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Co-funded by the **Erasmus+ Programme** of the European Union

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## **Green Hydrogen Production for Renewable Energy Storage**

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#### Content





- Introduction
- Hydrogen
- Green hydrogen
- Electrochemical cell
- Fundamentals of electrolysis
- HER , OER and exchange current density
- Faraday law
- Water electrolyzers type
- HER and OER catalyst
- Water electrolysers: Alkaline, PEM, AEM and Solid Oxide



#### **Energy Resources**

#### How hydrogen empowers the energy transition



Hydrogen 2030: The Blueprint







Brussels, 8.7.2020 COM(2020) 301 final

COMMUNICATION FROM THE COMMISSION TO THE EUROPEAN PARLIAMENT, THE COUNCIL, THE EUROPEAN ECONOMIC AND SOCIAL COMMITTEE AND THE COMMITTEE OF THE REGIONS

A hydrogen strategy for a climate-neutral Europe





The Future of

Hydrogen

### Hydrogen as a fuel



#### Hydrogen is...

- not existing freely in nature,
- an invisible, extremely flammable gas
- colorless, odorless gas,
- not an energy source,
- an energy carrier
- a secondary form of energy must be produced from a source
- a fuel with highest energy density, lowest volume density

H<sub>2</sub>

## Why hydrogen?





Hydrogen promises to lead to better, faster, more efficient, environmentally clean energy.

#### Potential uses for green hydrogen





https://hipaustralia.com.au/hydrogen-energy/

Around 120 million tonnes of hydrogen per year ( $MtH_2/yr$ ) are produced globally, 70 million tonnes pure hydrogen and the rest mixed with other gases.

- produced from fossil fuels
- responsible for CO<sub>2</sub> emissions of around 830 million tonnes of CO<sub>2</sub> per year (MtCO<sub>2</sub>/yr)
- Today's hydrogen production is mostly based on natural gas and coal, which together account for 95% of production
- 5% hydrogen is produced by electrolysis

Hydrogen is a chemical feedstock in petroleum refining and ammonia production.

- About 33 % of the hydrogen produced worldwide is used in refineries,
- 27 % for ammonia synthesis

## Color code of hydrogen



• Color code nomenclature is becoming commonly used for hydrogen based on the production process.



Source: IRENA 2020 Green Hydrogen Policy



## Green hydrogen for a climate-neutral strategy



EU's long-term plan for the goal to achieve a Carbon Neutral by 2050,

- From now to 2024, the installation of at least 6 GW of renewable hydrogen electrolysers
- From 2025 to 2030, the installation of at least 40 GW of renewable hydrogen electrolysers and the production of up to 10 million tonnes/yr of renewable hydrogen production in the EU.



Source: A Hydrogen Strategy for a climate-neutral Europe #EUGreenDeal

https://www.innovationnewsnetwork.com/a dvantages-green-hydrogen-fuel-cleanenergy-transition/22153/

## Hydrogen production

- Pure hydrogen does not naturally on the earth in large quantities, it takes a ٠ substantial amount of energy in its industrial production.
- Based on the source of energy, there are different ways to the production of ٠ hydrogen.

#### HYDROGEN PRODUCTION PROCESS

- Electrolysis
- Fossil Fuels and Biomass
- Thermochemical Process
- Direct Solar Water Splitting
- Biological Process







#### Historical perspective and technology status

- The principles were discovered about two centuries ago.
- A DC power source is required to split liquid water into gaseous hydrogen and oxygen.
- Alessandro Volta invented the first DC power source in Italy in 1800. It is called a voltaic pile (an early kind of non-rechargeable battery)
- William Nicholson and Anthony Carlisle in England used a volta pile as a DC power source for the electrolytic splitting of water using a woollen cloth soaked in alkaline.



Sergey A Grigoriev, Vladimir N Fateev, and Pierre Millet, Alkaline Electrolysers, Volume 4, Editor: Trevor M. Letcher, Comprehensive Renewable Energy, 2022, Elseiver

## **Electrochemical Cell Types**





# Electrolytic cell & Electrolyzer Term

"Electrolyzers" are sometimes devices.

It should be noted that the terms "electrolytic cell" and "electrolyzer" are often used interchangeably.

#### **ELECTROLYSIS** Anode Cathode 0 Anions Cations 0 0 Solution of 0electrolyte 0 0 0

- When the external power source is turned on, the cathode becomes negatively charged and attracts positively charged ions (cations) from the electrolyte.
- **Cathode:** reduction reactions occur, where the cations gain electrons and are transformed into their respective compounds or elements.
- Anode becomes positively charged and attracts negatively charged ions (anions) from the electrolyte.
- At the anode, oxidation reactions occur, where the anions lose electrons and undergo chemical transformations.

## Water Electrolyzer

A water electrolyzer uses electricity to split water or another aqueous solution into its constituent elements, typically hydrogen and oxygen.

