Modeling and Control of Electrolyzers

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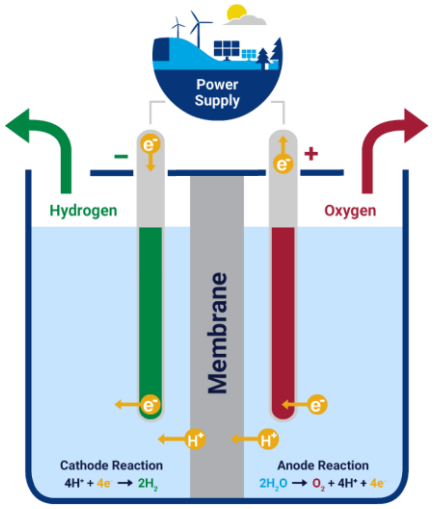
Summary

- Introduction
- Mathematical model of PEM electrolyzers
  - Static Electrochemical models
  - Dynamic Electrochemical models
  - Thermal models
- Efficiency
- Degradation

Water Electrolysis

$$H_2O(liquid) + electricity \rightarrow H_2(gas) + \frac{1}{2}O_2(gas)$$



- The molecules of water are split under the influence of the electric current resulting in the production of hydrogen and oxygen gases

- A water electrolysis system consists of:
  - two electrodes, one where oxidation takes place (anode) and at the other, the reduction reaction (cathode)
  - Electrolyte
  - Membrane to separate the produced gases
  - Direct Current (DC) power source

Electrolyzer Technologies

	Alkaline (AWE)	Polymeric PEM	Anionic AEM	Solid Oxid SOE
Advantages	Well stablished technologiy	High current densities	Advantages of PEM and AWE	It can be used as fuel cell
	Low capital cost	High voltage efficiency	Cheap components	High efficiency
	Stacks in the MW range	High operating pressures	High operating pressures	High operating pressures
	Long term stability	Rapid system response	Rapid system response	
		Compact and simple design	Compact and simple design	
		High H_2 purity		
Disavantages	Low H_2 purity	Use noble materials	Low membrane stability	Unstable electrodes
	Slow startup	High membrane cost	Low lifetime	Bulky system design
	Low current density	Low durability	Low current densities	Brittle material (ceramic)
	Corrosive liquid electrolyte	Acidic corrosive environment	Preliminary commercial status	Laboratory status
	Low operational pressures	Stacks below MW range		
	Slow dynamics			

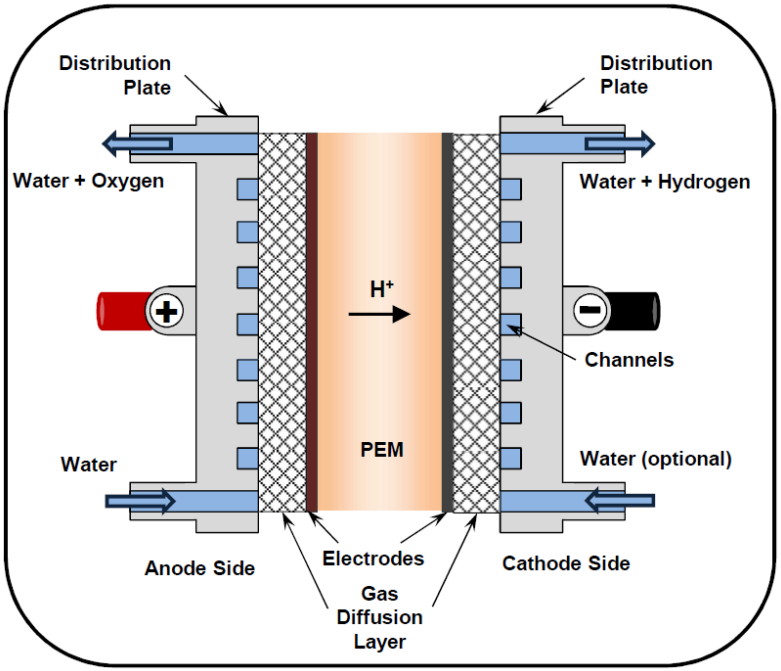
Technologies comparison

Specification	PEM	AWE	AEM	SOE
Maturity	Commercial	Commercial	Commercial	Early Commercial
Charger carrier	H^+	OH^-	OH^-	O^{2-}
Electrolyte	Solid polymer	Aqueous solution 10-40% KOH/NaOH	Solid polymer	Solid ceramic
Working fluid	Distilled water	High concentration solution	Distilled water or Low concentration solution	Steam
Anode material	Pt; Ir; Ru	Ni	Ni-based alloy	LSMYSZ; $CaTiO_3$
Cathode material	Pt; Pt-C	Ni alloys	Ni, Ni-Fe, $NiFe_2O_4$	Nicermets
Temperature, °C	70-90	65-100	50-70	650-1000
Operation pressure.	15-30 bar	2-10 bar	up to 35 bar	<30 bar
Efficiency, HHV	67-84%	62-82%	-	~90%
Cell voltage	1.80- 2.40 V	1.80- 2.40 V	~ 1.85 V	0.95- 1.30 V
Current density	0.6-2 A/cm^2	0.2- 0.4 A/cm^2	0.1-0.5 A/cm^2	0.3- 1 A/cm^2
Startup duration	<15 minutes	15 minutes	-	>60 minutes
Stack lifetime	< 40,000 hr	< 90,000 hr	> 10,000 hr	< 40,000 hr
Energy consumption, kWh/Nm^3	4.5-7.5	4.5-7	~ 4.8	2.5-3.5
Estimated cost by 2050.	~$750/kWch	~$600/kWch	-	~$200/kWch

A review of water electrolysis–based systems for hydrogen production using hybrid/solar/wind energy systems. M. Nasser *et al*. Environmental Science and Pollution Research (2022)

Proton Exchange Membrane Electrolyzer (PEM)

$$\text{Anode}: H_2O \rightarrow 2H^+ + \tfrac{1}{2}O_2 + 2e^-$$
$$\text{Cathode}: 2H^+ + 2e^- \rightarrow H_2$$



- Electrolite: Thin solid membrane
- Water is fed to the anode side of the cell where is reduced to oxygen, hydrogen protons and electrons.
- Oxygen is removed with the unconsumed water.
- Protons move through the electrolyte membrane towards the cathode where hydrogen gas is formed and removed

Proton Exchange Membrane Electrolyzer (PEM)

