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# **A Critical Review on the Definitions used to calculate the Energy Efficiency Coefficients of Water Electrolysis Cells Working under Near Ambient Temperature Conditions**

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### Glossary

#### Latin symbols

AEC = Alkaline Electrolysis Cell

AEM = Anion Exchange Membrane

AEMEC = Anion Exchange Membrane Electrolysis Cell

AFC = Alkaline Fuel Cell

$a_{H_2O}$  = activity of water.

BoP = Balance of Plant

$E_a(V)$  = anode potential.

$E_a^0(V)$  = anode potential under STP conditions.

$E_c(V)$  = cathode potential.

$E_c^0(V)$  = cathode potential under STP conditions.

$E_{cell}(V) = E_a - E_c$  = cell voltage.

$E_{\Delta G}(V) = E_a - E_c = E_{rev}$  = equilibrium Nernst cell voltage.

$E_{\Delta H}(V)$  = thermoneutral cell voltage.

$F (96485.4 \approx 96485 \text{ C mol}^{-1})$  = Faraday constant.

FCEV = Fuel Cell Electric Vehicles.

HER = Hydrogen Evolution Reaction

HOR = Hydrogen Oxidation Reaction

$HHV_{H_2}$  = HHV (J mol<sup>-1</sup>) = High Heating Value of hydrogen

$I$ (A) = current intensity.

$I_{loss}$ (A) = current loss associated to the flow of hydrogen lost during operation.

ICE = Internal Combustion Engine

$j$ (A cm<sup>-2</sup>) =  $I/S$  = current density.

$LHV_{H_2}$  = LHV (J mol<sup>-1</sup>) = Low Heating Value of hydrogen

$n$  = number of electrons exchanged.

NAT = Near-Ambient Temperature conditions

$\dot{n}_{H_2,loss}$  (mol s<sup>-1</sup>) =  $\Delta N_{H_2,loss} / \Delta t$  = molar flow rate of lost hydrogen.

$\dot{N}_{H_2,out}$  (mol s<sup>-1</sup>) =  $\dot{n}_{H_2}$  =  $\Delta N_{H_2} / \Delta t$  = molar flow rate of hydrogen at the cell/stack exhaust.

$\dot{N}_{H_2O,reacted}$  (mol s<sup>-1</sup>) = molar flow rate of reacted water.

OER = Oxygen Evolution Reaction

ORR = Oxygen Reduction Reaction

$p$ (Pa) = pressure.

$p^\theta$  (Pa) = reference pressure at the working temperature,

$p_{H_2}$  (Pa) = hydrogen partial pressure,

$p_{O_2}$  (Pa) = oxygen partial pressure,

$p_{H_2O}$  (Pa) = water partial pressure,

$p_{H_2O}^{sat}(T)$  (Pa) = water saturation pressure at the working temperature.

$p_{H_2O} / p^\theta = a_{H_2O}$  = activity of water.

$p^A$  (Pa) = pressure in the anodic compartment.

$p^C$  (Pa) = pressure in the cathodic compartment.

PEM = Proton Exchange Membrane

PEMEC = Proton Exchange Membrane Electrolysis Cell

PGM = Platinum Group Metal

$P_{elec}(W) = P_{electrical}$  = electrical power supplied.

$P_{thermal}(W)$  = heat power supplied.

$P_{auxi}(W)$  = electrical power consumed by auxiliary equipments.

$P_{total}(W) = W_{irrev}/\Delta t$  = total (thermal and electric) power supplied to the plant.

$P_{ideal}(W)$  = power thermodynamically required to split water at zero current.

$P_{real}(W)$  = real electrical power required for a given hydrogen production rate.

$\dot{Q}_{heat,PEM}(J\ mol^{-1})$  = rate of thermal energy input/output to/from the PEM electrolyzer.

$\dot{Q}_{heat,H_2O}(J\ mol^{-1})$  = heat flow supplied to the heat exchanger per mole of water

$R_e(\Omega)$  = electrical cell resistance.

$S$  = geometric surface area

SHE = Standard Hydrogen Electrode.

STP = Standard Temperature and Pressure conditions.

$S_{H_2}(J\ mol^{-1}\ K^{-1})$  = molar entropy of hydrogen.

$S_{O_2}(J\ mol^{-1}\ K^{-1})$  = molar entropy of oxygen.

$S_{H_2O}(J\ mol^{-1}\ K^{-1})$  = molar entropy of water.

$T(K)$  = absolute temperature.

$T^0(K)$  = standard absolute temperature.

$U_{cell}(V)$  = cell voltage.

$U_{rev}(V)$  = reversible cell voltage.

$U_{rev}^0(V)$  = reversible cell voltage under STP conditions.

$U_{tn}(V)$  = thermo-neutral cell voltage.

$U_{tn}^0(V)$  = thermo-neutral cell voltage under STP conditions.

$\dot{V}_{H_2}(Nm^3\ s^{-1})$  = volumetric hydrogen production rate.

$W_{rev}$  (J mol<sup>-1</sup>) = energy requirement to split one mole of water at  $I = 0$ .

$W_{irrev}$  (J mol<sup>-1</sup>) = energy requirement to split one mole of water at  $I \neq 0$ .

$W_e$  (J mol<sup>-1</sup>) =  $\Delta G_{irrev}$  = electrical energy requirement to split one mole of water.

### Greek symbols

$\Delta H(T,p)$  (J mol<sup>-1</sup>) = enthalpy change of the reaction

$\Delta H_{rev}^0$  (J mol<sup>-1</sup>) = enthalpy change of the reaction under STP conditions.

$\Delta G_{cell}(T,p)$  (J mol<sup>-1</sup>) = Gibbs free energy change of the reaction.

$\Delta N_{H_2}$  = number of hydrogen moles produced during time period  $\Delta t$ .

$\Delta p$  = pressure difference between anodic and cathodic compartments.

$\Delta Q_{rev}(T,p)$  (J mol<sup>-1</sup>) =  $T \Delta S(T,p)$  = reversible heat exchanged

$\Delta S(T,p)$  (J mol<sup>-1</sup> K<sup>-1</sup>) = entropy change of the reaction.

$\Delta Q_{H_2O}$  (J mol<sup>-1</sup>) = molar thermal energy used to heat-up water with an external heat exchanger.

$\Delta C_p$  (J mol<sup>-1</sup> K<sup>-1</sup>) = molar heat capacity at constant pressure and 298.15 K.

$\Delta Q_{irrev}$  (J mol<sup>-1</sup>) = irreversible heat exchanged associated to an irreversible transformation.

$\Delta Q_{cell}$  (J mol<sup>-1</sup>) = thermal balance of cell.

$\Delta t$  (s) = time period.

$\epsilon_{cell}$  (%) = energy efficiency coefficient of the cell.

$\epsilon_{cell,th}$  ( $\epsilon_{cell,th}^0$ ) = theoretical energy efficiency coefficient of the cell.

$\epsilon_{indus}$  = energy efficiency coefficient used in the industry.

$\epsilon_{indus}^{HHV}$  ( $\eta_{HHV}$ ) = energy efficiency coefficient using the HHV as reference.

$\epsilon_U = \eta_{Voltaic}$  = voltage efficiency coefficient used in the industry.

$\eta_F = \eta_{Faradic}$  (%) = Faradic efficiency coefficient used in the industry.

$\eta_{Thermal} = \epsilon_{thermal}$  = thermal efficiency coefficient used in the industry.

$\eta_{\text{cell}}$  = energy efficiency coefficient at the cell level.

$\eta_{\text{en}}$  = energy efficiency coefficient

$\eta(\text{V})$  = charge transfer overvoltage.

$\eta_{\text{act,a}}(\text{V})$  = activation overvoltage at the anode.

$\eta_{\text{act,c}}(\text{V})$  = activation overvoltage at cathode.

$\eta_{\text{ohm}}(\text{V})$  = voltage losses due to Joule effect.

$\eta_{\text{loss}}(\text{V})$  = overvoltages due to activation transfer and heat losses.

$\sigma(\text{J mol}^{-1})$  = specific heat production due to internal dissipations.

## **Abstract**

The accurate knowledge of the energy efficiency coefficient of near ambient temperature water electrolysis (Alkaline, PEM or AEM Electrolyzer) is a critical-point to estimate the total cost of electrolytic hydrogen. After describing the fundamentals of these three processes and presenting the main data of water electro-dissociation under given temperature and pressure conditions, the energy efficiency coefficient can be calculated by taking the ratio of the theoretical energy ( $\Delta H$ ) to decompose water under equilibrium conditions (no current) to the real energy used ( $\Delta H$  + energy losses) to electrolyze water at a given current intensity. Different approximations of this coefficient are discussed and compared to data from literature. Such coefficient can also be calculated by taking the ratio of the total energy of hydrogen collected at the exhaust of the electrolyzer to the total energy (electricity + heat) supplied to the complete system. It is demonstrated that both definitions are consistent and similar if all the energy involved is taken into account. It is also shown that some approximations, in particular those neglecting the thermal energy in the denominator of

this ratio, give efficiency coefficients larger than unity for cell voltages lower than the thermo-neutral voltage, which is a thermodynamic non-sense.

**Keywords:** Water Electrolysis; Thermodynamics; Electrochemical Kinetics; Energy Efficiency Coefficient; Comparison with Literature.

## 1. Introduction

Currently, up to 96 % of molecular hydrogen ( $H_2$ ) used in the industry is produced from fossil fuels, either by the cracking of natural hydrocarbons ( $\approx 30\%$ ) or by steam methane reforming ( $\approx 48\%$ ) or by coal gasification/reforming processes ( $\approx 18\%$ ) [1].  $H_2$  is currently used at the Mton/year scale as a multi-purpose chemical reactant in various industries, mainly in the refining industry as a petrochemical for hydrocracking and desulphurization processes, but also as a precursor of ammonia and fertilizer production for agriculture. It is also used for the production and fabrication of metals, for methanol synthesis, for food processing and in the electronics sectors. Since the first oil crisis in 1973, new applications have been developed for the energy sector. Nowadays, the situation is such that  **$H_2$  is now** considered as a key molecule for energy production and storage in the framework of the energy transition. Its large scale production, distribution to end-users and exploitation as a versatile energy carrier are expected to solve main environmental issues, to respond to the growing energy demand of human societies, and at the same time, to favor economic growth and development. Current applications of  $H_2$  as an energy vector are found in the sector of power generation, where it is used as a chemical fuel to produce electricity by air-combustion in fuel cells [2]. There are several fuel cell technologies available on the market. They display high chemical-to-power conversion efficiencies, larger than those of internal combustion engines (ICE), even when the fuel cell is operated under near-ambient temperature (NAT) [3]. An increasing number of car manufacturers already propose, or will soon be proposing, fuel cell electric vehicles (FCEV). In this context, it is expected that the  $H_2$  demand for energy applications will continue to rise in the near future and the development of methods for producing and delivering the appropriate amounts of hydrogen in a safe and economically profitable way are becoming of paramount importance.

Hydrogen currently available on the market and used in the industry is not decarbonized, nor environmentally friendly nor sustainable, since it is obtained mainly from natural fossil resources. A more appropriate alternative, to get rid of carbon and associated CO<sub>2</sub> problems, is to extract H<sub>2</sub> from water. This is why the splitting of a water molecule into its elemental components, molecular hydrogen and oxygen, is a chemical reaction of great practical interest in the framework of the energy transition. Water dissociation is considered as one of the best options to store renewable and intermittent energy sources, by using molecular hydrogen as a new and multi-purpose energy vector. A thermodynamics analysis of the energetics of the water dissociation reaction tells us that this is a non-spontaneous chemical transformation over an extended range of operating temperatures and pressures of practical interest for applications in the industry. The Gibbs free energy change of this reaction becomes negative at high temperatures of at least 2000 K (1 bar) and temperatures up to 4260 K are required to obtain a 50 % hydrogen yield. The design of reactors that could operate under such harsh conditions and could successfully separate the resulting H<sub>2</sub>-O<sub>2</sub> gas mixtures is a very challenging task, which has not yet been overcome. This is why there is no real technical option for direct water thermo-dissociation in spite of some attempts [4]. Instead, several hybrid thermochemical cycles, such as the ZnO/Zn cycle or the Iodine-Sulfur cycle (also called the Westinghouse process) can be used [5]. Another option for producing decarbonized hydrogen is the electrolysis of water. This is the main path to the so-called hydrogen economy [6]. A water electrolysis cell is the base unit of an electrochemical reactor used for the electro-dissociation of water. As in any electrochemical cell, two metallic electrodes (electron conductors) are placed face-to-face and separated by a thin layer of ion-conducting medium (electrolyte). The resulting galvanic chain contains two metal/electrolyte interfaces connected in series, the seats of the two half cell reactions. During operation, an external DC power supply is used to adjust the Fermi levels of these two electrodes in order to bracket those of

the two redox couples (protons / H<sub>2</sub> at the cathode and water / O<sub>2</sub> at the anode) in the intrapolar electrolytic region.