The electrolysis process involves passing an electric current through the electrolyte, which is the conductive solution.



https://tenor.com/search/electrolysis-gif-gifs

## **Fundamentals of water electrolysis**



#### Water electrolysis fundamentals

**Overall reaction**:  $H_2O(l) \rightleftharpoons H_2(g) + 1/2O_2(g) E^o_{rev(decomp.)} = 1.229 V \cong 1.23 V$ 

The standard reversible decomposition voltage for the electrolysis  $E_{rev}^o$  can be calculated, at standard conditions  $\Delta G^o = 237.13 \text{ kJ mol}^{-1}$  as:

$$E_{rev}^o = -\frac{\Delta G^o}{nF} = -\frac{\Delta H^o - T\Delta S^o}{nF} = -1.23V$$

The positive value of change in Gibbs free energy indicates that the reaction is nonspontaneous.

This is reflected in the negative sign in reversible decomposition voltage.

An absolute value of  $E_{rev}^o$  of 1.23 V is commonly reported.

$$E_{decomp}^{o} = E_A - E_C = 1.23V$$



The thermoneutral decomposition voltage  $E_{th}^o$  can be determined using  $\Delta H^o = 285.83 \text{ kJ mol}^{-1}$  at standard conditions.

 $\Delta H^o$  is the enthalpy of liquid water decomposition or known as the molar high heating value (HHV) enthalpy of hydrogen combustion for the reverse reaction of water formation:

$$|E_{th}^{o}| = \left|\frac{\Delta H^{o}}{nF}\right| = 1.48V$$

Typically, electrolyzer cells are operated above the thermoneutral voltage.  $E_{th}$ , (but above the reversible decomposition potential,  $E_{rev}$ ,), an energy from the surrounding in the form of heat equal to nF ( $E_{th}$ -  $E_{cell}$ ) will be required to maintain a constant operating temperature.





*E<sub>th</sub> at high temperatures:* 1.48 V at 25°C to 1.49 V at 1000 °C (1832°F).

A water electrolysis cell operating at 2.5 V, for example, at 25°C,

*Energy efficiency :* (1.48/2.5) x 100 = 59.2%

at 2.1V ; 70%

J. O'M. Bockris, Brian E. Conway, Ernest Yeager, and Ralph E. White, Comprehensive Treatise of Electrochemistry Volume 2: Electrochemical Processing (1981)



#### **Electrolysis Half-Cell Reactions**

The electrolysis half-cell reactions depend on the electrolyte used or on the mobile ion e.g., solvated hydroxide, solvated proton, carbonate, or oxide ion.

$$E_{decomp}^{o} = E_A - E_C = 1.23V$$

#### In alkaline electrolyte:

Cathode reaction :  $2H_2O(l) + 2e^- \Rightarrow H_2(g) + 2OH^-(aq)$   $E^o = -0.828V$  SHE Anode reaction :  $2OH^-(aq) \Rightarrow H_2O(l) + 1/2O_2(g) + 2e^ E^o = +0.402V$  SHE  $H_2O(l) \Rightarrow H_2(g) + 1/2O_2(g)$   $E_{rev}^o = 1.23V$ 

#### In acidic electrolyte:

Cathode reaction :  $2\mathcal{H}^+(aq) + 2e^- \rightleftharpoons H_2(g)$ Anode reaction :  $H_2O(l) \rightleftharpoons 2\mathcal{H}^+(aq) + 1/2O_2(g) + 2e^- E^o = +1.23V$  SHE  $H_2O(l) \rightleftharpoons H_2(g) + 1/2O_2(g)$  $E_{rev}^o = 1.23V$ 



#### In alkaline electrolyte:

Cathode reaction :  $2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$   $E^o = -0.828V$  SHE Anode reaction : $2OH^-(aq) \rightleftharpoons H_2O(l) + 1/2O_2(g) + 2e^ E^o = +0.402V$  SHE  $H_2O(l) \rightleftharpoons H_2(g) + 1/2O_2(g)$   $E^o_{rev} = 1.23V$ In acidic electrolyte: Cathode reaction : $2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$   $E^o = 0.00V$  SHE Anode reaction : $H_2O(l) \rightleftharpoons 2H^+(aq) + 1/2O_2(g) + 2e^ E^o = +1.23V$  SHE  $H_2O(l) \rightleftharpoons H_2(g) + 1/2O_2(g)$   $E^o_{rev} = 1.23V$ 

## $\Delta \mathbf{G}^{\circ} = \mathbf{237.13 \ kJ \ mol^{-1}}$ $E_{rev}^{o} = -\frac{\Delta G^{o}}{nF} = -\frac{\Delta H^{o} - T\Delta S^{o}}{nF} = -1.23V$