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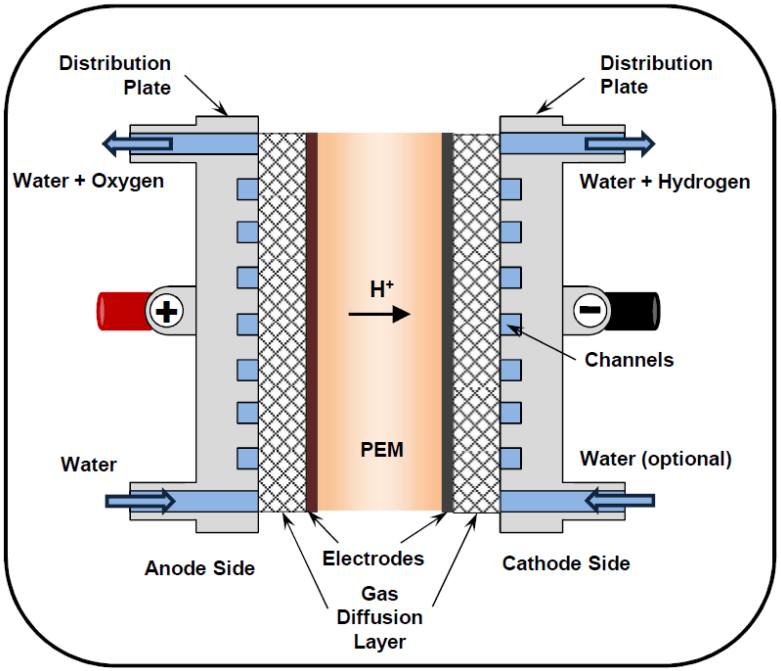
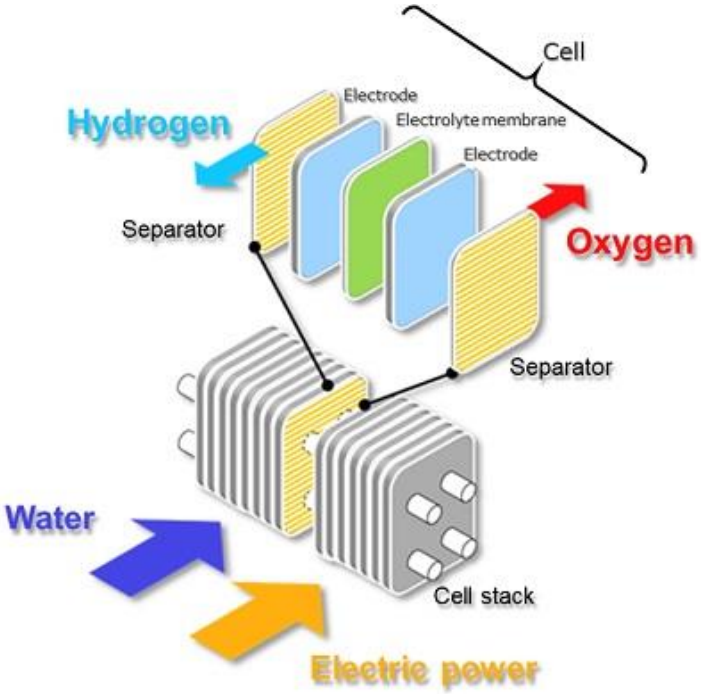
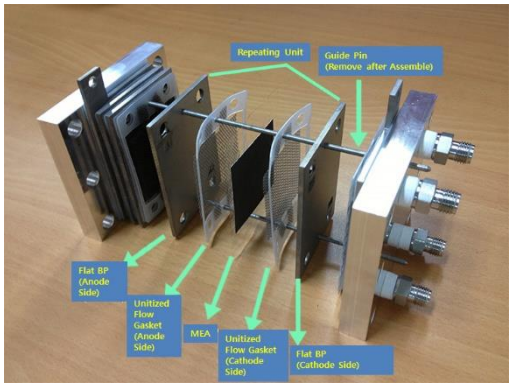
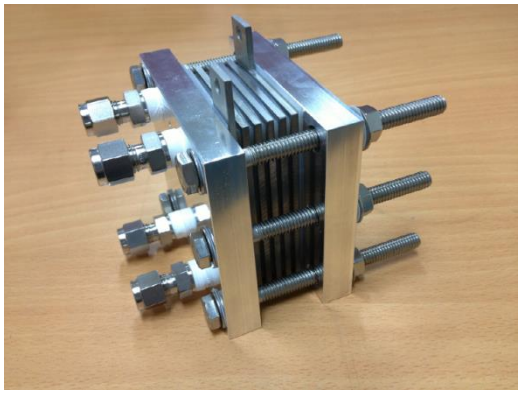


- Greater safety and reliability over AWE (no caustic electrolyte).
- Operate at high differential (produced hydrogen at the required pressure for storing)
- Faster startup times, very fast dynamic load change during its operation (more adequate for intermittent energy sources).
- Can operate at higher current densities.
- Membrane is the key limiting factor for the lifetime (degradation with the impurities in the water).
- Cost is high (noble metals are used as catalyst due to acidic environment)

