3.15. Key performance indicator

Metric parameter used to quantify the relevant process parameters for a specific task/process/system.

3.16. Operating conditions

Test or standardised operating conditions that have been predetermined to be the basis of the test in order to have reproducible, comparable sets of test data (2).

[*Source:* Modified from IEC TS 62282-1:2013, *Fuel cell technologies — Part 1*]

3.17. Operational mode

Any combination of operating conditions.

3.17.1. Constant current operation

Operational mode when the electrolyser is operated at a constant current (galvanostatic mode) (2).

[*Source:* Modified from IEC TS 62282-1:2013, *Fuel cell technologies — Part 1*]

3.17.2. Cold state

Non-operative state of a cell/stack/system when it is at ambient temperature with no power input or output (2).

[*Source:* Modified from IEC TS 62282-1:2013, *Fuel cell technologies — Part 1*]

3.17.3. Nominal operation mode

Operation of the device using the parameter setting defined to obtain the nominal performances as defined in the technical specifications.

3.17.4. Regulation mode

Mode of operation where the device is working using a variable power, i.e. provided by the network to compensate for grid imbalances.

3.17.5. Regulation profile

Variable power profile such as the grid power profile resulting from energy injection and withdrawal. This can be affected by renewable energy sources, energy fluctuations and network disturbances.

3.17.6. Shutdown

Sequence of operations, specified by the manufacturer, that occurs to stop the system and all its reactions in a safe and controlled manner.

3.17.6.1. Emergency shutdown

Control system actions, based on process parameters or manually activated, taken to stop the system and all its reactions immediately to avoid equipment damage and/or personnel hazards (2).

[*Source:* Modified from IEC TS 62282-1:2013, *Fuel cell technologies — Part 1*]

3.17.6.2. Scheduled shutdown

Shutdown of a power system for routine matters.

[*Source:* Modified from IEC TS 62282-1:2013, *Fuel cell technologies — Part 1*]

3.17.7. Standby state

System condition without hydrogen/oxygen output that allows a fast restart of the system.

3.17.7.1. Cold standby state

Non-operating state of equipment turned off and ready for immediate start.

3.17.7.2. Warm standby state

Operating state of equipment powered and warmed up at a temperature that allows a fast restart of the system.

3.17.7.3. Hot standby state

Operating state of equipment powered and warmed up and ready for immediate service operation.

3.17.8. Steady state

State of a physical system in which the relevant characteristics/operating parameters remain constant over time (2).

[*Source:* Modified from IEC TS 62282-1:2013, *Fuel cell technologies — Part 1*]

3.18. Operational parameters

3.18.1. Generating time

Cumulative duration of the time intervals required for hydrogen generation.

3.18.2. Initial response time

Time needed after a set-point change of a parameter to begin changing the output.

3.18.3. Total response time

Time needed after a set-point change of a parameter to reach a new value.

3.18.4. Operating profile

Description of the system power profile versus operating time.

3.18.4.1. Steady state profile

Mode of operation of the system when electrical power consumed or produced is constant over time.

3.18.4.2. Intermittent profile

Mode of operation of the system when electrical power consumed or produced is variable over time.

3.18.5. Operating temperature

Temperature at which the electrolyser (cell/stack/system) operates (8).

3.18.6. Overload capability

Overload capability is the ability of the electrolysis system to operate beyond the nominal operating and design point for a limited period of time, typically in the range of a few minutes to less than 1 hour. The overload capability is mainly used to provide greater flexibility in different grid-service applications (e.g. secondary control reserve).

3.18.6.1. Maximum overload capability

Maximum power, expressed in percentage of nominal power, at which the electrolyser can operate for limited time periods in cases of operational peaks (8).

3.18.7. Minimum partial load operation

Minimum partial load operation at which the system is designed to operate, as a percentage of rated nominal capacity, in terms of power input.

3.18.8. Minimum system power

Minimum power at which the system is designed to operate, as a percentage of nominal power (%) (8).

3.18.9. Reactivity

Time required for the electrolysis system to change from 0 to 100 % of power (ramp-up) or from 100 % of power down to 0 % (ramp-down).

3.18.10. Shutdown time

Duration between the point at which the power supply is removed and the point at which shutdown is completed, as specified by the manufacturer (2).