Stronger	$F_2(g) + 2e^-$	$\longrightarrow 2 F (aq)$	2.87	Weaker
oxidizing	$H_2O_2(aq) + 2 H^+(aq) + 2 e^-$	$\longrightarrow 2 H_2O(l)$	1.78	reducing
agent	$MnO_4^{-}(aq) + 8 H^{+}(aq) + 5 e^{-}$	$\longrightarrow$ Mn <sup>2+</sup> (aq) + 4 H <sub>2</sub> O(l)	1.51	agent
	$Cl_2(g) + 2e^-$	$\longrightarrow 2 \operatorname{Cl}^{-}(aq)$	1.36	
	$Cr_2O_7^{2-}(aq) + 14 H^+(aq) + 6 e$	$- \longrightarrow 2 \operatorname{Cr}^{3+}(aq) + 7 \operatorname{H}_2O(l)$	1.33	
	$O_2(g) + 4 H^+(aq) + 4 e^-$	$\longrightarrow 2 H_2O(l)$	1.23	
	$Br_2(l) + 2 e^-$	$\longrightarrow$ 2 Br <sup>-</sup> (aq)	1.09	
	$Ag^{+}(aq) + e^{-}$	$\longrightarrow Ag(s)$	0.80	
	$Fe^{3+}(aq) + e^{-}$	$\longrightarrow$ Fe <sup>2+</sup> (aq)	0.77	
	$O_2(g) + 2 H^+(aq) + 2 e^-$	$\longrightarrow$ H <sub>2</sub> O <sub>2</sub> (aq)	0.70	
	$I_2(s) + 2 e^-$	$\longrightarrow 2 I^{-}(aq)$	0.54	
	$O_2(g) + 2 H_2O(l) + 4 e^{-1}$	$\longrightarrow 4 \text{ OH}^{-}(aq)$	0.40	
	$Cu^{2*}(aq) + 2e^{-}$	$\longrightarrow$ Cu(s)	0.34	
	$Sn^{4+}(aq) + 2e^{-}$	$\longrightarrow$ Sn <sup>2+</sup> (aq)	0.15	
	$2 H^{*}(aq) + 2 e^{-}$	$\longrightarrow$ H <sub>2</sub> (g)	0	
	$Pb^{2+}(aq) + 2e^{-}$	$\longrightarrow Pb(s)$	-0.13	
	$Ni^{2+}(aq) + 2e^{-}$	$\longrightarrow$ Ni(s)	-0.26	
	$Cd^{2*}(aq) + 2e^{-}$	$\longrightarrow$ Cd(s)	-0.40	
	$Fe^{2+}(aq) + 2e^{-}$	$\longrightarrow$ Fe(s)	-0.45	
	$Zn^{2+}(aq) + 2e^{-}$	$\longrightarrow$ Zn(s)	-0.76	
	$2 H_2 O(l) + 2 e^{-1}$	$\longrightarrow$ H <sub>2</sub> (g) + 2 OH <sup>-</sup> (aq)	-0.83	
	$Al^{3+}(aq) + 3e^{-}$	$\longrightarrow$ Al(s)	-1.66	
Weaker	$Mg^{2+}(aq) + 2e^{-}$	$\longrightarrow$ Mg(s)	-2.37	Stronger
oxidizing	$Na^+(aq) + e^-$	$\longrightarrow$ Na(s)	-2.71	reducing
agent	$Li^{+}(aq) + e^{-}$	$\longrightarrow$ Li(s)	-3.04	agent

Weaker oxidizing agent

Stronger reducing agent

#### Alkaline Water Electrolysis

## $E = E^o - \frac{0.0592 \text{ V}}{n} \log Q$

## N UNIL FRSIT

#### In alkaline electrolyte:

Cathode reaction :  $2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq) E^o = -0.828V - 0.0592pOH$ Anode reaction :  $2OH^-(aq) \rightleftharpoons H_2O(l) + 1/2O_2(g) + 2e^- E^o = +0.402V - 0.0592pOH$ 

**Overall reaction**:  $H_2O(l) \rightleftharpoons H_2(g) + 1/2O_2(g)$   $E_{rev}^o \cong 1.23V$ 





$$E = E_{rev.}^{o} + \eta_{c} + \eta_{a} + \eta_{\Omega} + \eta_{hw}$$

 $\eta_{c}$ = cathodic overpotential  $\eta_{a}$ =anodic overpotential  $\eta_{\Omega}$ =the electrolyte ohmic drop between the anode and the cathode

 $\eta_{\rm hw}{=}{\rm the~ohmic~drop~through~the~hardware}$ 

#### Typical Components of Water Electrolyser Cell Voltage (150 mA cm<sup>-2</sup>; 75°C)

```
E_{rev.}^{o} = 1.19 V

\eta_{c}=0.30V

\eta_{a}=0.30V

\eta_{\Omega}=0.25V (anode-cathode gap ~4mm)

\eta_{hw}=0.11V

Cell voltage=2.15V
```

J. O'M. Bockris, Brian E. Conway, Ernest Yeager, and Ralph E. White, Comprehensive Treatise of Electrochemistry Volume 2: Electrochemical Processing (1981)

## Hydrogen evolution reaction (HER) activity



Volcano plot

## Exchange current density, *i*<sub>o</sub>

 $i_o$  is termed exchange current density which is the rate of oxidation and reduction at equilibrium.