Cells and stack



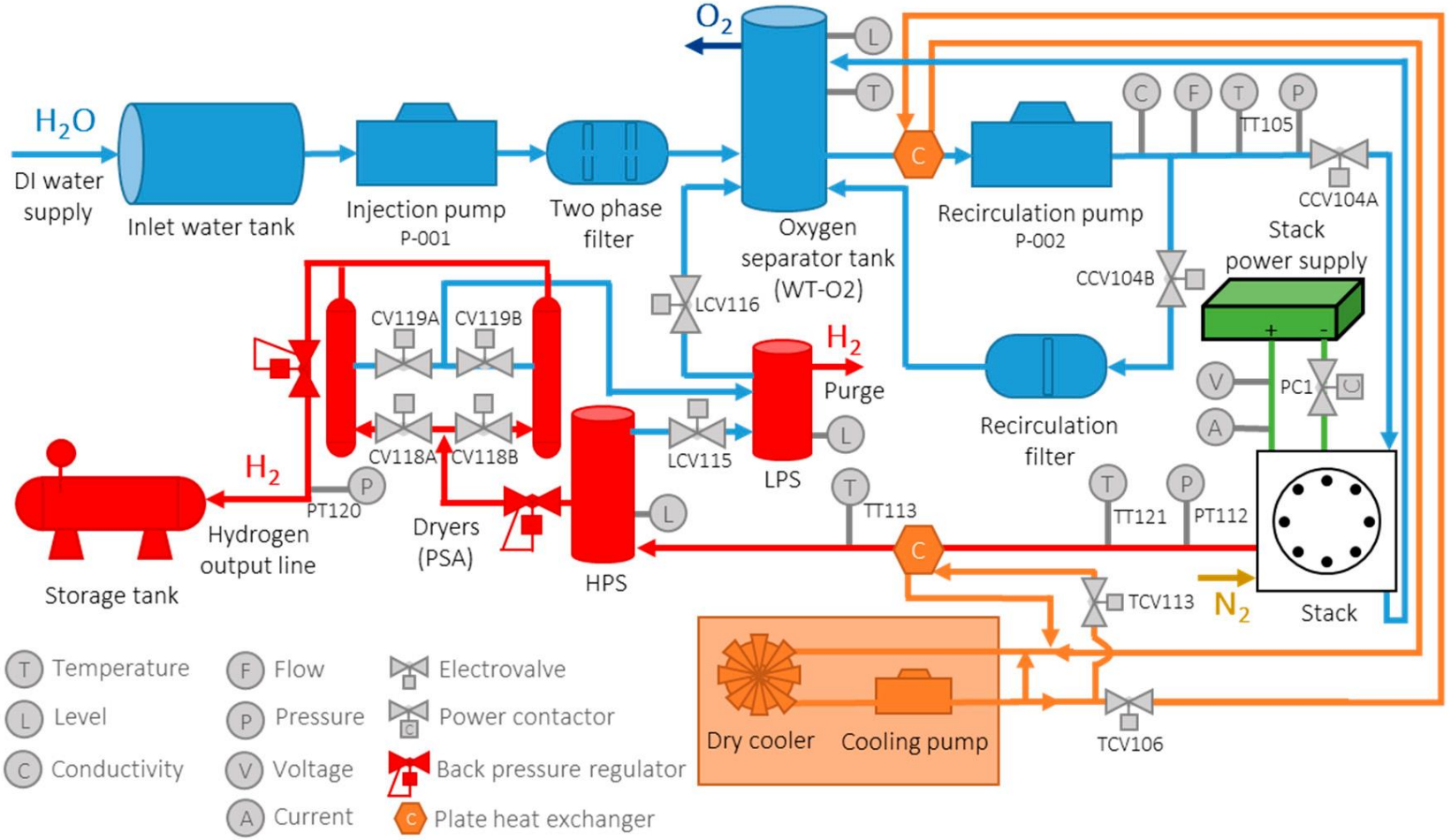




PEM Stack

3.2 MW Alkaline Stack

Balance of Plant (PEM)



An Optimized Balance of Plant for a Medium-Size PEM Electrolyzer: Design, Control and Physical Implementation. J.J. Caparrós *et al.* Electronics 2020, 9, 871

Summary

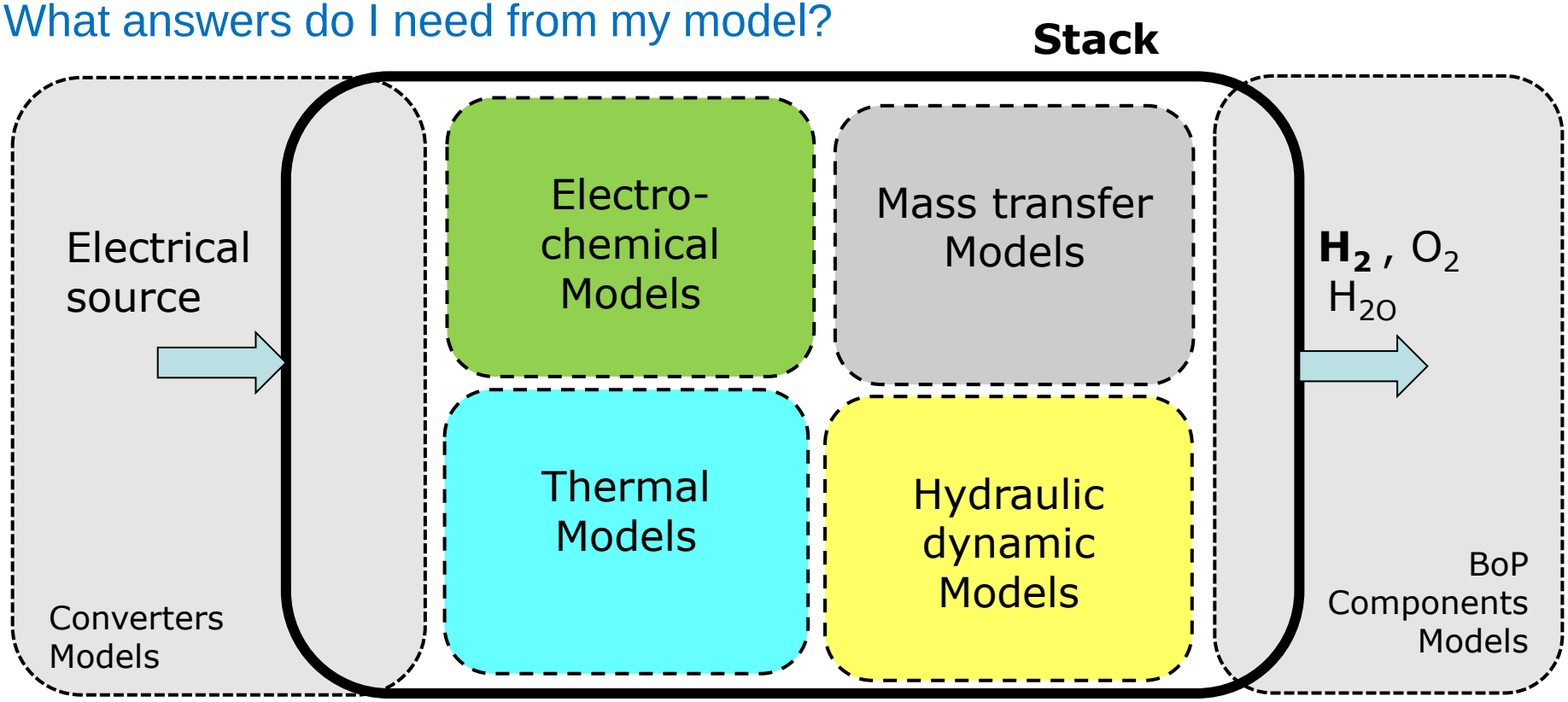
- Introduction
- **Mathematical model of PEM electrolyzers**
  - Static Electrochemical models
  - Dynamic Electrochemical models
  - Thermal models
- Efficiency
- Degradation

How to model an electrolyzer?

There is not a unique or simple answer to this question, previously:

What are the objectives of my models?