From an engineering viewpoint, it is necessary to avoid the direct contact of the reaction products (H<sub>2</sub> and O<sub>2</sub>) produced in the cell during the electrolysis process, a contact that would lead to their spontaneous recombination into water and would raise efficiency losses as well as safety issues, due to the possibility of spontaneous explosion. For that reason, a cell separator, permeable to ionic transport but impermeable to gas transport, is placed in the electrolyte between the two electrodes. When the two electrodes are not pressed against the separator, there is a gap filled with liquid electrolyte. Such gap-cells with gas-evolving electrodes cannot be operated to current densities larger than a few hundred of mA cm<sup>-2</sup>. Conversely, when the electrodes are pressed against the separator, higher current densities can be obtained. A last engineering option is to bind the electrodes directly onto an ion-conducting membrane. In such cells, the membrane plays the role of a solid electrolyte and of a gas-separator. Since the gaseous reaction products are evolved at the back side of the intrapolar gap, quite higher current densities (in the multi A cm<sup>-2</sup> range) can be reached.

From a technology viewpoint, water can be electrolyzed by using electrochemical reactors operating under near-ambient temperature conditions (NAT) (high temperature electrolysis of water steam using ceramic-based membrane is another option which is disregarded in this paper). From an historical survey, Alkaline Electrolysis Cell (AEC) technology was the first to be on the market because alkaline electrolytes are less corrosive than the acidic ones [7]. But the successful development of proton conducting ionomers in the 1960's (particularly Nafion® at the DuPont de Nemours Company) led to the concept of proton exchange membrane (PEM) electrolysis technologies. Because significantly higher current densities were reached compared to those obtained in AEC [8, 9], PEM electrolysis found applications in sectors where compactness is a decisive factor (e.g. O<sub>2</sub> generation in submarines or in

spacecrafts). The interest for PEM electrolysis to produce H<sub>2</sub> is somewhat more recent. Even more recently, an increasing number of hydroxyl-ion conducting polymers have been described in the literature and used in water electrolysis cells. Most of them need to be impregnated with molar KOH, in order to improve the membrane conductivity and the ionic contacts between the membrane and the catalyst layers. However, a short-term objective of research is to develop materials that could be operated without KOH, and could be operated in cells fed with only deionized water. A first class of polymer of interest is formed by poly-aryl-ether-ketone backbones and cyclic quaternized ammonium cationic moieties. They provide good mechanical properties, low ionic resistance ( $\approx 70 \text{ m}\Omega \text{ cm}^2$  for 60  $\mu\text{m}$  thick membranes) and limited hydrogen crossover. Performances outperform those of Nafion-115, the reference material for PEM technology. Platinum group metals (PGM) can be used as electrocatalysts but of course, the pH is such that cheaper transition metals, metal alloys or oxides can also be used. Best performing electrocatalysts developed in conventional alkaline technology can potentially be used in Anion-Exchange-Membrane (AEM) technology [10].

Many different materials have been reported as efficient electrocatalysts in alkaline media. For example, Ni [11], NiFe, NiMn<sub>2</sub>O<sub>4</sub> and NiCo<sub>2</sub>O<sub>4</sub> spinel oxides [12] and Ni phosphide [13] have been reported as active Oxygen Evolution Reaction (OER) catalysts. Ni, NiMo [14], Mn-doped Ni<sub>2</sub>P [15] and Ni/CeO<sub>2</sub> on carbon nanotubes [16] have been reported as efficient Hydrogen Evolution Reaction (HER) electrocatalysts.

Water electrolysis is a flexible technology, which can be powered by renewable intermittent primary energy sources, such as wind, solar, tidal, etc., to make hydrogen production a greener process. In particular, the Proton Exchange Membrane Electrolysis Cell (PEMEC) is known to be flexible enough to provide various services for the management of power grids [17]. One of the major characteristics of the water-H<sub>2</sub>-O<sub>2</sub> system is that the dissociation/formation of water molecules require a significant amount of energy ( $\Delta H^\circ =$

285.8 kJ mol<sup>-1</sup> and  $\Delta G^0 = 237.2$  kJ mol<sup>-1</sup> under standard conditions). Considering the light molecular weight of water, this is somewhat surprising but has long been recognized as due to strong intermolecular bonds (the hydrogen bond). As a result, the cell voltage required for water dissociation is 1.23 V under standard conditions. In fact, this is a useful characteristic for application in the energy sector. However, a main drawback, which limits the efficiency of the process, is the sluggish kinetics of the water-oxygen couple (both oxidation of water into oxygen and reduction of oxygen into water) under NAT conditions. When the electrolysis cell is operated at current densities of practical interest (at least 1 A cm<sup>-2</sup> to obtain a high hydrogen production rate at the cathode), high overvoltages are observed. As a result, cell voltages of 1.8 to 2.0 V are generally required to reach significant hydrogen production rates, leading to energy conversion efficiencies less than unity. These overvoltages are responsible for the energy cost of hydrogen production by water electrolysis. In PEM electrolysis cells, where strongly deionized water and expensive protonic membranes are used as acidic electrolytes, together with platinum group metal electrocatalysts (deposited on corrosion resistant supports such as titanium) as electrodes, the material costs are also significant. Therefore, a significant effort is still required to increase the electrical energy efficiency of these cells. This can be achieved mainly by developing more efficient electrocatalysts, by increasing the surface area of the catalyst/electrolyte interface with nanostructured materials, and by using thinner membranes.

The purpose of this review paper is to provide a detailed analysis of the various expressions of the water electrolysis energy efficiency coefficient for the three water electrolysis cells operating under NAT conditions. First, the design and principle of these different cells are briefly described and the thermodynamics of the water splitting reaction over (T,P) range conditions of practical interest is summarized. Then the water electrolysis energy efficiency coefficient is evaluated from theoretical considerations without any

simplifying assumption. A difference is made between the definitions used by academic Laboratories (the focus is on the efficiency of water dissociation itself at constant T,P conditions) and those used by the Industry sector (the focus is on the process efficiency and takes into account the energy content of the hydrogen-oxygen gases produced during electrolysis compared to the total energy used to split water). Approximate expressions are then deduced and the resulting loss of accuracy is quantified. Finally a critical analysis of some expressions of the water electrolysis efficiency found in the recent literature is provided.

## **2. Description of water electrolysis cells operating under near-ambient temperature conditions**

### **2.1 Principles of Proton Exchange Membrane Electrolysis Cell (PEMEC)**

In a Proton Exchange Membrane Electrolysis Cell (PEMEC) -see Fig.1- the anodic compartment of the cell is fed with liquid deionized water. Water molecules are oxidized at the catalytic anode (usually made of unsupported Ir-based oxide particles) according to the half-cell reaction (1a), leading to the production of dioxygen and protons:



where SHE is the Standard Hydrogen Electrode

Oxygen evolves in the gaseous phase and is extracted from the cell. Electrons circulate in the external circuit and hydrated protons migrate across the polymer membrane, down to the cathode (usually made of unsupported Pt particles or of carbon-supported Pt nanoparticles) where they are reduced by the electrons injected by the external DC power supply. As a result, dihydrogen is produced according to the half-cell reaction (1b):



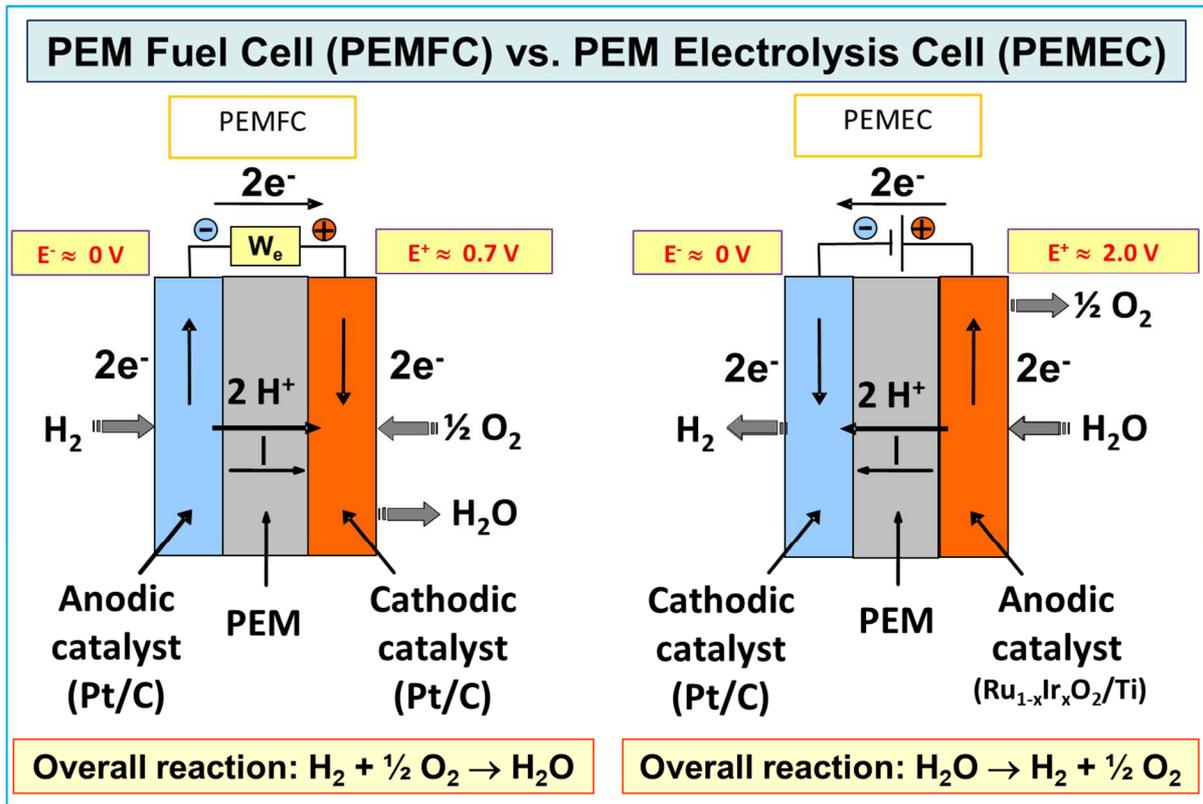


Fig.1: Schemes of a Proton Exchange Membrane Electrolysis Cell (PEMEC) and of a Proton Exchange Membrane Fuel Cell (PEMFC).

The electrical balance between reactions (1a) and (1b) corresponds to the electrochemical splitting of water into hydrogen and oxygen according to the overall reaction:



A thermodynamic analysis of the reaction yields the following data under standard conditions ( $T = 25 \text{ }^\circ\text{C}$ ,  $p = 1 \text{ bar}$ , liquid water):

$$\Delta H^0 = + 285.8 \text{ kJ (mole H}_2\text{O)}^{-1} \text{ and } \Delta G^0 = + 237.2 \text{ kJ (mole H}_2\text{O)}^{-1}$$

This is equivalent to a standard cell voltage  $U_{rev}^0 = E_a - E_c = \Delta G^0 / 2F = 1.229 \text{ V} \approx 1.23 \text{ V}$ .

These electrochemical half-cell reactions are exactly the reverse of those occurring in a fuel cell with an acid electrolyte (such as phosphoric acid, or a Proton Exchange Membrane – PEM, as shown in Fig.1 for the PEMFC). In either a PEM water electrolyzer or a PEM  $\text{H}_2/\text{O}_2$  fuel cell, the most popular membrane material is a perfluorosulfonic acid (PFSA)

ionomer. PFSA membranes are commercially available (e.g. Nafion® products) and membranes of different size (180 to 10 µm) can be used. The electrocatalysts used at the negative electrode for the HER or for the Hydrogen Oxidation Reaction (HOR) are similar (i.e. Pt/C nanoparticles) since the HER/HOR are quasi-reversible reactions. However, the electrocatalysts used at the positive electrode are different, i.e. Pt-based nanoparticles dispersed on large surface area carbon powder (e.g. Vulcan XC72R) for the Oxygen Reduction Reaction (ORR) and Ir-based oxides dispersed on a corrosion-proof support (e.g. a Ti mesh or foam) for the OER.

## 2.2 Principles of Alkaline Electrolysis Cell (AEC)

The design and layout of an Alkaline Electrolysis Cell (AEC) is shown in Fig. 2. The anode and cathode are immersed in a liquid electrolyte and a diaphragm (which is used to prevent the mixture of evolving gases (H<sub>2</sub> and O<sub>2</sub>) is placed between the two electrodes. The electrolyte is usually a 25–30 wt.% aqueous solution of potassium hydroxide (KOH). It is usually pumped through the cell to collect the bubbles of gaseous products and to extract the excess of heat. Alternatively, natural circulation (so-called pump-lift) resulting from temperature gradients and buoyancy effects of the gas bubbles can be used but only for operation in the low current density range. The electrolyte is stored in two separated drums, one for each gaseous product (O<sub>2</sub> and H<sub>2</sub>) which also serve as gas-liquid-separators. After drying, the typical purity of gases is in the 99.5–99.9% range for H<sub>2</sub> and in the 99–99.8% range for O<sub>2</sub>. Higher purity (above 99.999%) can be reached by using on-line catalytic gas purifiers (deoxidizer) [18].