[*Source:* Modified from IEC TS 62282-1:2013, *Fuel cell technologies — Part 1*]

3.18.11. Stack

Assembly of a number of repetitive cell production units.

3.18.11.1. Stack nominal capacity

Individual stack capacity, as rated by the manufacturer (8).

Note 1 to entry: it is expressed in kW direct current.

3.18.11.2. Stack nominal power capacity

Individual stack power capacity, as rated by the manufacturer.

Note 1 to entry: it is expressed in kW direct current.

3.18.11.3. Stack arrays

Number of stack arrays within the system that can be operated independently (8).

3.18.11.4. Stack cell number

Number of cells per stack (8).

3.18.12. Response time

Time required for a power system to transfer from one defined state to another (4).

3.18.12.1. Start-up time

Time required for starting the device from a cold state to nominal operating conditions.

3.18.12.2. Cold start time to nominal power

The time required to reach nominal power when starting the device from cold standby mode (8).

3.18.12.3. Cold start time to nominal capacity

Time required to reach the nominal hydrogen output rate operating capacity when starting the device from cold standby mode (8).

3.18.12.4. Warm start time to nominal power

Time required to reach nominal power when starting the device from warm standby mode (8).

3.18.12.5. Warm start time to nominal capacity

Time required to reach nominal capacity (in terms of H_2 production rate) when starting the device from warm standby mode (system already at operating temperature).

3.18.12.6. Transient response time

Average time to ramp up from 30 % to 100 % load at nominal power and operating pressure and temperature.

Note 1 to entry: it is expressed in s.

3.19. Pressure

Expression of force exerted on a surface per unit area.

Note 1 to entry: it is expressed in Pa.

3.19.1. Differential cell pressure

Difference in pressure across the electrolyte membrane as measured from one electrode to the other (1).

[*Source:* IEC TS 62282-1:2013, *Fuel cell technologies — Part 1*]

3.19.2. Hydrogen output pressure

Gas pressure measured on the cathode side at the outlet of the electrolysis cell/stack.

3.19.3. Maximum differential working pressure

Maximum differential pressure between the anode and cathode sides, specified by the manufacturer, which the electrolyser cell can withstand without any damage or permanent loss of functional properties (2).

[*Source:* Modified from IEC TS 62282-1:2013, *Fuel cell technologies — Part 1*]

3.19.4. Maximum operating pressure

Maximum gauge pressure, specified by the manufacturer of a component or system, at which it is designed to operate continuously (1).

[*Source:* IEC TS 62282-1:2013, *Fuel cell technologies — Part 1*]

3.19.5. Operating pressure

Pressure at which the electrolyser (stack) operates (8). metric

3.20. Purity of gas

Metric used to indicate the amount of other gases in a particular gas. It is expressed as the molar or volumetric percentage of the gas, which is equal to 100 % minus the sum of the other gas impurities. There are different ways to express purity, as a percentage, for example 99.99 or with a grade, for example N4.0 for 99.99 %.

The first digit of the grade classification indicates the 'number of nines' purity, for example. N4.0 = 99.99 % purity.

The second digit is the number following the last nine, for example N4.6 oxygen has a guaranteed minimum purity level of 99.996 %.

3.20.1. Hydrogen purity

Allowable or tolerated amount of specific impurities (e.g. carbon monoxide) to define the hydrogen purity, which depends on the scope of use of the hydrogen produced. For fuel cell operation the hydrogen quality requirement is defined in **ISO fuel quality 14687-2:2012a**

3.20.2. Oxygen purity

Allowable or tolerated amount of specific impurities in oxygen, which depends on the scope of use of the oxygen produced.

3.21. Reliability

Ability of an item to perform a required function under stated conditions for a stated period of time (4).

3.21.1. Rated system lifetime

Period of time, expected or measured, for an item of equipment to be able to operate within specified process limit parameters, as rated by the manufacturer (8).

3.21.2. Stack availability

Ratio of the time that the stack is operated compared with the time that it was required to operate.

3.21.3. System availability

Ratio of the time that the system operated compared with the time that it was required to operate.

3.22. Resistance (electrical)

Material's opposition to the flow of electric current, resulting in the loss of cell voltage, the so-called ohmic drop, due to charge carrier (electrons, ions) transport processes occurring in the components of the cell or stack (4).