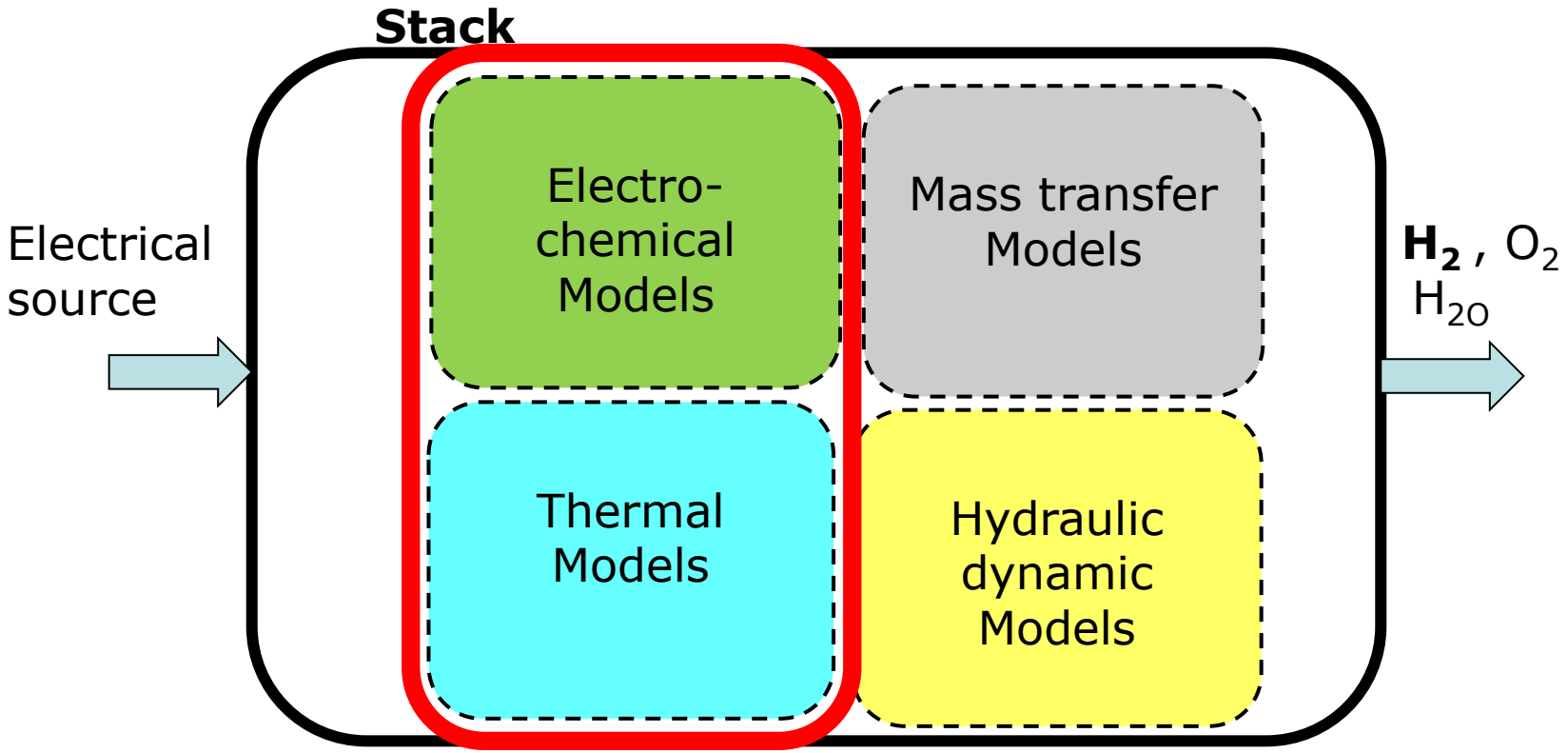
What answers do I need from my model?



Pierre Olivier et al. Low-temperature electrolysis system modelling: A review, Renewable and Sustainable Energy Reviews, Volume 78, 2017

Objective of the models

- Model for design and testing of control systems
- Mainly focused on Energy Management Systems

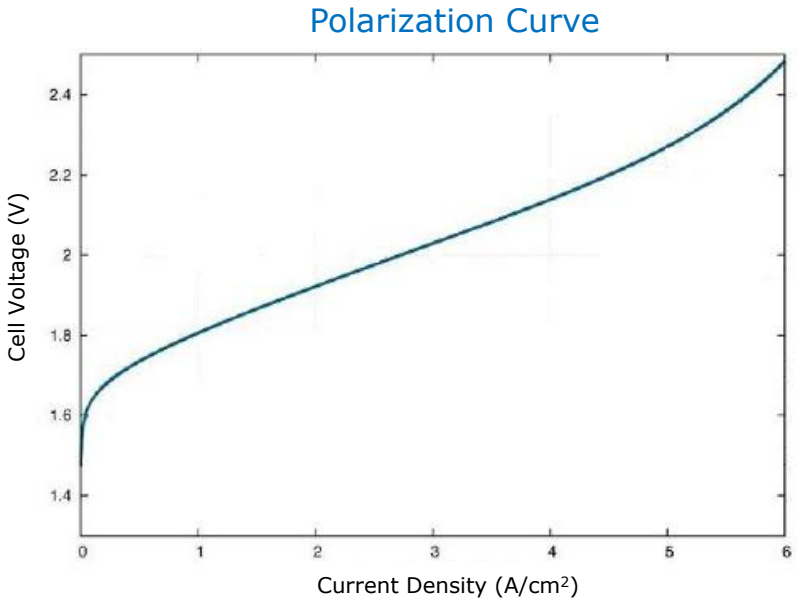


Pierre Olivier et al. Low-temperature electrolysis system modelling: A review, Renewable and Sustainable Energy Reviews, Volume 78, 2017