The half-cell electrochemical reactions are:



leading to the overall reaction:

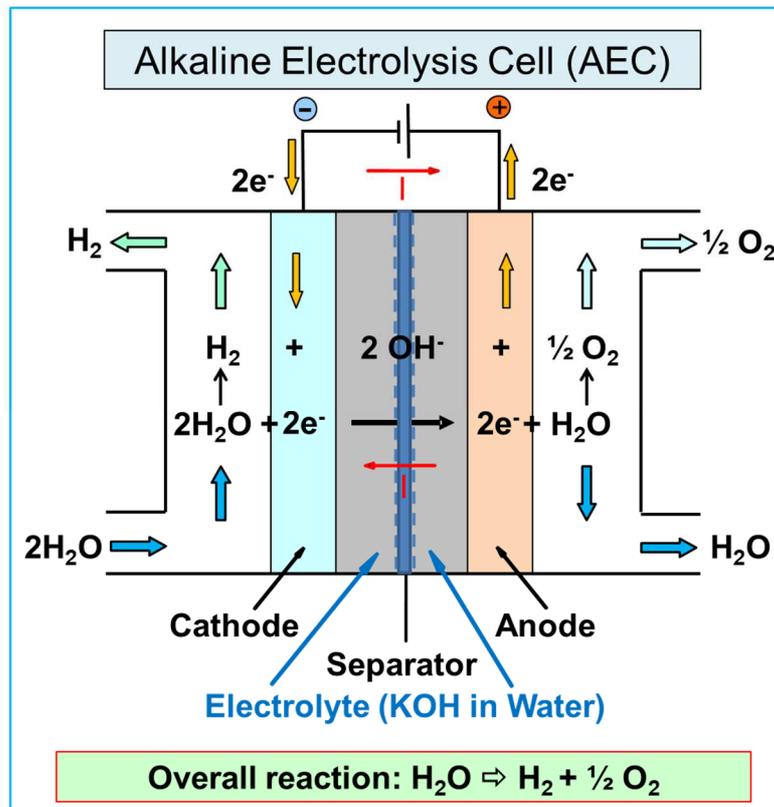
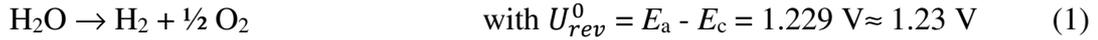


Fig.2: Schematic diagram of an Alkaline Electrolysis Cell (AEC).

These electrochemical processes are again exactly the reverse of those occurring in an Alkaline Fuel Cell (AFC). The anode is usually made of nickel or nickel-based catalysts, with two or three non-noble elements (Co, Mn, NiMoFe, etc.) or even noble metal elements (Pt, Pd, IrO<sub>2</sub> and RuO<sub>2</sub>), while the cathode is made of nickel, or Ni-based catalysts. The advantage of non-precious metal electrocatalysts, such as Ni-based catalysts, is that they are cheaper than Platinum Group Metal (PGM) and are particularly stable and active in alkaline medium.

### 2.3 Principles of Anion Exchange Membrane Electrolysis Cell (AEMEC)

AEM electrolysis is the electrochemical splitting of water into hydrogen and oxygen using an Anion Exchange Membrane (AEM) as electrode separator and solid electrolyte. Ionic conduction is provided by the transport of hydroxyl anions (OH<sup>-</sup>) [19].

Fig. 3 shows the principle of an AEMEC, with an Anionic Exchange Membrane (such as A-201 from Tുകyama) on which are pressed the porous anode and cathode containing the electrocatalysts.

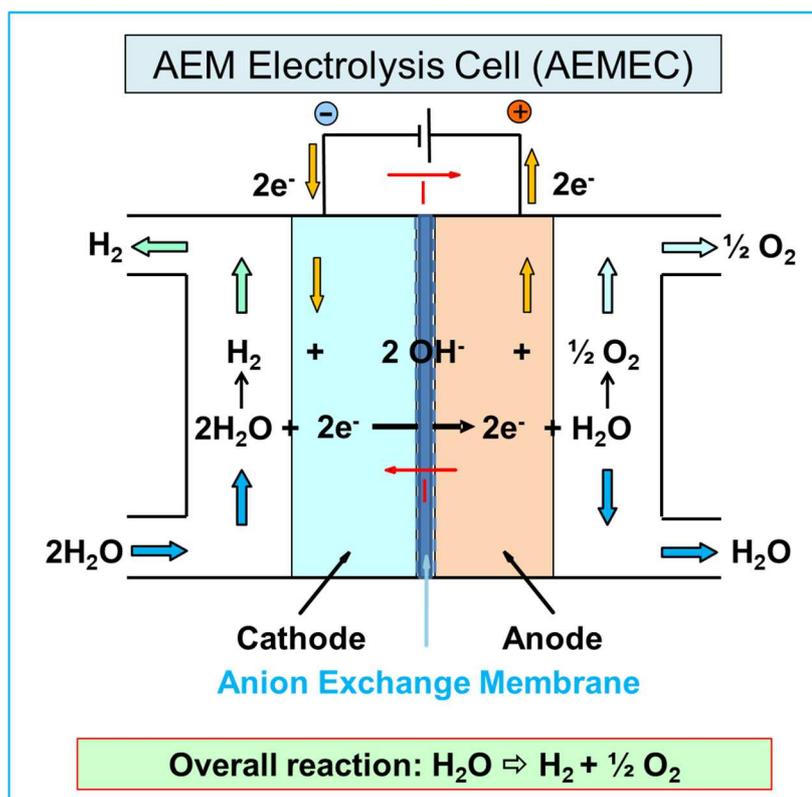


Fig.3: Schematic diagram of an Anion Exchange Membrane Electrolysis Cell (AEMEC).

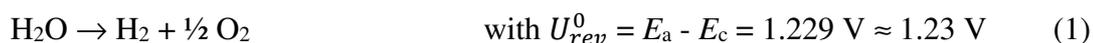
Typical electrocatalysts used at the anode for the OER are metal transition oxides ( $\text{Co}_3\text{O}_4$ ,  $\text{CuCo}_3\text{O}_4$ , etc.). Rare-earth metal oxides (e.g.  $\text{Ni/CeO}_2\text{-La}_2\text{O}_3$  deposited on a microporous carbon paper) are used at the cathode for the HER. Water is circulated through the cathode side where it is reduced to form hydrogen and hydroxyl ions by the addition of two electrons coming from an external DC power supply. Hydroxyl ions migrate across the anionic membrane up to the anode, while the electrons are transported to the cathode through the external circuit. In the anode chamber, the hydroxyl ions are oxidized into water and oxygen by losing electrons. Oxygen bubbles are released from the surface of the anode. Both

half-cell reactions require electrocatalysts to form and release the respective gases from the electrode surfaces.

The partial electrochemical reactions are the following [19]:



leading to the overall reaction :



Despite the larger pH, a theoretical thermodynamic cell voltage of 1.23 V is also required to split the water molecules into hydrogen and oxygen at 25°C. However, in practice, the requirement of the cell voltage for efficient hydrogen production is greater than 1.23 V, since an additional voltage (overvoltage) is required to overcome both the electrode kinetics and the ohmic resistance of electrolyte and components of the electrolyzer. Typical operational cell voltages for alkaline and PEM electrolysis are 1.85–2.05 V and 1.75 V at 70–90°C [20]. The typical operational cell voltage for an AEM electrolysis cell is 1.9 V for current density of 400 mA cm<sup>-2</sup> at 40°C. Typical current densities range from 200 to 500 mA cm<sup>-2</sup>.

AEM electrolysis cells have several advantages compared to PEM and alkaline cells.

1. Only transition metal catalysts are used instead of PGMs.
2. Distilled water or a low concentration of alkaline solution (1% K<sub>2</sub>CO<sub>3</sub> solution) can be used as electrolyte instead of concentrated KOH. The use of a low concentrated alkaline solution eliminates the precipitation of K<sub>2</sub>CO<sub>3</sub> (a side-reaction resulting from the dissolution in KOH of CO<sub>2</sub> from the air atmosphere).
3. The quaternary ammonium ion exchange-group-containing membrane, which is used in AEM electrolysis, is less expensive than the Nafion<sup>®</sup> based membranes.
4. Interaction between CO<sub>2</sub> and the AEM is low due to the absence of metal ions in the AEM.
5. Furthermore, the absence of a corrosive liquid electrolyte offers advantages such as the

absence of leakage, volumetric stability, ease of handling, and a reduction in the size and weight of the electrolyzer. 6. Overall, AEM electrolysis is considered as a less expensive and more stable technology for hydrogen production [21].

### 3. Thermodynamics of the water electro-dissociation reaction under equilibrium conditions

#### 3.1 The cell voltage at equilibrium ( $I=0$ ) for different T and p operating conditions

##### 3.1.1 Expressions of the thermodynamic and electrochemical data

The total energy required to split one mole of water in an electrolysis cell is the opposite of the enthalpy of formation,  $\Delta H_{\text{cell}}(T,p)$ , of one mole of water from its constituents (hydrogen and oxygen). This is the sum of the electrical energy requirement  $\Delta G_{\text{cell}}(T,p)$  and the thermal energy requirement  $\Delta Q_{\text{rev}}(T,p)$ :

$$\Delta H_{\text{cell}}(T,p) = \Delta G_{\text{cell}}(T,p) + \Delta Q_{\text{rev}}(T,p) \quad (3)$$

where  $\Delta Q_{\text{rev}}(T,p) = T \Delta S(T,p)$  and  $\Delta G_{\text{cell}}(T,p) = nFU_{\text{cell}}$  where the cell voltage  $U_{\text{cell}} = E_a - E_c$  is the difference of electrode potentials at the anode and cathode, respectively.

The entropy change  $\Delta S(T,p)$  associated with the decomposition reaction of one mole of water (according the overall reaction (1)) can be calculated from the elementary entropy of each constituents, i.e.:

$$\Delta S(T,p) = S_{\text{H}_2} + 0.5 S_{\text{O}_2} - S_{\text{H}_2\text{O}}$$

Under (STP) conditions (current intensity  $I = 0$ , liquid water,  $T^\circ = 25^\circ\text{C}$ , i.e. 298.15 K and  $p^\circ = 10^5 \text{ Pa} = 1 \text{ bar}$ ), the entropy change is:

$$\Delta S^\circ(298) = 130.7 + 0.5 \times 205.1 - 69.9 = 163.2 \text{ J (mol K)}^{-1}.$$

As a result  $\Delta Q_{\text{rev}}^\circ(298) = T^\circ \Delta S^\circ(298) = 298.15 \times 163.2 = 48.6 \text{ kJ mol}^{-1}$ . Thus:

$$\Delta H_{\text{cell}}(T^\circ, p^\circ) = \Delta G_{\text{cell}}^\circ(T,p) + \Delta Q_{\text{rev}}^\circ(T,p) = 237.2 + 48.6 = 285.8 \text{ kJ mol}^{-1} \quad (4)$$

From a thermodynamic viewpoint, the minimum but necessary cell voltage required for the onset of the water electrolysis reaction under reversible STP conditions,  $U_{rev}^0$ , is defined as:

$$U_{rev}^0 = \Delta G^0 / (n F) \quad (5)$$

where  $n$  is the number of electron 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,  $F=96485.4 \approx 96485 \text{ C mol}^{-1}$ ).

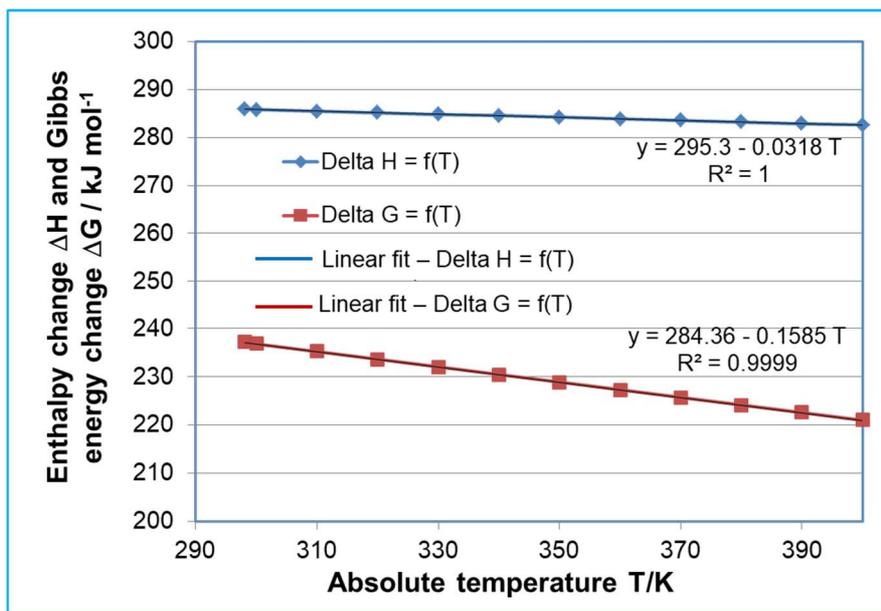
The cell voltage  $U_{rev}^0$  at equilibrium (no current flowing) under standard conditions, is

$$U_{rev}^0 = \frac{\Delta G^0}{nF} = E_a^0 - E_c^0 = 1.229 \text{ V} \approx 1.23 \text{ V} \quad (6)$$

Hydrogen generation by electrolysis cannot take place when the cell voltage  $U_{cell} < U_{rev}^0$ .