There is no net current under the above conditions even through the concept is a useful method of representing rates at equilibrium.

 $i_o$  for H<sup>+</sup>/H<sub>2</sub> reaction  $2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$ 



Exchange current densities are determined experimentally.



## Hydrogen Evolution Reaction (HER)

It is generally accepted that the hydrogen evolution reaction in alkaline solutions takes place through the following three steps :

The first step is the formation of the adsorbed hydrogen on the metal

 $H_2O + M + e \Leftrightarrow MH_{ads} + OH^-$  (Volmer step)

The second step is formation of hydrogen gas by desorption of the adsorbed hydrogen with reduction of water molecule.

 $MH_{ads} + H_2O + e \Leftrightarrow M + OH^- + H_2$  (Heyrovsky step)

The third step is the formation of hydrogen gas by chemically desorption of the adsorbed hydrogen.

 $2MH_{ads} \leftrightarrow 2M + H_2$  (Tafel step)

The strength of metal hydrogen bond has a key role in the reaction mechanism and in the rate of hydrogen evolution.

## **Oxygen Evolution Reaction (OER)**



(a) The OER mechanism in alkaline conditions. (b) Volcano plot showing activity for O2 production on catalysts surfaces versus the enthalpy changes of catalysts in acidic (■) and basic (□) solutions.



 $40H^{-}(aq) \rightleftharpoons H_2O(l) + O_2(g) + 4e^{-}$ 

Jia-Xin Li, Li-Gang Feng, 2022, J. Electrochem. 2022, 28(9), 2214001

## Electrode electrolyte interface



$$O + e^- \rightleftharpoons R$$



## **Decomposition Potential**

## FARADAY LAW & ELECTROLYZER

- Faraday's laws: The relationship between the amount of matter that is changed at the electrodes and the amount of current flowing through the circuit is given by two expressions known as Faraday's laws.
- 1. In an electrolysis system, the amount of matter changed at the electrodes is directly proportional to the amount of electricity passing through the circuit.
- 2. The same amount of electricity causes the same equivalent amounts of matter conversion at the electrodes.

$$i \text{ (amperes)} = \frac{dQ}{dt} \text{ (coulombs/s)}$$
$$\frac{Q}{nF} \frac{\text{(coulombs)}}{\text{(coulombs/mol)}} = N \text{ (mol electrolyzed)}$$

$$N_{mol\ electrolyzed} = \frac{It}{nF}$$

$$N_{mole\ electrolyzed} = \frac{Q}{nF}$$
$$N_{mole\ electrolyzed} = \frac{It}{nF}$$

m: mass of the electrolyzed
M: molar mass
Q: charge (coulomb)
n: mole electron
F: 96485 C mol<sup>-1</sup>
t: time

$$m = \frac{QM}{nF}$$
$$m = \frac{ItM}{nF}$$

Calculation the hydrogen mole and mass for 1 A current to pass the water electrolyzer for 1 hour.

$$\begin{split} N_{mole\ electrolyzed} &= \frac{Q}{nF} \qquad N_{mole\ electrolyzed} = \frac{It}{nF} \\ n_{H_2} &= (1.0A) \left(\frac{1 coulomb/sec}{1A}\right) \left(\frac{1\ mol\ e^-}{96485\ coulombs}\right) \left(\frac{1\ mol\ H_2}{2\ mol\ e^-}\right) \left(\frac{3600sec}{1hr}\right) \\ &= 0.018655\ mol\ H_2(per\ 1A) \end{split}$$

$$m = \frac{QM}{nF} \qquad m = \frac{ItM}{nF}$$
$$m_{H_2} = (0.018655molH_2) \left(\frac{2.0157gH_2}{1 molH_2}\right) = 0.0376 \frac{gH_2}{1A}$$

Calculation the produced hydrogen mole and mass for a 2kW water electrolyzer for 1 hour. The single cell potential is taken 2.1 V

$$I = \frac{P}{V} = \frac{2000W}{2.1V} = 952.38A$$
  $m = \frac{ItM}{nF}$ 

$$m_{H_2} = (952.38A) \left( 0.0376 \frac{gH_2}{1A} \right) = 35.80 \ gH_2$$

$$n_{H_2} = 35.80 \ gH_2 \left(\frac{1 \ molH_2}{2.0157 \ gH_2}\right) = 17.76 \ molH_2$$

Calculation of the required hydrogen mole and mass for a 2kW fuel cell. The single cell potential is taken at 0.9 V

$$I = \frac{P}{V} = \frac{2000W}{0.9V} = 2222.22A$$
 m

$$m_{H_2} = (2222.22A) \left( 0.0376 \frac{gH_2}{1A} \right) = 83.55 \ gH_2$$

$$n_{H_2} = 83.55 \ g_{H_2} \left( \frac{1 \ molH_2}{2.0157 \ g_{H_2}} \right) = 41.45 \ molH_2$$