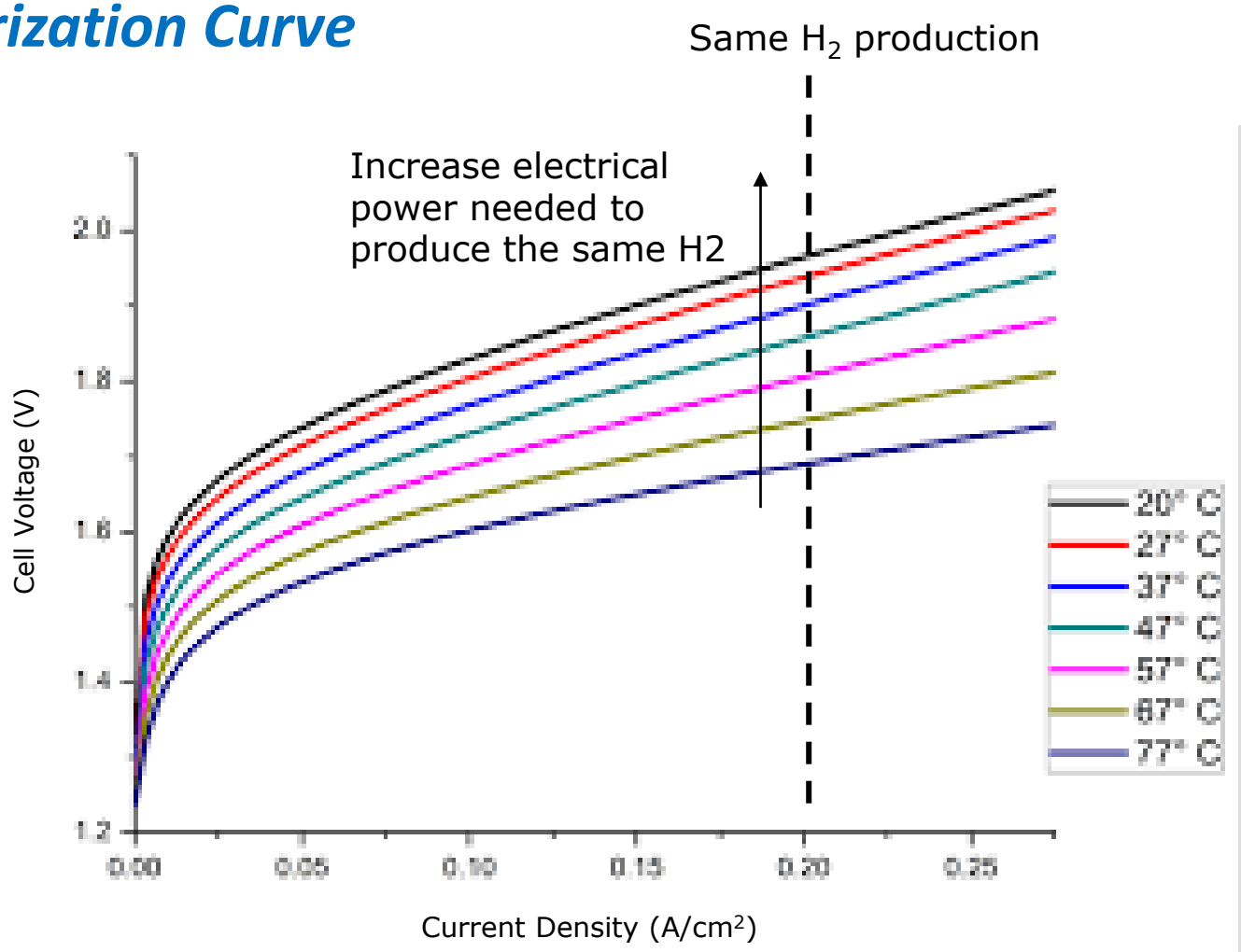
- **Model the electrical response of electrolisys cells (and stack) and the produced hydrogen**

➢ Simplifications:

- All the cells have the same electrical and termal behaviour
- Temperature homogeneity across the stack
- Oxygen and hydrogen behave as ideal gases. In addition, the gas and liquid phases are separated
- Electrochemical dynamics can be neglected, so a static model is used (algebraic equation)
- Drops and pressure effects are neglected



Polarization Curve



Static Electrochemical Model

Faraday´s Law: production rate of hydrogen is proportional to the cell current

$$\dot{n}_{H_2} = \frac{I_{cell}}{2\,F}\,\eta_F$$

η_F Faraday Efficiency
F Faraday Constant

Voltage equation: polarization curve

$$V_{cell} = V_{ocv} + V_{act} + V_{ohm} + V_{con}$$

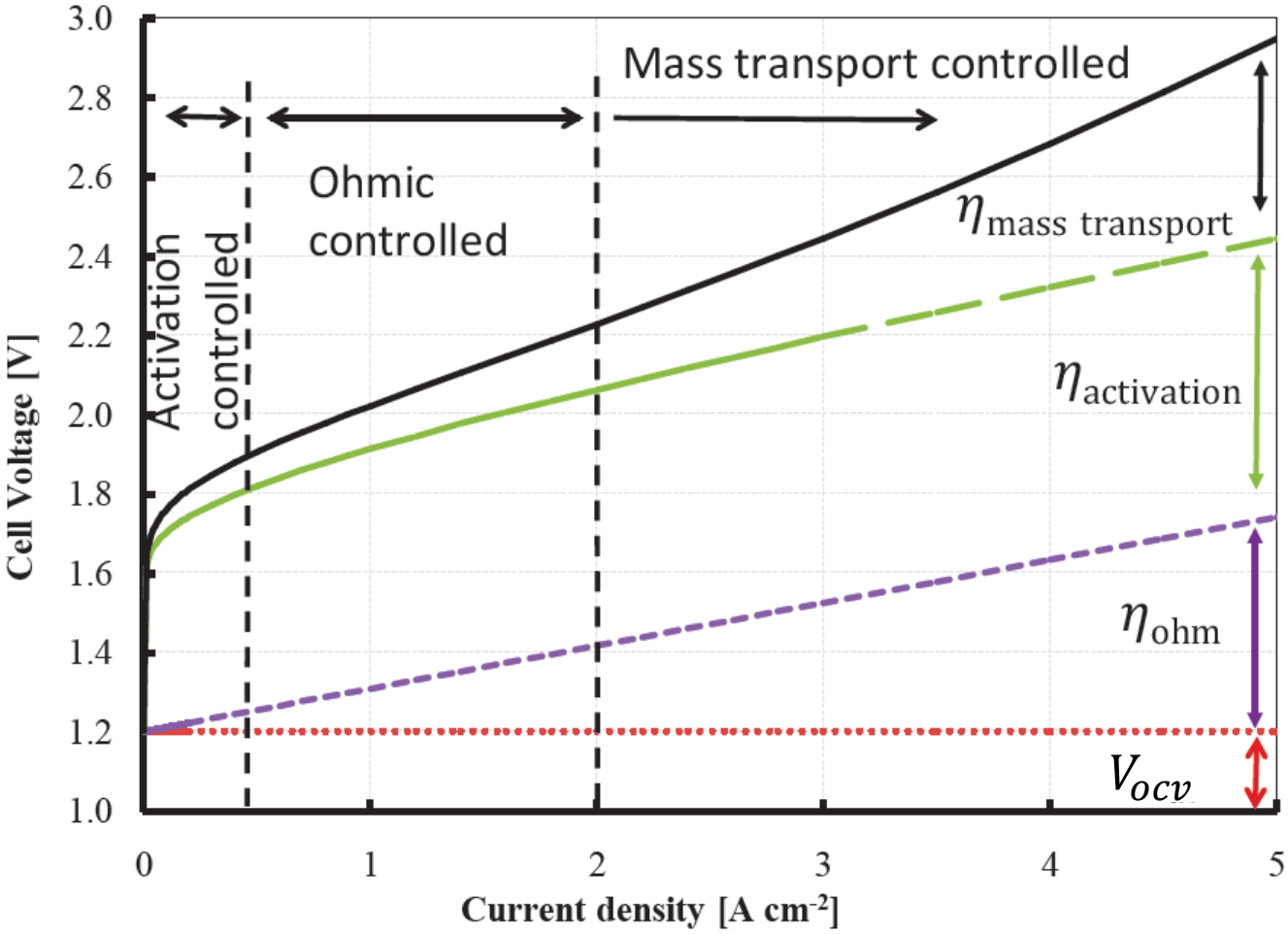
V_{ocv} Open circuit voltage
V_{act} Activation overvoltage
V_{ohm} Ohmic losses overvoltage
V_{con} Concentration overvoltage (mass transport losses)