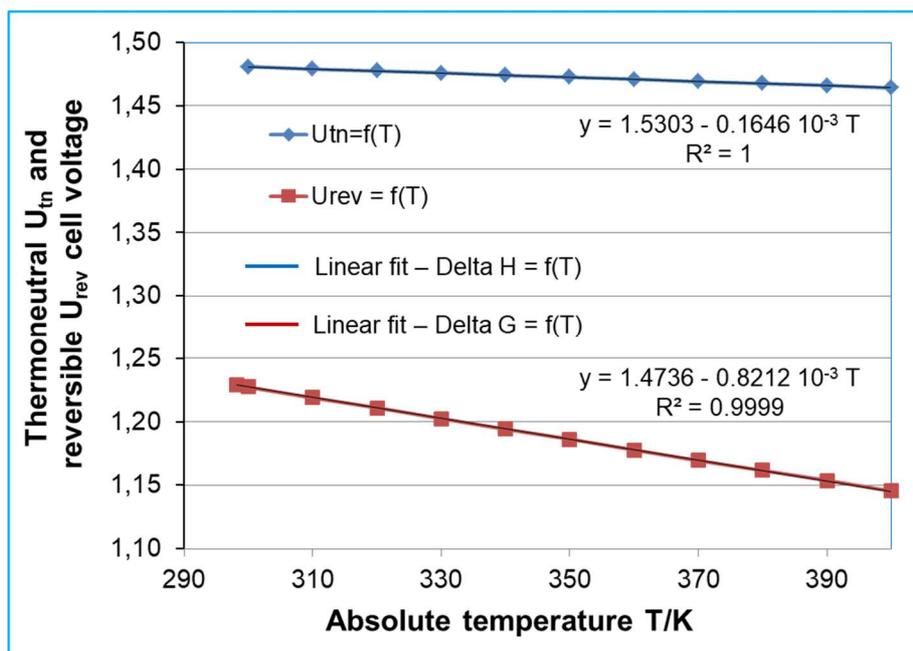
However the thermodynamic data to consider, ( $\Delta H$ ,  $\Delta G$ ,  $\Delta S$ ), are those at the working temperature of the electrolysis cell/stack, i.e. the 300-400 K temperature range for the PEMEC, the AEC and the AEMEC. Absolute temperature ( $T$ ) and pressure ( $p$ ) are the two main physical 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 at any ( $T, p$ ) operating conditions of interest in order to be able to calculate the efficiency of the electrolyser (at the cell, stack or system level) under such conditions.

Figure 4 shows the plots of the enthalpy change  $\Delta H(T, 1)$  and the Gibbs energy change  $\Delta G(T, 1)$  associated with the decomposition of liquid water as a function of absolute temperature together with their linear fits.



**Fig 4 :** Enthalpy change  $\Delta H$  and Gibbs energy change  $\Delta G$  of the decomposition of liquid water as a function of absolute temperature (from 298.15 K to 400 K).

Figure 5 shows the plots of the thermo-neutral cell voltage  $U_{tn}(T,1) = \Delta H/2F$  and the reversible cell voltage  $U_{cell}(T,1) = \Delta G/2F$  as a function of absolute temperature from 298.15 to 400 K and at 1 bar.



**Fig 5:** Plot of the thermo-neutral voltage  $U_{tn}$  and the reversible voltage  $U_{rev}$  required for the decomposition of liquid water as a function of absolute temperature (298.15 K to 400 K).

### 3.1.2 Simplified expression of thermodynamic data under STP conditions

When water dissociation takes place under NAT conditions (0 – 100°C and 1 – 100 bars), the enthalpy change  $\Delta H(T,p)$  of the water splitting reaction can be considered as constant. Thus, in a first approximation  $\Delta H(T,p)$  is equal to the standard enthalpy change  $\Delta H^0 = \text{HHV} = 285.8 \text{ kJ mol}^{-1} = nF U_{tn}^0$ , where HHV is the Higher Heating Value (in  $\text{J mol}^{-1}$ ), i.e. the absolute value of the heat of combustion of hydrogen with oxygen under a pressure of 1 bar, at 15°C, leading to the formation of liquid water. Hence, using this simplifying assumption, the energy efficiency coefficient  $\epsilon_{\text{cell}}$  of a water electrolysis cell/stack can be evaluated by using for reference the STP values of the cell voltages, i.e.  $U_{rev}^0 = \Delta G^0/nF = 237.2/(2 \times 96.485) = 1.23 \text{ V}$  and  $U_{tn}^0 = \Delta H^0/nF = 285.8/(2 \times 96.485) = 1.48 \text{ V}$ .

### 3.1.3 Expression of the thermodynamic data as a function of temperature at $p = 1 \text{ bar}$

For a more accurate calculation of energy efficiencies, it is necessary to take into account the effect of operating temperature on  $\Delta H(T,1)$  and  $\Delta G(T,1)$ . Empirical polynomial expressions have been reported in the literature [22] to calculate accurately the thermodynamic voltage  $U_{rev}(T,1)$  based on Gibbs free energy change, and the thermo-neutral voltage  $U_{tn}(T,1)$ . For water under liquid state, in the range 0 to 100°C and  $p = 1.013 \times 10^5 \text{ bar}$  (1 atm.), these expressions are:

$$U_{rev}(T, 1 \text{ atm.}) = \Delta G(T)/2F = 1.5184 - 1.5421 \times 10^{-3} \times T + 9.523 \times 10^{-5} \times T \times \ln(T) + 9.84 \times 10^{-8} T^2 \quad (7)$$

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

where T is expressed in Kelvin in both cases and  $T^0 = 273.15 \text{ K}$ . It should be noted here that these two equations are valid for  $p = 1 \text{ atm.}$ , and not  $p = 1 \text{ bar}$ . However, the difference in pressure is 1 %. Therefore, Eqs. (7) and (8) can be used when the pressure is 1 bar. A plot of the corrected thermo-neutral voltage value,  $U_{tn}$ , as a function of the reaction temperature, at atmospheric pressure, is shown in Fig. 5 (valid for liquid water only). 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 validity of the above simplifying assumption that temperature effect can be neglected in a first approximation). A similar linear behavior applies to the variation of the cell voltage,  $U_{rev}$ , under reversible conditions (Fig.5), but with a relatively larger change of approximately 5 % ( $U_{rev} = 1.229$  V at 25°C and 1.167 V at 100°C).

### 3.1.4 Thermodynamics of the water splitting reaction as a function of the pressure

#### a) Assuming that dry and ideal gases are formed

It should be first noted that only the Gibbs free energy change ( $\Delta G$ ) of the water dissociation reaction varies with pressure. The enthalpy change ( $\Delta H$ ) is constant because the effect of pressure on the free-energy and the entropy changes cancel out each other. Assuming that the gaseous products ( $H_2$  and  $O_2$ ) produced during electrolysis and collected at the exhaust of the electrolyser are dry and ideal gases, the minimal electric energy required to evolve one mole of hydrogen  $W_t = \Delta G_{rev}(T, p, I=0)$  (in J (mol $_{H_2}$ ) $^{-1}$ ) can be determined by calculating  $\Delta U_{cell}$ , the variation of the cell voltage when the pressures of reacting species ( $p_{H_2O}$ ) and products ( $p_{H_2}$  and  $p_{O_2}$ ) differ from the reference state, as follows:

$$\Delta G_{rev}(T, p, I = 0) = nF U_{rev}(T, p, I = 0) = \Delta G_{rev}(T, p^\theta) + RT \ln \left[ \left( \frac{p_{O_2}}{p^\theta} \right)^{\frac{1}{2}} \left( \frac{p_{H_2}}{p^\theta} \right) / \left( \frac{p_{H_2O}}{p^\theta} \right) \right] = nF (U_{rev}(T, p^\theta) + \Delta U_{cell}) \quad (9)$$

$$\text{with } \Delta U_{cell} = U_{rev}(T, p, I = 0) - U_{rev}(T, p^\theta) = \frac{RT}{2F} \ln \left[ \left( \frac{p_{O_2}}{p^\theta} \right)^{\frac{1}{2}} \left( \frac{p_{H_2}}{p^\theta} \right) / \left( \frac{p_{H_2O}}{p^\theta} \right) \right] \quad (10)$$

The different pressures (expressed in bar), in Eqns. (9) and (10), have the following meaning:

- $p^\theta$  = reference pressure at the working temperature T,
- $p_{H_2}$  = hydrogen partial pressure,
- $p_{O_2}$  = oxygen partial pressure,

- $p_{H_2O}/p^\theta = a_{H_2O} = 1$  for PEM and alkaline water electrolysis (where  $a_{H_2O}$  is the activity of water).

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 of water vapour,
- $p^C$  = pressure of the cathodic compartment =  $p + \Delta p$ , assuming a differential pressure  $\Delta p$  between the two compartments.

b) Assuming that water saturated ideal gases are formed

Since gases produced during electrolysis are usually saturated with water vapour, equations (9) and (10) need corrections. These corrections are made by considering the fact that the pressure in both compartments might be different. For ideal wet gases:

$$nFU_{rev}(T, p, I = 0) = \Delta G_{rev}(T, p^\theta) + RT \ln \left[ \left( \frac{p^A - p_{H_2O}^{sat}}{p^\theta} \right)^{\frac{1}{2}} \left( \frac{p^C - p_{H_2O}^{sat}}{p^\theta} \right) / \left( \frac{p_{H_2O}^{sat}}{p^\theta} \right) \right] = 2F(U_{rev}(T, p^\theta) + \Delta U_{cell}) \quad (11)$$

$$\text{with } \Delta U_{cell} = \frac{RT}{2F} \ln \left[ \left( \frac{p^A - p_{H_2O}^{sat}}{p^\theta} \right)^{\frac{1}{2}} \left( \frac{p^C - p_{H_2O}^{sat}}{p^\theta} \right) / \left( \frac{p_{H_2O}^{sat}}{p^\theta} \right) \right] \quad (12)$$

where  $U_{rev}(T, p^\theta)$  is the cell voltage at reference pressure  $p^\theta$  and temperature  $T$ , and  $p_{H_2O}^{sat}(T)$  is the water saturation pressure at the operating temperature  $T$ .

c) Assuming equi-pressure conditions of operation

When the operating pressure in the same in both cell chambers ( $p^A = p^C = p = p^\theta$ ) and assuming that there is no gas leakages across the cell separator (membrane), it is possible to simplify equation (12) to take into account the effect of pressure on the cell voltage  $U_{rev}$  derived from the Nernst equation:

$$\Delta U_{cell} = U_{rev}(T, p, I = 0) - U_{rev}(T, p^\theta) = \frac{RT}{2F} \ln \left[ \left( \frac{p - p_{H_2O}^{sat}}{p^\theta} \right)^{\frac{1}{2}} \right] \quad (13)$$

### 3.1.5 General expression of the cell voltage as a function of $T$ and $p$

The equilibrium cell voltage  $U_{cell}$  ( $I=0$ ) can thus be evaluated from the Nernst potential at each electrode:

$$U_{cell} (I=0) = E_a - E_c = \Delta G/2F = \Delta G^0/2F + (RT/2F) \text{Ln}\{(p_{O_2})^{1/2} (p_{H_2}) / p_{H_2O}\}$$

$$U_{cell} = U_{rev}^0 + (RT/2F) \text{Ln}\{(p_{O_2})^{1/2} (p_{H_2}) / p_{H_2O}\}$$

with  $U_{rev}^0 = \Delta G^0/2F$  the standard cell voltage, i.e.  $U_{rev}^0 = E_a^0 - E_c^0 = 1.229 \text{ V}$  at  $25^\circ\text{C}$ ,

increasing the pressure of the reactant ( $\text{H}_2\text{O}$ ) and decreasing the pressure of the products ( $\text{H}_2$  and  $\text{O}_2$ ) one can decrease the cell voltage. The variation of  $U_{rev}$  with  $T$  comes mainly from the entropic term, i.e.  $\Delta S^0 = nF (dU^0/dT)$  which is the temperature coefficient of the electrolysis cell. Thus, assuming that  $\Delta H$  and  $\Delta S$  are nearly independent of temperature one may calculate  $U_{rev}$  as follows:

$$U_{rev}(T) = \Delta G/nF = (\Delta H - T \Delta S) / nF = 1.481 - 0.000846 T \quad (\text{in V})$$

for  $\text{H}_2\text{O}$  in the liquid state at  $25^\circ\text{C}$  ( $\Delta H^0 = 285.8 \text{ kJ mole}^{-1}$  and  $\Delta S^0 = 163.2 \text{ J mole}^{-1} \text{ K}^{-1}$ ).