3.23. Safeguarding

Procedure for actions of the controlling system based on monitoring of the technical process in order to avoid process conditions which would be hazardous to personnel, the plant, the product or the environment (4).

3.24. Testing

3.24.1. Acceptance test

Contractual test to prove to the customer that the item meets certain conditions of its specifications (1).

[*Source:* IEC TS 62282-1:2013, *Fuel cell technologies — Part 1*]

3.24.2. Conditioning test

Preliminary step that is required to properly operate an electrolyser cell or a stack and that is realised following a protocol specified by the manufacturer.

3.24.3. Initial response time test

Test to measure the time necessary to begin changing load, following a set-point change.

3.24.4. Process and control test

System test that is carried out before operation to verify the integrity of component performance and control function (2).

3.24.5. Polarisation curve test

Test to measure electrolyser performance that is carried out by applying a predefined set of currents (galvanostatic test) or electric potentials (potentiostatic test) to the electrolyser and measuring the voltage output or supplied current, respectively, as a function of input parameter during a period under steady-state conditions.

3.24.6. Polarisation curve (I-V curve)

Performance plot of the water electrolysis process incorporating thermodynamics and kinetic and electrical resistance effects.

It is typically a plot of the output voltage of an electrolyser as a function of the input current at defined reactant conditions for galvanostatic tests or supplied current for potentiostatic tests.

Note 1 to entry: the polarisation curve plot is expressed in V versus $A \cdot cm^{-2}$.

3.24.7. Overpotential

Amount of potential energy needed to overcome energy-barrier or voltage losses typical of electrical resistance processes occurring at the interface between electronic conductor and electrolyte, resulting in nonlinear behaviour of a polarisation curve.

3.24.7.1. Activation losses

Overpotential contribution due to catalyst material electrodes properties and related activation energy requirements.

3.24.7.2. Bubble losses

Overpotential contribution due to the reduction of the effective active area available for the electrolysis reaction where the produced gas bubbles remain in contact with electrodes' surfaces. A second phenomenon owing to the presence of gas bubbles is the reduction of electrolyte conductivity.

3.24.7.2.1 Bubble coverage

Percentage of the electrode active area covered by gas bubbles.

3.24.7.2.2 Bubble void fraction

Gas volume fraction present in the electrolyte solution.

3.24.7.3. Concentration losses

See mass transport limitation losses.

3.24.7.4. Diffusion losses

See mass transport limitation losses.

3.24.7.5. Exchange current density

Rate of oxidation or reduction at an equilibrium electrode expressed in terms of current density. At equilibrium potential, electron transfer processes continue at the electrode–solution interface in both directions, meaning that the cathodic current is balanced by the anodic current, therefore the net current flow is zero.

3.24.7.6. Kinetic losses

See activation losses.

3.24.7.7. Mass transfer limitation losses

Overpotential contribution due to transport reactants or diffusion limitations.

3.24.7.8. Ohmic losses

Overpotential contribution due to the properties of electrolysis cell materials, i.e. ionic conduction in the electrolyte, separator/contact resistance, electronic conduction and bubble effect.

3.24.7.9. Ohmic resistance

Sum of the contribution of constituent materials to electrical resistance through the electrolytic cell.

3.24.7.9.1 Ohmic resistance -- electrolyte

Electrical resistance contribution due to the electrolyte, depending on its ionic concentration.

3.24.7.9.2 Ohmic resistance -- electronic

Electrical resistance contribution due to electron conductive components, such as bipolar plates, end plates and current distributors.

3.24.7.9.3 Ohmic resistance -- separator

Electrical resistance contribution due to the separator present in the alkaline electrolyser. The resistance of the separator is constant due to its constant thickness and resistivity.

3.24.7.10. Reactant starvation losses

See mass transfer limitation losses.

3.24.8. Overvoltage

The difference between the actual cell voltage at a given current density and the reversible cell voltage for the reaction (overpotential when referring to a single electrode).

3.24.9. Routine control test

Conformity test performed on each individual item during or after manufacture (2).

[*Source:* Modified from IEC TS 62282-1:2013, *Fuel cell technologies — Part 1*]

3.24.10. Short-stack test

Electrolyser stack test with a significantly smaller number of cells than the designed stack with rated power, but with a high enough number of cells to represent the scaled characteristics of the full stack.

3.24.11. Single cell test

Parametric tests for the assessment of performance and degradation behaviour performed on one single cell.