In a stack with *n cells (in series):*

$$\dot{n}_{H_2} = \frac{n\,I_{el}}{2\,F}\,\eta_F$$

$$V_{el} = n\,(V_{ocv} + V_{act} + V_{ohm} + V_{con})$$

Static Electrochemical Model



Static Electrochemical Model

$$V_{cell} = V_{ocv} + V_{act} + V_{ohm} + V_{con}$$

The **Open Circuit Voltage (Nernst or Reversible voltage)** is the lowest potential level that facilitates the electrolysis process

Nernst Equation

$$V_{ocv} = E_0 + \frac{RT_{el}}{2F}\left[\ln\left(\frac{a_{H_2(g)}\, a_{O_2(g)}^{\frac{1}{2}}}{a_{H_2O(l)}}\right)\right]$$

T_{el} Temperature of electrolyzer (K)
a_i Activity of substance i
E_0 Reversible voltage (standard conditions)
R Universal Constant of gases (J/ mol K)

Standard reversible potential E_0:

Typically experimental equations

$$E_0 = 1.299 - 085 \cdot 10^{-3}(T_{el} - 298)$$

Other expressions for E_0:

$1,5184 - 1,5421.10^{-3}.T + 9,523.10^{-5}.T.\ \ln(T) + 9,84.10^{-8}.T^2$
$1,5241 - 1,2261.10^{-3}.T + 1,1858.10^{-5}.T.\ \ln(T) + 5,6692.10^{-7}.T^2$
$1,50342 - 9,956.10^{-4}.T + 2,5.10^{-7}.T^2$
$1,229 - 8,5.10^{-4}.(T - 298)$
$1,449 - 0,0006139.T - 4.592.10^{-7}.T^2 + 1.46.10^{-10}.T^3$

P. Olivier *et al*. Low-Temperatore electrolysis system modelling: A Review. Renewable and Sustainable Energy Reviews 78 (2017)

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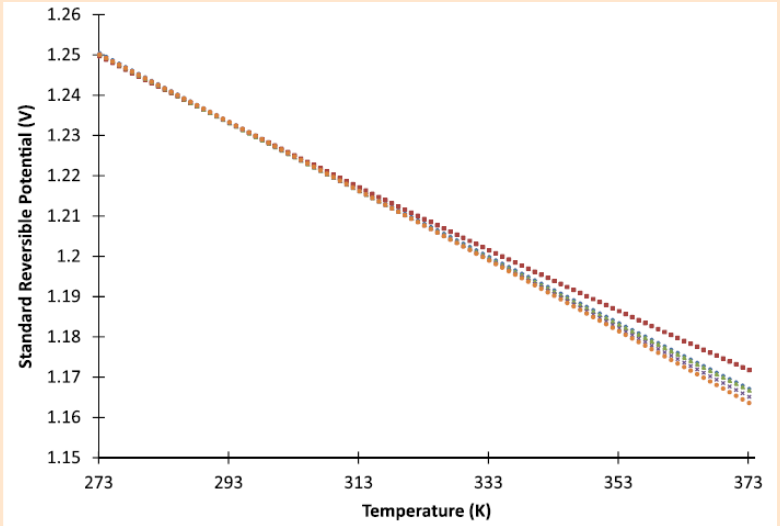

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Nernst Equation

$$V_{ocv} = E_0 + \frac{RT_{el}}{2F}\left[\ln\left(P_{H_2} \cdot P_{O_2}^{\frac{1}{2}}\right)\right]$$

Activities:

- For hydrogen and oxygen (gases), $a = p\ (bar)/p_0$, being $p_0 = 1\ bar$
- For water, it approaches 1

Standard reversible potential E_0:

Typically experimental equations

$$E_0 = 1.299 - 085 \cdot 10^{-3}(T_{el} - 298)$$

Other expressions for E_0:

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Static Electrochemical Model

$$V_{cell} = V_{ocv} + V_{act} + V_{ohm} + V_{con}$$

The **Activation Voltage** represents the voltage needed to overcome the reaction energy barriers to initiate a sufficiently high reaction rate

Simplification of Butler-Volmer Equation

$$V_{act} = V_{act,a} + V_{act,c}$$

$$V_{act,i} = \frac{RT_{el}}{\alpha_i F} \sinh^{-1}\left(\frac{i}{2i_{0,i}}\right), \qquad i = a, c$$

T_{el} Temperature of electrolyzer (K)
α_i Charge transfer coeficient
$i_{0,i}$ Exchange current density
i Electrolyzer current density

Parameters α_i , $i_{0,i}$

- Can be used for electyrolyzer characterization
- Typical Values:
  - $\alpha_a \approx 2$
  - $\alpha_c \approx 0.5$
  - $i_{0,a}$ [10^{-6} - 10^{-12}]
  - $i_{0,c}$ [10^{-5} - 10^{-1}]

L. Jarvinen *et* al. Automized parametrization of PEM and alkaline wáter electrolyzer polarization curves. International journal o f hydrogen Energy 47 (2022)

Static Electrochemical Model

$$V_{cell} = V_{ocv} + V_{act} + V_{ohm} + V_{con}$$

The **Ohmic Voltage** is due to resistances of different types, mainly ionic (electrolyte) and electric

Ohm's Law

$$V_{ohm} = i\,R_{ohm} = i\,(R_{elec} + R_{mem})$$

R_{elec} Electric resistente. Difficult to obtain experimentally. It can be neglected or used as a fit parameter

R_{mem} Ionic resistence. More significant than electric one

Ionic resistence R_{mem}

$$R_{mem} = \frac{100\,t_m}{\sigma_m}$$

t_m Membrane thickness

σ_m Conductivity

$$\sigma_m = (0.005139\,\lambda_m - 0.00326)\,e^{1268\left(\frac{1}{303} - \frac{1}{T_{el}}\right)}$$