In summary the minimum cell voltage  $U_{rev}$  required for the electrolysis of liquid water can be expressed as a function of operating temperature and pressure by using the following equations:

$$U_{rev}(T,P) = 1.481 - 0.000846 T + 0.0000431 T \text{Ln}\{(p_{O_2})^{1/2} (p_{H_2}) / p_{H_2O}\} \quad \text{in V} \quad (14)$$

or 
$$U_{rev}(T,P) = 1481 - 0.846 T + 0.0431 T \text{Ln}\{(p_{O_2})^{1/2} (p_{H_2}) / p_{H_2O}\} \quad \text{in mV}$$

### 3.2 Thermal balance of the cell

The calculation of the thermal balance of the cell,  $\Delta Q_{cell}$ , is an important point to evaluate the energy balance, which will determine the operating conditions of an electrolysis process: if  $\Delta Q_{cell}$  is positive the necessary heat  $\Delta Q_{rev} = T \Delta S$  is provided by the surrounding, using either a thermostat (Research Laboratories) or an heat exchanger (Industrial Companies); if  $\Delta Q_{cell}$  is negative the excess heat must be evacuated with an heat exchanger.

In order to calculate the total energy needed to decompose water by electrolysis under practical working conditions ( $I \neq 0$ ) at any given temperature  $T$  and pressure  $p$ , it is necessary to evaluate the thermal balance of the cell to know the amount of heat exchanged between the electrolysis cell and the surroundings. Usually the temperature of the electrolysis cell is controlled to a constant value (this could be that of air when the electrolysis takes place at ambient temperature, but in most laboratory experiments, it could be that of a thermostated bath, or in the industry that of an external heat exchangers). It is thus possible to evaluate the irreversible heat produced by the different irreversible processes taking place when  $I \neq 0$ , such as the charge transfer process at each interface (associated with the elementary electrochemical reactions) and the transport of charge carriers (electrons and ions) inside the cell (leading to the cell resistance).

Under any specific and constant  $T, p$  operating conditions, the heat balance  $\Delta Q_{\text{cell}}$  (in  $\text{J mol}^{-1}$ ) of the cell can be defined as the difference between the reversible heat  $\Delta Q_{\text{rev}}$  (in  $\text{J mol}^{-1}$ ) associated with the entropy change of the reaction,  $\Delta Q_{\text{rev}} = T\Delta S(T, p)$ , which is spontaneously transferred from the surroundings to the cell (in response to a temperature gradient at the beginning of the water electrolysis process when  $T_{\text{cell}} < T_{\text{out}}$ ), and the internal energy dissipation into heat via charge transfer overvoltages ( $\sum|\eta_i|$ ) and ohmic losses ( $R_e I$ ) (associated with the irreversible heat  $\Delta Q_{\text{irrev}}$ , which is transferred from the cell to the surroundings when  $T_{\text{cell}} > T_{\text{out}}$ ). Then:

$$\Delta Q_{\text{rev}} (\text{J mol}^{-1}) = T\Delta S = \Delta H_{\text{rev}} - \Delta G_{\text{rev}} = nF (U_{\text{tn}} - U_{\text{rev}}), \quad (15)$$

$$\Delta Q_{\text{irrev}} (\text{J mol}^{-1}) = nF (\sum|\eta_i| + R_e I) = nF \eta_{\text{loss}} = nF (U_{\text{cell}} - U_{\text{rev}}) \quad (16)$$

This leads to the expression of the heat balance  $\Delta Q_{\text{cell}}$ :

$$\Delta Q_{\text{cell}} = T\Delta S - \Delta Q_{\text{irrev}} = nF (U_{\text{tn}} - U_{\text{rev}}) - nF (U_{\text{cell}} - U_{\text{rev}}) = nF (U_{\text{tn}} - U_{\text{cell}}) \quad (17)$$

Under standard conditions one has  $U_{\text{cell}} = U_{\text{rev}}^0$ ,  $\Delta Q_{\text{rev}}^0 = nF (1.481 - 1.229) = 285.8 - 237.2 = 48.6 \text{ kJ mol}^{-1}$  and  $\Delta Q_{\text{rev}}^0/2F = 0.252 \text{ Volt}$ .

This expression of  $\Delta Q_{\text{cell}}$  gives the value of the total heat exchanged between the surrounding and the electrolysis cell. The value and sign of  $\Delta Q_{\text{cell}}$  depend on the value of  $U_{\text{cell}}$  vs. that of  $U_{\text{tn}}$ . The heat balance,  $\Delta Q_{\text{cell}}$ , for any operating conditions is function of the reversible heat ( $\Delta Q_{\text{rev}} = T\Delta S$ ) exchanged with the outside and of the irreversible heat ( $nF \eta_{\text{loss}}$ ) resulting from the overvoltages and the Joule effect (Ohmic drop  $R_e I$ ). It is not possible to distinguish between these two sources of heat but if  $U_{\text{cell}} < U_{\text{tn}}$  then the system needs an external heat input (via the thermostat) and if  $U_{\text{cell}} > U_{\text{tn}}$  then the excess heat is released to the environment (via the thermostat or by radiation, conduction, convection). However, the direction of the heat flow can be known (either to the system or to the surroundings). The algebraic sign of  $\Delta Q_{\text{cell}}$  shows the direction of the net heat flow:

- $\Delta Q_{\text{cell}} = 0$  (when  $U_{\text{cell}} = U_{\text{tn}}$ ), i.e. the cell operates isothermally without a net exchange of heat between the cell and the surroundings;
- $\Delta Q_{\text{cell}} > 0$  (when  $U_{\text{cell}} < U_{\text{tn}}$ ), heat is absorbed by the cell at low current intensity to maintain T constant;
- $\Delta Q_{\text{cell}} < 0$  (when  $U_{\text{cell}} > U_{\text{tn}}$ ), the excess heat produced at high current intensity is released from the cell to the surroundings and some external cooling may be needed to maintain T constant.

#### **4. Expressions of the energy efficiency coefficient for water electrolysis ( $I \neq 0$ )**

##### 4.1 Presentation of the academic and industry viewpoints

The first approach is mostly used by the research academic/scientific community. The focus is on the water electrolysis reaction only, under constant temperature and pressure

(T,p) conditions. The energy efficiency coefficient  $\epsilon_{\text{cell}}$  of a water electrolysis cell can be defined as the ratio of the minimum amount of energy  $W_{\text{rev}}$  (in  $\text{J mol}^{-1}$ ) required to split one mole of water under equilibrium (reversible) conditions (current intensity  $I = 0$ ) to the real amount of energy  $W_{\text{irrev}}$  (in  $\text{J mol}^{-1}$ ) required to split that mole of water (current intensity  $I \neq 0$ ) under constant (T,p) operating conditions.

$$\epsilon_{\text{cell}} = \frac{\text{energy requirement under reversible conditions}}{\text{energy requirement under irreversible conditions}} = \frac{W_{\text{rev}}(\text{J mol}^{-1})}{W_{\text{irrev}}(\text{J mol}^{-1})} \quad (18)$$

At equilibrium ( $I = 0$ ),  $W_{\text{irrev}} = W_{\text{rev}}$  and  $\epsilon_{\text{cell}} = 1$ . Under non-equilibrium conditions ( $I \neq 0$ ),  $W_{\text{irrev}}$  is larger than  $W_{\text{rev}}$ , and  $0 \leq \epsilon_{\text{cell}} \leq 1$ . The reason why  $W_{\text{rev}} < W_{\text{irrev}}$  is due to the second principle of thermodynamics since the transport of electric charges carriers (electrons and ions) across the cell induces irreversible energy degradation (dissipation). A fraction of the kinetics energy of these charge carriers is converted into heat due to frictions. Two main approaches that can be used to define and calculate the energy efficiency coefficient  $\epsilon_{\text{cell}}$  of water electrolysis cells operating under NAT conditions will be discussed in this section. Practically, the electrolysis cell is placed in a thermostat in order to maintain the temperature at a constant value.

The second approach is a more practical one, and is mainly used by the industry sector. Compared to the first definition, there are two main differences:

(i) all parasitic losses (those of the electrolysis unit cell/stack, such as the energy and current losses, heat losses, etc. but also those of auxiliary subsystems such as heat exchangers, pumps, etc.) are taken into account at the denominator of the definition of  $\epsilon_{\text{indus}}$ . Thus the energy efficiency coefficient is a characteristic of the complete electrolyser system;

(ii) the energy of reference (the numerator in the definition of  $\epsilon_{\text{indus}}$ ) is different: this is the energy content of the hydrogen/oxygen gases produced by electrolysis. Thus the energy efficiency coefficient is defined as the ratio of the energy content of the products obtained at

the exhaust of the device (cell, stack, or system plant) to the total energy that is provided to the system.

$$\varepsilon_{indus} = \frac{\text{energy content of products}}{\text{total energy requirements}} = \frac{W_{rev}(\text{J mol}^{-1})}{W_{irrev}(\text{J mol}^{-1})} \quad (19)$$

#### 4.2 Detailed expressions of the energy efficiency coefficient $\varepsilon_{cell}$

A theoretical definition of the energy efficiency coefficient  $\varepsilon_{cell}$  found in the literature is derived from Eq. (18). The numerator of Eq. (18) (the energy requirement under reversible conditions), is defined as the necessary electrical work ( $\Delta G_{rev} = nF U_{rev}$ ) + the necessary heat flow ( $\Delta Q_{rev} = T \Delta S$  in  $\text{J mol}^{-1}$ ) associated with the entropy change:

$$W_{rev} = nF U_{rev} (\text{electrical work}) + nF (U_{tn} - U_{rev}) (\text{reversible } Q) = nF U_{tn} = \Delta H_{rev} (\text{total energy})$$

The denominator of Eq. (18), the energy consumption under irreversible conditions, is defined as the real electrical energy consumption, i.e. the necessary minimum electrical work ( $\Delta G_{rev}$ ) + the necessary heat associated with the entropy increase ( $\Delta Q_{rev}$ ) + the extra amount of electrical work which is dissipated internally into heat ( $nF \eta_{loss}$ , where the total overvoltage  $\eta_{loss}$  results from all the irreversible process, i.e. the irreversibility of the electrochemical reactions involved and of the Ohmic drop). Therefore:

$$\begin{aligned} W_{irrev} &= nF U_{rev} (\text{electrical work}) + nF (U_{tn} - U_{rev}) (\text{reversible } Q) + nF \eta_{loss} (\text{irreversible loss}) \\ &= nF (U_{tn} + U_{cell} - U_{rev}) (\text{total energy}) = \Delta H_{rev} + nF \eta_{loss} \end{aligned}$$

with  $\eta_{loss} = (U_{cell} - U_{rev}) = \sum |\eta_i| + R_e I$

Therefore, the theoretical energy efficiency coefficient is given by [23]:

$$\varepsilon_{cell, th} = \frac{\Delta H_{rev}}{\Delta H_{rev} + nF \eta_{loss}} = \frac{\Delta G_{rev} + \Delta Q_{rev}}{nF U_{cell} + \Delta Q_{rev}} = \frac{U_{tn}}{U_{tn} + U_{cell} - U_{rev}} \quad (20)$$

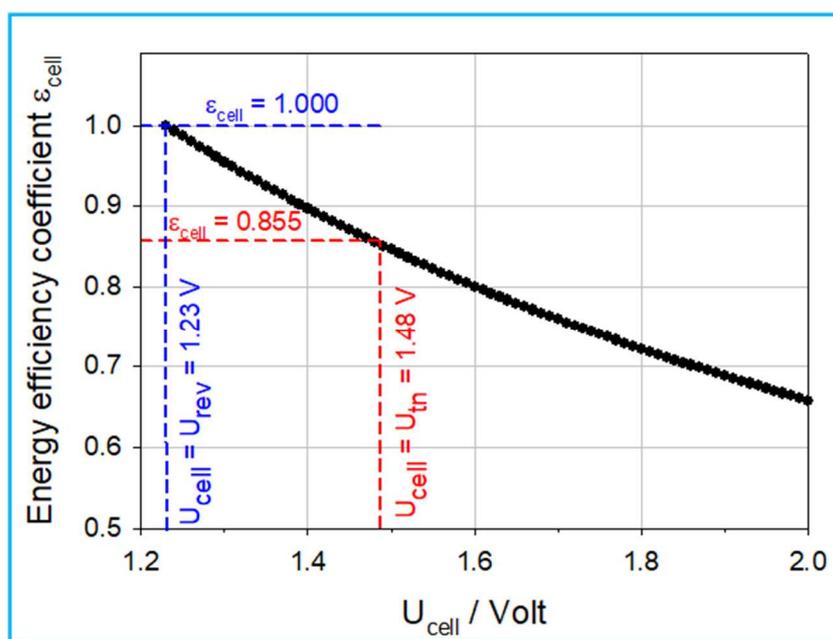


Fig.6: Plot of the theoretical energy efficiency coefficient  $\epsilon_{cell,th}$  vs.  $U_{cell}$ .