ItM

nF

## Calculate the current amount required to produce 1 kg of H<sub>2</sub> for an hour.

$$m = \frac{ItM}{nF}$$

Cathode reaction :  $2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$   $E^o = -0.828V$  SHE Anode reaction :  $2OH^-(aq) \rightleftharpoons H_2O(l) + 1/2O_2(g) + 2e^ E^o = +0.402V$  SHE **Overall reaction** :  $H_2O(l) \rightleftharpoons H_2(g) + 1/2O_2(g)$   $E^o_{rev} = 1.23V$ 

$$?A = 1kgH_2 \times \frac{1000 \ gH_2}{1 \ kg \ H_2} \times \frac{1 \ mol \ H_2}{2.016 \ g \ H_2} \times \frac{2 \ mol \ e^-}{1 \ mol \ H_2} \times \frac{96485 \ A.s}{1 \ mol \ e^-} \times \frac{1 \ h}{3600 \ s} = 26589 \ A$$

In the previous example, calculate the number of cells and required power for an alkaline electrolyzer system to produce hydrogen. (Electrode size  $10 \text{ cm}^2$ , Stack Resistance  $1 \Omega \text{ cm}^2$ , the optimal potential for electrolyzers is 2.0 V for each stack) (26589 A required for  $1 \text{ kg H}_2/1 \text{ hour}$ ) Stacks can be designed with parallel or series connections according to requirements and maximum electrical capacities. The efficiency of the electrolyzer is neglected.

#### Optimal Stack Resistance 1.0 $\Omega$ cm<sup>2</sup> for each stack.

 $V = I \times R$ 

$$I = V/R = 2.0 V / 1.0 \Omega cm^2 = 2.0 A cm^{-2}$$
 each stack

Stack Current =  $2.0 \text{ A cm}^{-2} \times 10 \text{ cm}^{2} = 20.0 \text{ A}$ 

26589/20.0= **1330 Cell required** 

 $P=A \times V$ 

P=26589 A x 2.0 V = 53177 W=53.2 kW

## **Type of water electrolyzer** *for large scale green hydrogen production*

#### Water Electrolyzers Type









Anode

2H,0

Anode:  $20^2 \leftrightarrow 0_2 + 4e^2$ 

Cathode: 2H,0+4e<sup>-</sup>↔2H,+2O<sup>2-</sup>

Cathode

g 2H2O





#### **Components of water electrolysers**

	Alkaline	PEM	AEM	Solid Oxide
Operating temperature	70-90 °C	50-80 °C	40-60 °C	700-850 °C
Operating pressure	1-30 bar	< 70 bar	< 35 bar	1 bar
Electrolyte	Potassium hydroxide (KOH)	PFSA membranes	DVB polymer support with	Yttria-stabilized Zirconia (YSZ)
	5-7 molL'		KOH or NaHCO3 1molL <sup>-1</sup>	
Separator	ZrO <sub>2</sub> stabilized with PPS mesh	Solid electrolyte (above)	Solid electrolyte (above)	Solid electrolyte (above)
Electrode / catalyst (oxygen side)	Nickel coated perforated stainless steel	Iridium oxide	High surface area Nickel or NiFeCo alloys	Perovskite-type (e. <i>g.</i> LSCF, LSM)
Electrode / catalyst (hydrogen side)	Nickel coated perforated stainless steel	Platinum nanoparticles on carbon black	High surface area nickel	Ni/YSZ
Porous transport layer anode	Nickel mesh (not always present)	Platinum coated sintered porous titanium	Nickel foam	Coarse Nickel-mesh or foam
Porous transport layer cathode	Nickel mesh	Sintered porous titanium or carbon cloth	Nickel foam or carbon Cloth	None
Bipolar plate anode	Nickel-coated stainless steel	Platinum-coated titanium	Nickel-coated stainless steel	None
Bipolar plate cathode	Nickel-coated stainless steel	Gold-coated titanium	Nickel-coated Stainless steel	Cobalt-coated stainless steel
Frames and sealing	PSU, PTFE, EPDM	PTFE, PSU, ETFE	PTFE, Silicon	Ceramic glass

Note: Coloured cells represent conditions or components with significant variation among different companies. PFSA = Perfluoroacidsulfonic; PTFE = Polytetrafluoroethylene; ETFE = Ethylene Tetrafluorethylene; PSF = poly (bisphenol-A sulfone); PSU = Polysulfone; YSZ = yttriastabilized zirconia; DVB = divinylbenzene; PPS = Polyphenylene sulphide; LSCF =  $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3-\delta$ ; LSM =  $(La_{1-x}Sr_x)_{1-y}MnO_3$ ; § = Crofer22APU with co-containing protective coating.