3.24.12. Stack test

Parametric tests for the assessment of performance and degradation behaviour performed on a stack.

3.24.13. Test input parameter

Process parameter value that can be modified in a controlled manner during an experiment.

3.24.14. Test output parameter

Measured value of a parameter that can change as a function of a modification to the operating conditions.

3.25. Thermal management system

Subsystem intended to provide cooling and heat rejection in order to maintain thermal equilibrium within the electrolyser cell system and, if necessary, to effect the recovery of excess heat and to assist in heating during start-up (4).

3.26. Voltage

Potential difference between two points in an electrical circuit.

3.26.1. Cell voltage

Potential difference between the positive and negative electrodes.

3.26.2. Maximum voltage

Highest voltage at which an electrolyser module is able to produce hydrogen and oxygen continuously at its rated power or under maximum permissible overload conditions (2)

[*Source:* Modified from IEC TS 62282-1:2013, *Fuel cell technologies — Part 1*]

3.26.3. Minimum voltage

Lowest voltage at which an electrolyser module is able to produce hydrogen and oxygen continuously at its rated power (2).

[*Source:* Modified from IEC TS 62282-1:2013, *Fuel cell technologies — Part 1*]

3.26.4. Open circuit voltage

Voltage across the terminals of an electrolysis cell or stack and in the absence of external current flow [units: V] (2).

[*Source:* Modified from IEC TS 62282-1:2013, *Fuel cell technologies — Part 1*]

3.27. Water

3.27.1. Water quality

Required input water quality for the hydrogen production operations to fulfil the rated durability/lifetime.

3.27.2. Water utilisation factor

Dimensionless ratio of the flow of water converted into hydrogen and oxygen to the total water flow supplied to the stack.

3.27.3. Water recirculation system

Subsystem intended to provide treatment and purification of recovered or added water for use within the electrolyser unit.

3.27.4. Water transport layer

Porous transport layer to facilitate water diffusion at the anode and cathode compartment sides.

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4. SYMBOLS

Table 6: Definition of symbols used in the document

Symbol	Unit	Description
A	m^2, cm^2	Active area of the cell
Cp	$Jg^{-1}K^{-1}$	Water heat capacity under standard conditions (Cp = 4.186 $Jg^{-1}K^{-1}$)
E	V	Electrical potential
F	C mol^{-1}	Faraday's constant (F = 96485.3 C mol^{-1})
G	j mol^{-1}	Gibbs free energy
H	j mol^{-1}	Molar enthalpy
LHV	j mol^{-1}	Lower heating value
HHV	j mol^{-1}	Higher heating value
I	A	Electrical current
I_{max}	A	Maximum electrical current
J	J	Energy unit (joules)
M		Molar mass
N		Number of objects in a series
n		Number of electrons exchanged in the reaction for 1 mole of gas
$\dot{n}$	mol s^{-1}	Molar flow rate
p	Pa, bar	Pressure
p^{θ}	Pa, bar	Reference pressure
p^{A}	Pa, bar	Anodic pressure
p^{C}	Pa, bar	Cathodic pressure
P	W	Electrical power
Q	j mol^{-1}	Heat
R	$Jmol^{-1}K^{-1}$	Universal gas constant (R = 8.31446 $J.mol^{-1}.K^{-1}$)
S	j $mol^{-1}k^{-1}$	Entropy
t	s	Time
T	K, °C	Temperature
$T_{x,\ y}$	K, °C	Temperature of cell fluid *x* at cell location *y* (inlet = in or outlet = out)
T_{env}	K, °C	Ambient temperature
T_{ehs}	K, °C	Temperature of an external heat source
T_c	K, °C	Cell temperature
U	V	Cell electrical potential
V	V	Voltage measurement
V_{tn}	V	Thermoneutral voltage
i	A/m^2, mA/cm^2	Current density ($i = I / A$)
w	j mol^{-1}	Work, electrical energy needed to transform 1 mole of reactant

Symbol	Unit	Description
Greek symbols		
α		Charge transfer coefficient, dimensionless
ε		Energy efficiency, dimensionless
ζ		Exergy yield, dimensionless
η		Current efficiency, dimensionless
ξ		Ratio between parasitic power and net power consumed by the electrolyser due to the energy consumption by the auxiliaries, dimensionless
Δ		Quantity variation

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