This expression shows clearly that the energy efficiency coefficient of a water electrolysis process is a homographic function of the cell voltage  $U_{cell}$ . Since the energy cost of the process is proportional to the energy efficiency coefficient, which is in turn inversely proportional to the irreversible energy  $nF \eta_{loss}$  losses associated with irreversible processes (overvoltages and heat losses), a key point to decrease the energy cost is to increase the energy efficiency by decreasing the irreversible losses. This can be achieved by decreasing both the electrochemical overvoltages  $\sum|\eta_i|$  and the overall cell resistance  $R_e$ . This is true for both energy efficiency coefficients ( $\epsilon_{cell}$  and  $\epsilon_{indus}$ ) since they are quite equivalent – see eqn.(18). To decrease the electrochemical overvoltages, it is necessary to select appropriate electrocatalytic materials, in particular on the anode side where the  $O_2/H_2O$  redox process is quite irreversible leading to low OER reaction rates.

Figure 6 shows the plot of Eq. (20) for  $p = 1$  bar from the STP conditions ( $U_{tn}^0 = 1.48$  V and  $U_{rev}^0 = 1.23$  V) up to  $U_{cell} = 2.0$  V. There is a continuous decrease of  $\epsilon_{cell,th}$  vs.  $U_{cell}$ . When  $U_{cell} = U_{tn} = 1.48$  V under STP conditions, then  $\epsilon_{cell,th} = 0.855 \approx 85.5\%$ .

In this case, both the numerator and denominator of Eq. (20) are consistent since they both contain an electricity term and a heat term.

Under STP conditions at zero current:

$$\varepsilon_{cell,th}^0 = \frac{U_{tn}^0}{U_{tn}^0 + U_{cell}(STP) - U_{rev}^0} = 1 \quad \text{since } U_{cell}(STP) = U_{rev}^0.$$

Under any (T,p) conditions :

$$\varepsilon_{cell,th} = \frac{U_{tn}(T,p)}{U_{tn}(T,p) + U_{cell}(T,p) - U_{rev}(T,p)} < 1$$

#### 4.3 Simplified expressions of the energy efficiency coefficient $\varepsilon_{cell}$ . used in research laboratories

Some simplifying assumptions can be used to obtain handy expressions of  $\varepsilon_{cell}$ .

\* Constant enthalpy change  $\Delta H \approx \Delta H^0 = HHV$ .

In a first approximation the relative enthalpy change  $\Delta(\Delta H)$  between 25 and 100°C is very small, i.e.  $\Delta(\Delta H) = (\Delta H_{25} - \Delta H_{100})/\Delta H_{62} = (285.8 - 283.46)/284.66 = 0.00832 \approx 0.83\%$ , so that the numerator of equation (18) can be considered as constant, i.e.  $\Delta H \approx \Delta H^0 = HHV = 285.8 \text{ kJ mole}^{-1}$  ( $U_{tn}^0 = 1.48 \text{ V}$ ). The expression of  $\varepsilon_{cell}$  thus becomes, for any (T,p) conditions:

$$\varepsilon_{cell} = \frac{\Delta H_{rev}^0}{\Delta H_{rev}^0 + nF\eta_{loss}} = \frac{HHV}{HHV + nF\eta_{loss}} = \frac{U_{tn}^0}{U_{tn}^0 + U_{cell} - U_{rev}}$$

\* Reversible heat small compared to enthalpy change.

Equation (20) can be written as follows:

$$\varepsilon_{cell} = \frac{\Delta G_{rev} + \Delta Q_{rev}}{nFU_{cell} + \Delta Q_{rev}} = \frac{\Delta G_{rev}(1 + \Delta Q_{rev}/\Delta G_{rev})}{\Delta G_{irrev}(1 + \Delta Q_{rev}/\Delta G_{irrev})}$$

If  $\Delta Q_{rev}/\Delta G_{rev} < \Delta Q_{rev}/\Delta G_{irrev} \ll 1$ , this equation simplifies to :

$$\varepsilon_{cell} = \frac{U_{rev} (1 + \Delta Q_{rev} / \Delta G_{rev})}{U_{cell} (1 + \Delta Q_{rev} / \Delta G_{irrev})} \approx \frac{U_{rev}(T,p)}{U_{irrev}(T,p)} = \varepsilon_U \leq 1 \quad (21)$$

The energy efficiency coefficient is thus easily calculated as the ratio of the reversible cell voltage  $U_{rev}$  to the working cell voltage  $U_{irrev}$ . In the literature this ratio is usually called the **voltage efficiency**  $\varepsilon_U$  and is always less than unity since  $U_{rev}$  is the minimum cell voltage required to split one water molecule by electrolysis. Figure 7 shows the plot of Eq. (21), the thermodynamic voltage efficiency, as a function of  $U_{cell}$  under STP conditions. Starting at  $U_{cell} = U_{rev}$ , there is a continuous decrease of  $\varepsilon_{cell}$  vs.  $U_{cell}$  from  $\varepsilon_{cell}^{\circ} = 100\%$  (for  $U_{cell} = U_{rev} = 1.23$  V) to  $U_{cell} = 2.0$  V. When the cell voltage is equal to the thermo-neutral voltage ( $U_{cell} = U_{tn} = 1.48$  V under STP conditions),  $\varepsilon_{cell} \approx 83.1\%$ .

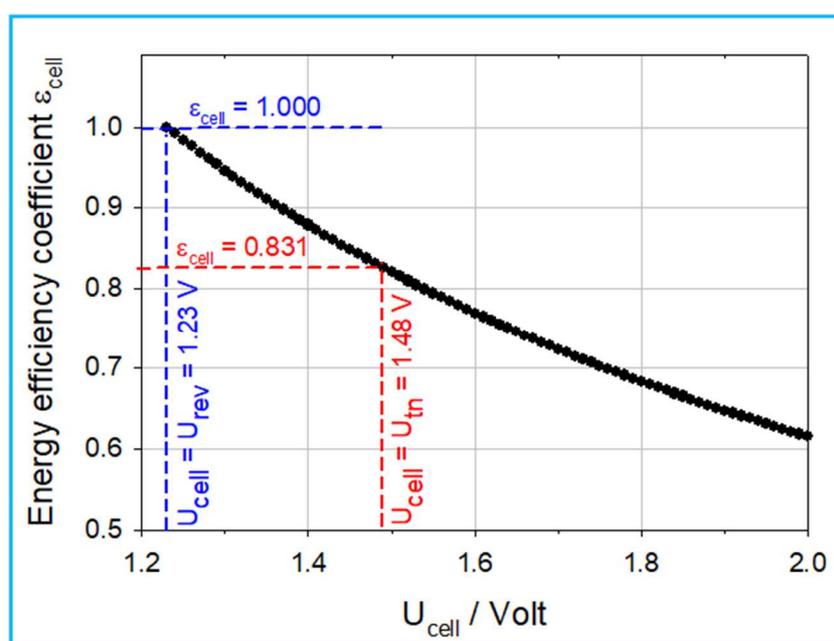


Fig.7: Plot of the practical energy efficiency coefficient  $\varepsilon_{cell}$  vs.  $U_{cell}$ .

This definition is correct since it is homogeneous: only the electrical work is taken into account at the numerator and denominator. But heat flows, in particular the reversible heat exchanged between the cells and the surrounding, are disregarded. This is acceptable for NAT electrolysis only since the relative error at 25°C or 100°C is small:

At 25°C one has  $\Delta Q_{rev}/\Delta G_{rev} = (285.83 - 237.17)/237.17 = 0.205 \approx 20\%$ , so that the practical energy efficiency coefficient at 25°C and 1 A cm<sup>-2</sup> under  $U_{cell} = 1.8$  V would be  $\epsilon_{cell} = 1.229/1.8 = 0.682 \approx 68\%$ , whereas the theoretical cell efficiency coefficient is  $\epsilon_{cell,th} = 1.481/(1.481 + 1.8 - 1.229) = 0.722 \approx 72\%$ , corresponding to a relative error of  $(0.722 - 0.682)/0.722 = 5.5\%$ . For  $U_{cell} = 2.0$  V one has  $\epsilon_{cell,th} = 1.481/(1.481 + 2.0 - 1.229) = 0.657 \approx 66\%$  and a practical energy efficiency coefficient  $\epsilon_{cell} = 1.229/2 = 0.615 \approx 62\%$ , i.e. a relative error of 6.4%.

At 100°C  $\Delta Q_{rev}/\Delta G_{rev} = (283.46 - 225.24)/225.24 = 0.259 \approx 26\%$ . Thus at 100°C under  $U_{cell} = 1.6$  V one obtains  $\epsilon_{cell,th} = 1.469/(1.469 + 1.6 - 1.167) = 0.772 \approx 77\%$  and a practical energy efficiency  $\epsilon_{cell} = 1.167/1.6 = 0.729 \approx 73\%$ , corresponding to a relative error of  $(0.772 - 0.729)/0.772 = 0.0557 \approx 5.6\%$ .

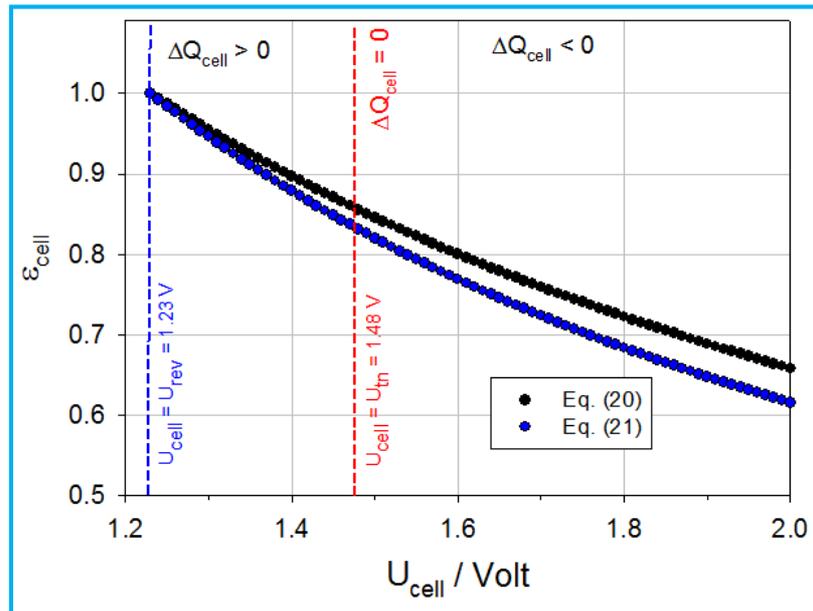
\* Some papers [7] also mention another voltage ratio, obtained by the combination of the two previous approximations. This leads to another definition of the energy efficiency coefficient, i.e. a thermal efficiency:

$$\epsilon_{thermal} = \frac{\Delta H_{rev}^0}{\Delta G_{rev}^0 + nF\eta_{loss}} = \frac{U_{tn}^0}{U_{cell}} = \frac{1.48 V}{U_{cell}} \quad (22a)$$

The blind use of this expression to calculate the energy efficiency coefficient can lead to values greater than unity, in particular when when  $U_{rev} < U_{cell} < U_{tn}$  [24]. A value of  $\epsilon_{cell} > 1$  is of course a thermodynamic non-sense [25], since the heat flow, particularly the reversible heat exchanged between the cells and the surrounding, is neglected in the denominator whereas it is taken into account in the numerator. This definition must be avoided.

#### 4.4 Comparison of water electrolysis efficiency definitions

A comparison of the plots of the STP energy efficiency coefficient  $\epsilon_{cell}$  vs.  $U_{cell}$ , defined in Eqns. (20) and (21), is given in Figure 8 for a cell voltage from  $U_{rev}^0 = 1.23$  V to 2.0 V.



**Fig.8:** Comparative plots of  $\epsilon_{\text{cell}}$  (the STP energy efficiency coefficient) vs.  $U_{\text{cell}}$  according to Eqs. (20) and (21).

For any  $U_{\text{cell}}$  value, Eq. (20) shows slightly higher values of the efficiency coefficient compared to those calculated by Eq. (21) with a difference of 0% at  $U_{\text{cell}} = 1.23$  V and up to 6.4 % for  $U_{\text{cell}} = 2.0$  V.

#### 4.5 Expressions of the energy efficiency coefficient used in the industry

The energy efficiency coefficient usually found in the industry is a definition derived from Eq. (19). The energy content of reaction products at the numerator of this equation is usually the HHV of hydrogen combustion in oxygen (not in air), which is by definition the opposite of the standard enthalpy of formation of a water molecule at 25°C, i.e.  $\text{HHV} = \Delta H^0 = 285.8 \text{ kJ mol}^{-1}$ . There are potentially different practices among users 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:

- Some authors use the heating value of hydrogen combustion in air instead of oxygen.
- Some authors use the High Heating Value (HHV) of hydrogen combustion in oxygen/air (leading to the formation of liquid water) and some other use the Low Heating Value (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 products.
- The usual practice in industry is not to calculate the efficiency coefficient in percent (as in the academic community) but instead to calculate the specific energy consumption of a system (e.g. in kWh/kg<sub>H2</sub> or in kWh/Nm<sup>3</sup><sub>H2</sub>).