		20	20			20	50	
	Alkaline	PEM	AEM	SOEC	Alkaline	PEM	AEM	SOEC
Cell pressure [bara]	< 30	< 70	< 35	< 10	> 70	> 70	> 70	> 20
Efficiency (system) [kWh/KgH <sub>2</sub> ]	50-78	50-83	57-69	45-55	< 45	< 45	< 45	< 40
Lifetime [thousand hours]	60	50-80	> 5	< 20	100	100-120	100	80
Capital costs estimate for large stacks (stack-only, > 1 MW) [USD/kW <sub>el</sub> ]	270	400	-	> 2 000	< 100	< 100	< 100	< 200
Capital cost range estimate for the entire system, >10 MW [USD/kW <sub>el</sub> ]	500- 1000	700- 1400	-	-	< 200	< 200	< 200	< 300

Note: PEM = Polymer Electrolyte Membrane (commercial technology); AEM = Anion Exchange Membrane (lab-scale today); SOEC = Solid Oxide Electrolysers (lab-scale today). Key performance indicators for four electrolyzer technologies today and in 2050.

Innovation is crucial to reduce costs and improve the performance of the electrolyzer.

#### The ultimate goals are to:

- reduce cost by standardizing and simplifying manufacturing and design to allow for industrialization and scale-up;
- improve efficiency to reduce the amount of electricity required to produce one unit of hydrogen;
- increase durability to extend the equipment lifetime and spread the cost of the electrolyzer facility over a larger hydrogen production volume.

Based on IRENA analysis.



## Historic examples of large-scale electrolysis hydrogen production plants

Plant location (country, city)	Capacity (MW)	Commissioning year
Norway (Rjukan)	165	1929
Canada (Trail)	90	1939
Norway (Glomfjord)	160	1953
💶 India (Nangal)	125	1958
Peru (Cuzco)	25	1958
Egypt (Aswan)	160	1960
🔀 Zimbabwe (Que Que)	95	1974

#### Source: IRENA 2022

All of these plants except the plant in Peru have been closed or have switched to fossil fuels.



#### - By 1902, more the 400 industrial alkaline electrolysers

- Primarily for ammonia production (fertilizer industry)
- Plants based on low-cost hydroelectricity



Aswan Dam – Egypt

#### Aswan Electrolyser (KIMA) 165MW - 37000 m<sup>3</sup>H<sub>2</sub>/h



- The most popular and commonly used set of performance indicators used for water electrolyzers are
  - (i) the cell voltage (or the mean cell voltage for a stack of several cells)
    (ii) the specific energy consumption (in kWh per kg of hydrogen or per Nm<sup>3</sup> of hydrogen).
- The thermodynamic cell voltage equals 1.23 Volt in standard conditions, and the specific energy consumption is 2.94 kWh Nm<sup>-3</sup>.

- The cell efficiency is a function of the operating current density and temperature.
- A high operating current density is required to decrease capital expenses. Still, at the same time, a low current density is required to reduce operational expenses (the electric energy consumption per mass of produced hydrogen).
- A high operating temperature is preferable to reduce the electric energy consumption, but at temperatures about 100 °C, gas purity and separator lifetime are reduced.

## **Diaphragms (Seperators)**

- One of the key components of an alkaline water electrolysis cell is the diaphragm separator.
- Porous diaphragms based on asbestos  $(Mg_3Si_2O_5(OH)_4)$  were used for many decades, until the mid-1970s, before being banned due to health hazards.
- These materials were not stable enough, and their structure did not fully prevent the formation of gas mixtures.
- Various alternative diaphragm materials have been developed because asbestos is a toxic material and is permeable to dissolved gases and gas bubbles.



#### **Electrodes**

- Steel is used as a main cell frame material, and steel grids are often used as electrode materials.
- To improve the charge transfer kinetics (especially kinetics of anode reaction), these grids are covered with a layer of porous nickel produced by the leaching of zinc from the Ni-Zn alloy (Raney nickel).
- They are distinguished by high catalytic activity in the reaction of the cathodic evolution of hydrogen.

The main disadvantages of Raney nickel and alloys based on it are

- the manufacturer's complexity
- the degradation of the amorphous structure during operation.



### **Hydrogen Evolution Reaction (HER)**

- Ni-based alloys are widely used as catalysts for the cathodic hydrogen evolution reaction (HER).
- These such as NiCo, NiFe, NiMo, NiW, NiCu, NiAl, NiZn, NiMoFe, and



	Alkaline	PEM	
Operating temperature	70-90 °C	50-80 °C	
Operating pressure	1-30 bar	< 70 bar	
Electrolyte	Potassium hydroxide (KOH) 5-7 molL <sup>-1</sup>	PFSA membranes	1
Separator	ZrO <sub>2</sub> stabilized with PPS mesh	Solid electrolyte (above)	
Electrode / catalyst (oxygen side)	Nickel coated perforated stainless steel	Iridium oxide	
Electrode / catalyst (hydrogen side)	Nickel coated perforated stainless steel	Platinum nanoparticles on carbon black	
Porous transport layer anode	Nickel mesh (not always present)	Platinum coated sintered porous titanium	
Porous transport layer cathode	Nickel mesh	Sintered porous titanium or carbon cloth	
Bipolar plate anode	Nickel-coated stainless steel	Platinum-coated titanium	T.L.
Bipolar plate cathode	Nickel-coated stainless steel	Gold-coated titanium	
Frames and sealing	PSU, PTFE, EPDM	PTFE, PSU, ETFE	