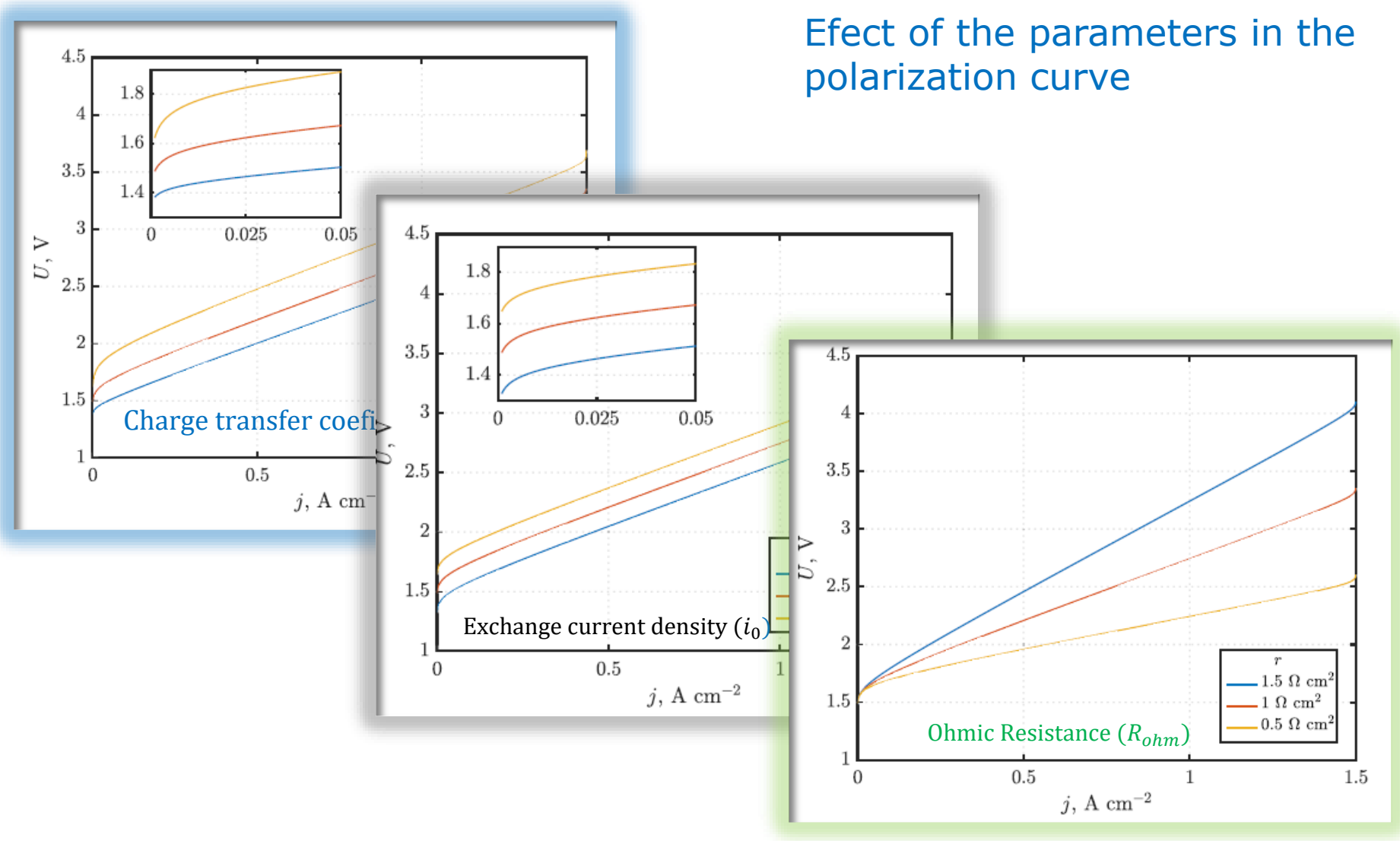
λ_m Water content of membrane.

. Typically in the range 7-14

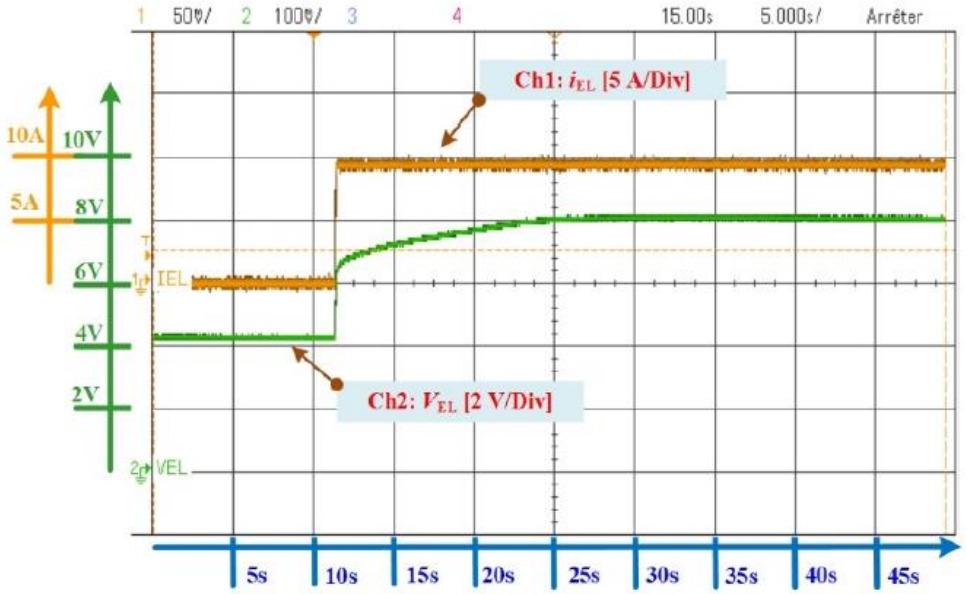
Springer TE, Zawodzinski TA, Gottesfeld S. Polymer electrolyte fuel cell model. JElectrochem Soc 1991;138:2334–42

Static Electrochemical Model

Efect of the parameters in the polarization curve



Dynamic Electrochemical Model



Response of voltage to a step input (current)

Voltage response:
Sudden rise followed by a slow rise before reaching the steady-state