The reason for such discrepancies is clear: the reference state is not unique but dictated by the applications. Therefore, the same electrolyzer 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 at 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 eventually compression). Specifically, the instantaneous hydrogen production energy efficiency (based on the HHV) is defined as the ratio between the flow rate of the produced hydrogen,  $\dot{n}_{H_2}$ , expressed in mole per second multiplied by the HHV expressed in Joule per mole of hydrogen and the total electric and thermal power provided to the system expressed in Watt, i.e.:

$$\varepsilon_{indus}^{HHV} = \frac{HHV(T,P) \dot{n}_{H_2}}{P_{electrical} + P_{thermal} + P_{auxi}} \quad (23)$$

where  $P_{auxi}$  is the power used in auxiliary equipments for the stack plant (Balance of Plant - BoP). In the following discussion this power will only concerns the heat exchanger connected to the stack and that one involved in the BoP will not be considered

Equation (23) provides a practical and general (energy + current) value of the efficiency. An integral form of Eq. (23) is needed to calculate the specific energy consumption in kWh (kg<sub>H2</sub>)<sup>-1</sup>, i.e.:

$$W_e = \int_0^{\Delta t} \varepsilon_{indus} (P_{elec} + P_{therm}) = \Delta H \times \Delta N_{H_2}.$$

When the system is operated under stationary conditions, the expression (over a given time interval  $\Delta t$ ) is simply:

$$\varepsilon_{indus}^{HHV} = \frac{HHV \dot{n}_{H_2} \Delta t}{W_e + \Delta Q_{rev} + \Delta Q_{H_2O}} = \frac{HHV \Delta N_{H_2}}{W_e + \Delta Q_{rev} + \Delta Q_{H_2O}} = \frac{\Delta H_{rev} \Delta N_{H_2}}{W_{irrev}} \quad (24)$$

where  $W_{irrev} = W_e + \Delta Q_{rev} + \Delta Q_{H_2O}$  with

- $\dot{n}_{H_2} = \Delta N_{H_2} / \Delta t$  the rate of hydrogen production, i.e. the ratio of the number of moles of hydrogen produced by time  $\Delta t$  (molar flow rate),
- $\Delta N_{H_2}$  = the number of hydrogen moles produced over the considered time period  $\Delta t$ ,
- $P_{total} = W_{irrev} / \Delta t$  the total thermal and electric power provided to the system,
- $W_e = \Delta G_{irrev} = nF U_{cell}$  the electric energy input,
- $\Delta Q_{rev}$  = the reversible heat exchanged (T $\Delta$ S) between the surrounding and the system,
- $\Delta Q_{H_2O}$  = the thermal energy input of an additional heat exchanger (external to the system) for further water heat up.

The last term of eq. (24) corresponds to the theoretical energy efficiency coefficient defined in section 4.1 – see eqn. (18) -, but for  $\Delta N_{H_2}$  number of moles of hydrogen produced over the time period  $\Delta t$ . Thus one may write for the production of one mole:

$$\varepsilon_{indus}^{HHV} = \frac{\Delta H_{rev} \times \Delta N_{H_2}}{W_{irrev} \times \Delta N_{H_2}} = \frac{W_{rev} \times \Delta N_{H_2}}{W_{irrev} \times \Delta N_{H_2}} = \frac{W_{rev}}{W_{irrev}} = \varepsilon_{cell} \quad (18)$$

This expression is exactly the same as that one used in academic Laboratories - see eq. (18).

## 5. Critical analysis of some theoretical efficiency expressions found in the literature

### 5.1 Energy efficiency coefficient definitions used in research laboratories

Concerning the definition and calculation of the energy efficiency coefficient of the water electrolysis reaction, there is a lack of homogeneity in the literature, with different symbols for the same coefficient. Various expressions have been reported in the detailed calculation of the energy efficiency coefficient for Alkaline, PEM or AEM water electrolysis cells. They have different meaning and depend on the operating conditions [26]. This is why it is difficult to make comparisons between experimental results from different authors. For example, Zeng et al. [7] use three different efficiency definitions: voltage, Faradic and thermal efficiencies. Their definition of the voltage efficiency is given by Equation (22b):

$$\% \text{voltage efficiency} = \frac{E_{anode} - E_{cathode}}{E_{cell}} \times 100 \quad (22b)$$

Eq. (22b) is strictly equivalent to the definition that we proposed above for the voltage efficiency (see Eq.(21) in Section 4.3) if the reference cell voltage  $E_a - E_c$  is the reversible cell voltage  $U_{rev}$  (at any T and p conditions) and if the exchanged reversible heat is small compared to the enthalpy change of water decomposition. In this equation, the voltage efficiency is the ratio of the reversible cell voltage  $U_{rev}(I = 0)$  required to split one mole of water to the total cell voltage  $U_{cell}(I \neq 0)$  applied to the whole electrolysis cell. This is a good approximation of the efficiency of the electrolysis system, if the entropic heat exchanged between the cell and the surroundings,  $\Delta Q_{rev}$ , is small and can be neglected.

The definitions of the Faradic and thermal efficiencies reported in Ref. [7] use the Gibbs free energy change and the enthalpy change of the water decomposition reaction under reversible conditions as the theoretical energy input in the numerator and the theoretical energy requirement plus energy losses as the energy input in the denominator, according to Equations (22c) and (22a), respectively:

$$\eta_{\text{Faradic}} = \frac{\Delta G}{\Delta G + \text{Losses}} = \frac{E_{\Delta G}}{E_{\text{cell}}} = \frac{1.23 \text{ (V)}}{E_{\text{cell}}} \quad \text{at } 25^\circ\text{C} \quad (22c)$$

$$\eta_{\text{Thermal}} = \frac{\Delta H}{\Delta G + \text{Losses}} = \frac{E_{\Delta H}}{E_{\text{cell}}} = \frac{1.48 \text{ (V)}}{E_{\text{cell}}} \quad \text{at } 25^\circ\text{C} \quad (22a)$$

where  $E_{\text{cell}}$  is the cell voltage.  $E_{\Delta G}$  and  $E_{\Delta H}$  are the equilibrium Nernst voltage and thermoneutral voltage under reversible conditions, respectively.

A similar analysis of the water electrolysis efficiency can be found in Ref. [27].

The physical meaning of Equation (22a) is that the efficiency coefficient is the ratio of the theoretical energy needed to split one water molecule to the real cell voltage under working conditions. This is a physical non-sense since  $\eta_{\text{thermal}}$  can be greater than 1 if  $E_{\text{cell}} < 1.48 \text{ V}$ . On the other hand eqn. (22c) is exactly the same as eqn. (22b) since  $\Delta G/nF = E_{\Delta G} = E_a - E_c = E_{\text{rev}}$  so that the efficiency called  $\eta_{\text{Faradic}} = E_{\text{rev}}/E_{\text{cell}}$  is exactly the **voltage efficiency** of the electrolysis cell, as defined in Eq. (21) - section 4.3. Thus it is not correct to use the term Faradic efficiency for this definition. The Faradic efficiency is not an energy efficiency but a mass conservation efficiency. This is the ratio of the total amount of hydrogen mole ( $\Delta N_{\text{H}_2}$ ) effectively produced at a current intensity  $I$  during a time interval  $\Delta t$  (measured at the exit of the electrolyzer), i.e.  $\Delta N_{\text{H}_2} = I\Delta t/2F - \Delta N_{\text{H}_2\text{loss}}$ , to the theoretical number of hydrogen mole deduced from the Faraday's conservation law, i.e.  $\Delta N_{\text{th}} = I\Delta t/2F$ , so that:

$$\eta_{\text{Faradic}} = \frac{I\Delta t/2F - \Delta N_{\text{H}_2\text{loss}}}{I\Delta t/2F} = \frac{I - 2F\left(\frac{\Delta N_{\text{H}_2\text{loss}}}{\Delta t}\right)}{I} = \frac{I - 2F\dot{n}_{\text{H}_2\text{loss}}}{I} = \frac{I - I_{\text{loss}}}{I} \quad (25)$$

where  $I_{\text{loss}} = 2F\dot{n}_{\text{H}_2\text{loss}}$ , with  $\dot{n}_{\text{H}_2\text{loss}} = \Delta N_{\text{H}_2\text{loss}}/\Delta t$ , is the flow of hydrogen lost during operation (e.g. due to parasitic electrochemical reactions or to hydrogen leakage from the anodic compartment to the cathodic one by cross-permeation through the electrolyte separator). If there is no hydrogen leakage, then the measured amount of produced hydrogen is equal to its theoretical amount and the Faradic efficiency reaches a maximum of 100%.

In Eq. (22a), an additional cell voltage (added to the reversible voltage) is required to maintain the thermal balance of the cell. The energy efficiency coefficient defined in such a way is sometimes called the thermal efficiency. However, a blind use of this equation can yield efficiency values larger than 100% (when  $U_{\text{rev}} < U_{\text{cell}} < U_{\text{tm}}$ ) since the electrolysis cell can absorb heat from the environment at ambient temperature if it operates in endothermic mode. Such a definition, eqn. (22a), is not correct and should not be used since the numerator contains the reversible heat exchanged,  $\Delta Q_{\text{rev}} = T \Delta S$ , embedded in the enthalpy term  $\Delta H$  in addition to the Gibbs energy change  $\Delta G_{\text{rev}} = nF U_{\text{rev}}$ , whereas the denominator only contains the electrical energy  $W_e = \Delta G_{\text{irrev}} = nF U_{\text{cell}}$ .

## 5.2 Energy efficiency coefficient definitions used in the industry

A typical example of the definition of the water electrolysis energy efficiency coefficient used in the industry can be found in Ref. [28]. According to the Faraday's law, the hydrogen production rate is proportional to the current intensity. If parasitic reactions take place, it is necessary to take into account the Faradic efficiency  $\eta_F$  (or current efficiency) which can be lower than 100%. The parasitic currents increase at lower electric resistance caused by lower current densities, higher operating temperature and larger pressure difference between cell compartments. A strong decrease in Faradic efficiency is observed below a current density of 50–100 mA cm<sup>-2</sup> for AEC. Grigoriev *et al.* [29] report a decrease of the Faradic efficiency of a PEM electrolyzer from nearly 100% at pressures up to 20 bars to 90% at a pressure of 130 bars. At nominal current density, the Faradic efficiency of AEC and PEMEC is reported to be close to 100% (98–99.9%).

The total hydrogen production rate (in  $\text{Nm}^3 \text{h}^{-1}$ ) of a stack equipped with bipolar plates and containing  $n_c$  electrolysis cells electrically connected in series and operated at a current intensity  $I$ , is given by:

$$\dot{V}_{H_2} = \eta_F \frac{n_c I}{2F} V_{mol} = \eta_F \frac{n_c I}{2F} (24.465 \cdot 10^{-3} \times 3600) \quad \text{in } \text{Nm}^3 \text{h}^{-1} \quad \text{at } 25^\circ\text{C and } 1 \text{ atm.} \quad (26)$$

The energy efficiency of such an electrolyzer is then defined as:

$$\eta_{HHV} = \frac{\dot{V}_{H_2} HHV_{H_2}}{P_{el}} \quad (27)$$

where  $\dot{V}_{H_2}$  is the volume flow rate of hydrogen in  $\text{Nm}^3 \text{h}^{-1}$ ,  $HHV_{H_2}$  is the higher heating value of hydrogen ( $HHV = \Delta H^\circ = 285.8 \text{ kJ mol}^{-1} = 3.24 \text{ kWh } (\text{Nm}^3)^{-1}$ ) and  $P_{el}$  the total power in kW. While the current intensity is approximately proportional to the theoretical hydrogen production rate (as long as the Faradic efficiency is close to 100%), the energy efficiency is inversely proportional to the cell voltage  $U_c$ :

$$\eta_{HHV} = \frac{\eta_F \frac{n_c I}{2F} HHV_{H_2}}{n_c U_c I} = \frac{1.48}{U_c} \eta_F \quad (27a)$$

The efficiency of NAT electrolyzers is often given by considering the high heating value of hydrogen. However, for the evaluation of an overall process chain, the partial efficiencies of the process steps and fuel prices are usually referred to the lower heating value ( $LHV_{H_2} = \Delta H_{\text{gas}} = 2.74 \text{ kWh } (\text{Nm}^3)^{-1}$ ). Therefore, it might be convenient in some cases to calculate the efficiency coefficient of the electrolyzer by taking into account the lower heating value  $LHV_{H_2}$ :

$$\eta_{LHV} = \frac{\dot{V}_{H_2} LHV_{H_2}}{P_{el}} = \frac{2.74}{3.24} \eta_{HHV} = \frac{1.25}{U_c} \eta_F \quad (27b)$$

However, these definitions of  $\eta_{HHV}$  (or  $\eta_{LHV}$ ) are not fully homogeneous since the denominator contains only the electric power  $P_{el} = U_c I$ , whereas the numerator  $HHV_{H_2} = \Delta H_{\text{liquid}}$  (or  $LHV_{H_2} = \Delta H_{\text{gas}}$ ) also contains the reversible heat  $\Delta Q_{\text{rev}} = T \Delta S$ .