#### HER catalysts studies (1M KOH)

Catalyst	Tafel slope	Current	Overpoten	Reference
	(mV/dc)	Density (mA	tial η (mV)	
		cm <sup>-2</sup> )		
FeNiP/NF	119.1	20	183	Li et al., 2020
Ni-MoO <sub>2</sub>	120	10	93	Faid et al., 2021
NiCoO-NiCo/C	69	10	123	Park et al., 2021
Gd-CeO <sub>2</sub>	211	10	99	Swathi et al., 2022
FeSe/NF	145	10	200	Chandan et al.,
				2020
FeSe <sub>2</sub> /CoFe <sub>2</sub> O	88.76	10	231	Zhang et al., 2020
NiFe-MOF		10	163	Mou et al., 2021
Ni–Fe–S	108	10	115	Yin et al <i>,</i> 2021
ZnCoNi/(Ppy/CNTs) <sub>4</sub>	127.1	10	189	Lu et al., 2022
NCNT/NiNiMn <sub>2</sub> O <sub>4</sub> /N	76	10	188	Qin et al., 2019
R-Mn-CoP	54	10	117	Li et al ., 2021
R-Mn-CoP@Mn-CoOOH	45		110	
NCNT/NiNiFe <sub>2</sub> O <sub>4</sub> /Ni	85	10	140	Qin et al., 2019

### **Oxygen Evolution Reaction (OER)**

- Nickel electrodes with a highly developed surface such as Raney nickel, and porous nickel electrodes possess high catalytic activity.
- Low overpotential of oxygen evolution is noted on Ni-Fe, Ni-Co alloys, as well as mixed oxides such as spinel or perovskite.

	Alkaline	PEM
Operating temperature	70-90 °C	50-80 °C
Operating pressure	1-30 bar	< 70 bar
Electrolyte	Potassium hydroxide (KOH) 5-7 molL <sup>-1</sup>	PFSA membranes
Separator	ZrO <sub>2</sub> stabilized with PPS mesh	Solid electrolyte (above)
Electrode / catalyst (oxygen side)	Nickel coated perforated stainless steel	Iridium oxide
Electrode / catalyst (hydrogen side)	Nickel coated perforated stainless steel	Platinum nanoparticles on carbon black
Porous transport layer anode	Nickel mesh (not always present)	Platinum coated sintered porous titanium
Porous transport layer cathode	Nickel mesh	Sintered porous titanium or carbon cloth
Bipolar plate anode	Nickel-coated stainless steel	Platinum-coated titanium
Bipolar plate cathode	Nickel-coated stainless steel	Gold-coated titanium
Frames and sealing	PSU, PTFE, EPDM	PTFE, PSU, ETFE

#### OER catalysts studies (1M KOH)

Catalyst	Tafel slope	Current Density	<b>Overpotential</b> η	Reference
	(mV/dc)	(mA cm <sup>-2</sup> )	(mV)	
NiFe-LDH/CoO <sub>4</sub> NF	81	50	274	Zhang et al., 2022
RuO <sub>2</sub> /CeO <sub>2</sub>	74	10	350	Galani et al., 2019
FeSe/NF	109	100		Chanda et al., 2020
Gd-CeO <sub>2</sub>	183	10	369	Swathi et al., 2022
PA-Gd-Ni(OH) <sub>2</sub> Cl	40	10	220	Haq et al.,2020
Gd-NiFe-LDH@CC	40.9	10	210	Li et al., 2020
FeCo@C	75	10	302	Wu et al., 2020
		50	423	
NiFe-MOF	42	10	168	Mou et al., 2021
Ni–Fe–S	41	10	223	Yin vd., 2021
ZnCoNi/(Ppy/CNTs) <sub>4</sub>	123.1	10	189	Lu et al., 2022
NCNT/Ni-NiMn2O4	89	10	300	Qin et al., 2019
NCNT/Ni-NiFe2O4/N	51	10	250	Qin et al., 2019
R-Mn-CoP@ Mn-CoOOH	72	10	251	Li et al., 2021



https://www.finh2.fi/electrolyser-technologies/



https://gfycat.com/uk/gentlehonestkentrosaurus

## Alkaline Water Electrolyzer

- Alkaline electrolysis stack (most common) materials
- Diaphragm: ZIRFON
- Electrolyte: potassium hydroxide (KOH)
- Electrode catalysts: nickel mesh
- Bipolar plates: nickel-coated stainless steel
- Alkaline electrolyser system components
- Stack
- O<sub>2</sub>-liquid separator
- H<sub>2</sub>-liquid separator
- Electrolyte pumps + heat exchangers
- H<sub>2</sub> purification system
- Water treatment system
- Power electronics + automation system



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## **PEM Water Electrolyzer**

- PEM electrolysis stack (most common) materials
- Proton exchange membrane: Nafion<sup>®</sup>
- Electrode catalysts: ٠
  - Anode catalyst: iridium oxide (IrO<sub>2</sub>)
  - Cathode catalyst: platinum (Pt)
- PTL, porous transportation layers: •
  - Anode: titanium (Ti)
  - Cathode: carbon paper (C), titanium (Ti)
- Bipolar plates:
  - Anode: titanium (+ platinum coating)
  - Cathode: titanium (+ gold coating)

#### **PEM electrolyser system components**

•Stack

•Anode side: water purification unit, water circulation pump, ion exchange filters, heat exchanger,  $O_2/H_2O$  separation unit •Cathode side:  $H_2/H_2O$  separation unit,  $O_2$  removal unit from product hydrogen, drying unit •Power electronics (grid electricity DC) 53 Automation system

## Solid Oxide Electrolyzers



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- SOEC electrolysis stack (most common) materials
- Electrolyte: YSZ
- Fuel electrode: Ni + YSZ
- Air/O<sub>2</sub> electrode: LSC, LSM, LSCF
- Interconnect plate: Crofer and other high-temperature ferritic stainless steels with protective coating
- Seals: glass, glass-ceramic, mica
- SOEC electrolyser system components
- Stack
- Steam generator
- Air blower
- Fuel recycling pump
- Heat exchangers + condensers
- Supporting structures + piping (gas and stack max. temperature 700-800 °C)
- High temperature insulation materials
- Power electronics + automation system

### AEM Water Electrolyzer



- One alternative electrolysis technology being researched is anion exchange membranes (AEMs), in which the separating membrane allows negatively charged OH<sup>-</sup> ions to pass through instead.
- These are attracted to the anode, where they combine to form oxygen and water molecules, as the hydrogen atoms gravitate to the cathode for collection as  $H_2$  gas.

AEMs can operate under alkaline conditions, so they don't need noble metals – the materials involved are, thus, some 3000 times less expensive.

A relatively young technology, AEMs have not found commercial success in hydrogen electrolysis

#### How sustainable hydrogen energy works:



Electrolysis is a sustainable and environmentally friendly method of producing green hydrogen using renewable electricity sources, such as solar or wind power.



Water can be transported to the anode side by the solvated species and charges. A mixing pipe is also installed between the anode and cathode water/gas separator to balance the OH- charges consumed/ produced and the electrochemical reaction.

Equipment around the electrolyser is affected by technology choice. There needs to be an integrated design for various components to achieve a low cost while satisfying demand requirements

The requirement to balance the charges between anode and cathode makes the stack more challenging to operate at differential pressures, as in PEM.

For the high-pressure configuration, more resistance cell frames and balance of plant (BoP) materials are needed, which impact on CAPEX.

#### Typical system design and balance of plant for an alkaline electrolyser.



Note: This configuration is for a generic system and might not be representative of all existing manufacturers.

Based on IRENA analysis.

#### Water and land use for green hydrogen production

 Green hydrogen production uses water as a key feedstock and renewable electricity as an energy source to separate hydrogen and oxygen from water in an electrolyser.

Water use is not a barrier to scaling up electrolysis. Even in places with water stress, seawater desalination can be used with limited penalties on cost or efficiency

- Water, as pure as possible, is, therefore a key input.
- While the purity level required varies depending on the technology, the cost of water purification is marginal, starting from desalinated sea water (well below USD 1/cubic metre (m3) of water (Reddy and Ghaffour, 2007)).
- Impurities in the water, however, will have a major impact on the lifetime of the electrolyser stack which can in turn affect hydrogen cost by increasing the annuity of the electrolyser in the cost of hydrogen.
- In addition to desalination costs, the need for any water treatment in the electrolyser stack requires additional costs (e.g. deioniser).
- These can potentially become significant, depending on the purity level required, but are still of low impact on the overall cost of hydrogen, as in general they remain around USD 1/m3 (Hand, Guest and Cusick, 2019), or less than USD 0.01/kg H2.

## A brief look at the historical development of electrolysers

Electrolysers have been known for over two centuries. While the fundamental technology has remained the same, different trends have affected its development, with these splitting the period into roughly five generations.



Based on IRENA analysis.



As a result, many large scale electrolysers will be operation in near future to produce green hydrogen as a fuel and also feed stock.



Arsad AZ et al., Int J Hydrogen Energy, https://doi.org/10.1016/j.ijhydene.2022.11 .023



SECOND EDITION



VOLUME 4 Fuel Cells and Hydrogen Technology

Comp	rehensive
Treati	se of
Electr	<i>cochemistry</i>
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Volume 1 THE DOUBLE LAYER Volume 2 ELECTROCHEMICAL PROCESSING Volume 3 ELECTROCHEMICAL ENERGY CONVERSION AND STORAGE Volume 4 ELECTROCHEMICAL MATERIALS SCIENCE

#### Thank you very much for your attention

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