The operating temperature has a strong influence on performance but its maximum value is dictated by degradation issues of the electrolysis cells and by material constraints. The nominal current density of operation of a water electrolyzer is a trade-off between two contradictory trends [30], namely operating and capital costs, since higher current densities result in:

- an increase of hydrogen production per cell area corresponding to reduced specific capital costs per Nm<sup>3</sup> of hydrogen production;
- a decrease in performance corresponding to an increase in operational costs;
- an increase in the deactivation rate due to higher overpotentials.

According to Schalenbach *et al.* [31] the most general definition of the energy efficiency coefficient of water electrolysis  $\eta$  can be calculated by the ratio of the chemical energy associated with a given amount of produced hydrogen to the energy that was spent to produce such an amount. Under steady state operating conditions this ratio is equal to the power  $P_{\text{ideal}}$  that is thermodynamically required for a given hydrogen production divided by the real electrical power  $P_{\text{real}}$  supplied to the process:

$$\eta = P_{\text{ideal}} / P_{\text{real}} \quad (28)$$

The efficiency aspects discussed in this study concern the efficiency of water electrolysis cells, where the energy consumption of system components such as water pumps and power electronics are not included. At the cell level, the power consumption is equal to the product of the applied voltage  $U_{\text{cell}}$  and the resulting cell current intensity  $I$  plus the power consumed for the heat balance of the cell. The efficiency at the cell level will be denoted as  $\eta_{\text{cell}}$ . The thermodynamic power required for the hydrogen production equals the thermodynamic reference voltage  $U_{\text{ref}}$  times the current intensity that contributes to the hydrogen output of the water electrolyzer. The reference thermodynamic voltage used to calculate the efficiency coefficient of the electrochemical water decomposition reaction, is

typically either the reversible cell voltage  $U_{rev} = 1.23$  V (corresponding to the Gibbs free energy change  $\Delta G^0$ ), or the lower heating value  $U_{LHV} = LHV/(2 \times 98485) = 1.25$  V, or the thermoneutral voltage  $U_{tn} = HHV/(2 \times 98485) = 1.48$  V (corresponding to the enthalpy change  $\Delta H^0$  or higher heating value HHV) under standard ambient temperature and pressure conditions. The thermoneutral voltage (HHV) includes the irreversible heat of evaporation for the phase transition of liquid water to gaseous hydrogen and oxygen, a contribution which is not included in the reversible voltage. For cell voltages less than the thermoneutral voltage, water electrolysis is an endothermic process, whereas for cell voltages larger than the thermoneutral voltage, water electrolysis is an exothermic process.

The current loss  $I_{loss}$  is defined here as the amount of current applied which does not result in viable cathodic hydrogen output of the cell. This current loss is mainly attributable to the hydrogen and oxygen cross-permeation through the separator (as already discussed previously). Accordingly, the current that achieves a viable hydrogen output is equal to the difference between the total current  $I$  applied and the current loss  $I_{loss}$ . By employing the present definitions, the latter equation can be rewritten as:

$$\eta_{cell} = \frac{U_{ref} (I - I_{loss})}{U_{cell} I} = \frac{U_{ref} (I - I_{loss})}{U_{cell} I} = \eta_U \eta_F \quad (21a)$$

where  $\eta_U$  is the voltage efficiency – see eqn. (21) - and  $\eta_F$  is the current efficiency (also commonly referred to the Faradic efficiency), defined as :

$$\eta_F = \frac{I - I_{loss}}{I} = 1 - \frac{I_{loss}}{I}$$

A more complete definition of the energy efficiency of a water electrolysis system (electrolysis stack + balance of plant), containing both the heat exchanged with the electrolyzer and with the heat exchanger, can be found in the work of Ni *et al.* [32]. First of

all, it is necessary to calculate the theoretical energy demand for the electrolytic hydrogen production. The total energy demand for PEM electrolysis can be calculated as:

$$\Delta H = \Delta G + T\Delta S$$

The minimum energy demand is the theoretical energy required for H<sub>2</sub>O electrolysis without any losses ( $I = 0$ ). In real systems ( $I \neq 0$ ), losses are inevitable and the performance of the system concerned can be evaluated in terms of the energy efficiency ( $\eta_{en}$ ). The energy efficiency can be defined from an energy balance of the system, as follows:

$$\eta_{en} = \frac{LHV_{H_2} \dot{N}_{H_2,out}}{P_{elec} + \dot{Q}_{heat,PEM} + \dot{Q}_{heat,H_2O}} \quad (29)$$

where  $LHV_{H_2}$  is the lower heating value of H<sub>2</sub>;  $\dot{N}_{H_2,out} = \Delta N_{H_2,out} / \Delta t$  is the outlet flow rate of H<sub>2</sub> during time  $\Delta t$ ;  $P_{elec}$  and  $\dot{Q}_{heat,PEM}$  are the rate of electric energy input and the rate of thermal energy input for the PEM electrolyzer, respectively;  $\dot{Q}_{heat,H_2O}$  is the rate of thermal energy input to the heat exchanger for heating up H<sub>2</sub>O.

The H<sub>2</sub> flow rate at the exhaust of the electrolyzer for a Faradic efficiency of 100% can be determined by:

$$\dot{N}_{H_2,out} = \frac{I}{2F} = \dot{N}_{H_2O,reacted}$$

where  $I$  is the current intensity;  $F$  is the Faraday constant ( $F = 96485 \text{ C}$ ); and  $\dot{N}_{H_2O,reacted}$  is the rate of H<sub>2</sub>O which reacted in the process. Similarly, the flow rate of H<sub>2</sub>O and O<sub>2</sub> at the PEM electrolyzer outlet can be evaluated as:

$$\dot{N}_{O_2,out} = \frac{I}{4F} \quad \text{and} \quad \dot{N}_{H_2O,out} = \dot{N}_{H_2O,in} - \dot{N}_{H_2O,reacted} = \dot{N}_{H_2O,in} - \frac{I}{2F}$$

where the flow rate of H<sub>2</sub>O at the PEM electrolyzer inlet ( $\dot{N}_{H_2O,in}$ ) is a known parameter.

The overpotentials (irreversibilities) associated with the charge transfers and the ohmic losses during operation ( $I \neq 0$ ) will contribute to heat production due to an entropy generation term  $\sigma$ :

$$\sigma = 2F (\eta_{\text{act,a}} + |\eta_{\text{act,c}}| + \eta_{\text{ohm}}) \quad (30)$$

where  $\eta_{\text{act,a}}$  and  $|\eta_{\text{act,c}}|$  are the activation overvoltage and  $\eta_{\text{ohm}}$  the Joule heat losses.

For  $U_{\text{cell}} > U_{\text{tn}}$ , i.e.  $\sigma \geq T \Delta S$ , the heat produced inside the cell by irreversible processes is equal to (or exceeds) the heat required for the water-splitting reaction. In such a case, the cell is working exothermally and no external heat is needed for the PEM electrolyzer. The excess heat must be evacuated from the cell and transferred to the reference environment via heat exchange with a thermostat. If  $\sigma \leq T \Delta S$ , the heat produced inside the cell is less than the thermal requirement, so that external heat must be provided from the thermostat to maintain the cell temperature at a constant value. The heat balance of the PEM electrolyzer is then calculated as:

$$\dot{Q}_{\text{heat,PEM}} = (T\Delta S - \sigma) \dot{N}_{\text{H}_2\text{O,reacted}} = (T\Delta S - \sigma) \frac{I}{2F} \quad (17a)$$

This last equation corresponds exactly to the heat balance derived above in Section 3.2 – see eqns. (15) to (17). Therefore, it can be concluded that Eq. (29) may lead to the correct expression of the energy efficiency taking into account a complete energy input for an electrolysis time  $\Delta t$ , i.e. an electrical energy input  $\Delta W_{\text{elec}} = P_{\text{elec}} \Delta t = (\Delta G_{\text{rev}} + \sigma) \Delta N_{\text{H}_2,\text{out}} = W_{\text{elec}} \Delta N_{\text{H}_2,\text{out}}$  from the electric supply and the entropic heat exchanged,  $\Delta Q_{\text{rev}} = T\Delta S \Delta N_{\text{H}_2,\text{out}}$  with the reference environment and  $\sigma$  with the thermostat, i.e.  $\dot{Q}_{\text{heat,H}_2\text{O}} \Delta N_{\text{H}_2,\text{out}}$ . Thus eqn. (29) will give:  $\eta$

$$\eta_{en} = \frac{LHV_{H_2} \dot{N}_{H_2, out}}{P_{elec} + \dot{Q}_{heat, PEM} + \dot{Q}_{heat, H_2O}} = \frac{LHV_{H_2} \Delta N_{H_2, out}}{W_{elec} \Delta N_{H_2, out} + \Delta Q_{rev} \Delta N_{H_2, out} + \Delta Q_{heat, H_2O} \Delta N_{H_2, out}}$$

$$= \frac{LHV_{H_2}}{W_{irrev} + \Delta Q_{heat, H_2O}} \quad (31)$$

Equation (31) is very similar to Eqn. (24) for  $\varepsilon_{indus}^{HHV}$  but the heat exchanged with the thermostat is added. The only difference is that the LHV is used instead of the HHV for the reference state (when  $I = 0$ ). This is the most general expression of the energy efficiency of a water electrolysis system that can be used for industrial electrolyzers.

## 6. Conclusions

The energy efficiency coefficient is a key performance indicator of major interest to compare the energetic performances of water electrolysis cells, stacks and plants and to calculate the cost of electrolytic hydrogen. However, different definitions are available in the literature and therefore the comparison of performances obtained by Research Laboratories to those used in Industrial Companies is not straightforward and not always possible. The purpose of this research paper is to provide a critical review of the definitions used by both communities to calculate this energy efficiency coefficient. The discussion is restricted to the three main water electrolysis technologies which operate under near ambient temperature conditions: (i) Proton Exchange Membrane (PEM) water electrolysis cells; (ii) conventional alkaline water electrolysis cells with liquid electrolyte (AEC); (iii) Anion-Exchange Membrane (AEM) water electrolysis cells.

Expressions of the energy efficiency coefficient  $\varepsilon_{cell}$  can be derived from basic thermodynamic analysis of the water electro-dissociation reaction under equilibrium ( $I = 0$ ) and non-equilibrium ( $I \neq 0$ ) conditions when the kinetics of the redox processes is taken into account. The different expressions used by both the scientific and industrial communities have

been derived and compared. Their differences have been outlined and their significance discussed in details. Since both electricity and heat are required to electrolyze water, the most appropriate definitions of  $\epsilon_{\text{cell}}$  are those which have homogeneous numerator and denominator expressions, i.e. which contain either the electricity and heat contributions together, or only the electricity terms. Expressions of  $\epsilon_{\text{cell}}$  that use the thermoneutral voltage at the numerator should be handled carefully. This is because the thermoneutral voltage contains both the electrical energy and the reversible heat necessary to decompose one water molecule. If the expression used at the denominator contains only the electrical contribution,  $\epsilon_{\text{cell}}$  values larger than 100% are obtained when the cell voltage is less than the thermoneutral voltage. This is a thermodynamic non-sense. Such definitions are theoretically inconsistent and should not be used.

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### Legend of the Figures

Fig.1: Schemes of a Proton Exchange Membrane Electrolysis Cell (PEMEC) and of a Proton Exchange Membrane Fuel Cell (PEMFC).

Fig.2: Schematic diagram of an Alkaline Electrolysis Cell (AEC).

Fig.3: Schematic diagram of an Anion Exchange Membrane Electrolysis Cell (AEMEC).

Fig 4: Enthalpy change  $\Delta H$  and Gibbs energy change  $\Delta G$  of the decomposition of liquid water as a function of absolute temperature (from 298.15 K to 400 K).

Fig 5: Plot of the thermo-neutral voltage  $U_{tn}$  and the reversible voltage  $U_{rev}$  required for the decomposition of liquid water as a function of absolute temperature (298.15 K to 400 K).

Fig.6: Plot of the theoretical energy efficiency coefficient  $\epsilon_{cell,th}$  vs.  $U_{cell}$ .

Fig.7: Plot of the practical energy efficiency coefficient  $\epsilon_{cell}$  vs.  $U_{cell}$ .

Fig.8: Comparative plots of  $\epsilon_{cell}$  (the STP energy efficiency coefficient) vs.  $U_{cell}$  according to Eqs. (20) and (21).

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