The sudden voltage stack rise is related to the ohmic over-potentials

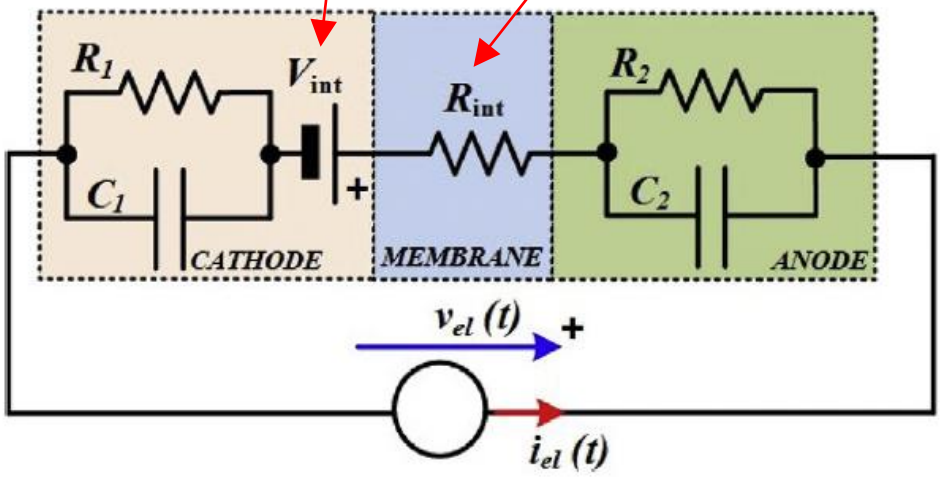
The slow rise is related to the activation over-potentials at the anode and cathode (related to the activation over-potentials)

The dynamics strongly depends on the current (the parameters of the model can not be considered constants)

A. Hernández-Gómez *et al.* Development of an adaptive static-dynamic electrical model based on input electrical energy for PEM water electrolysis, International Journal of Hydrogen Energy, Volume 45, Issue 38, 2020

Dynamic Electrochemical Model

$$V_{el} = V_{ocv} + V_{act} + V_{ohm}$$



$$V_{act} = V_{act,a} + V_{act,c}$$

$$\frac{dV_{act,a}}{dt} = \frac{1}{C_1} I_{el} - \frac{1}{\tau_1} V_{act,a}$$

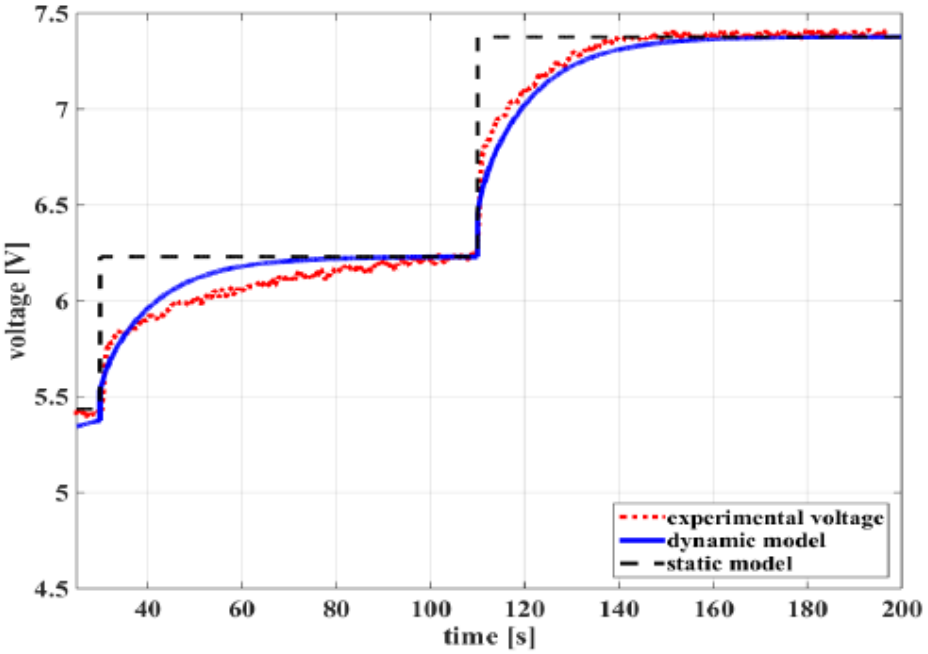
$$\frac{dV_{act,c}}{dt} = \frac{1}{C_2} I_{el} - \frac{1}{\tau_2} V_{act,c}$$

Parameters experimentally adjusted

A. Hernández-Gómez *et al.* Development of an adaptive static-dynamic electrical model based on input electrical energy for PEM water electrolysis, International Journal of Hydrogen Energy, Volume 45, Issue 38, 2020

Dynamic Electrochemical Model

Several works consider constant parameters, experimentally adjusted



$$\begin{cases} R_1 = 0.035\,\Omega; & C_1 = 37.26\,F \\ R_2 = 0.318\,\Omega; & C_2 = 37.26\,F \end{cases}$$

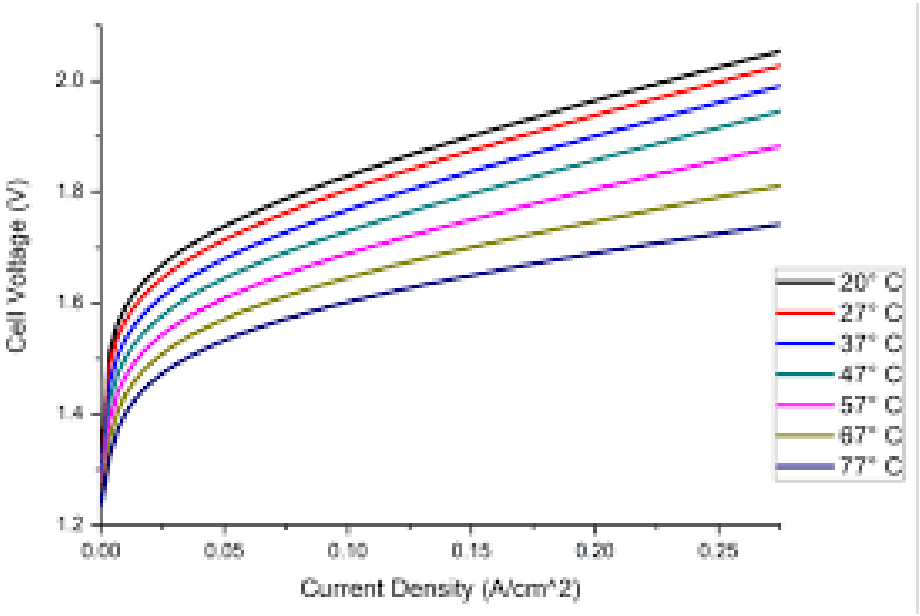
D. Guilbert *et al.* Experimental Validation of an Equivalent Dynamic Electrical Model for a Proton Exchange Membrane Electrolyzer *2018 IEEE Int. Conf. on Environment* Palermo, Italy, 2018,

B. Yodwong *et al*. Proton Exchange Membrane Electrolyzer Modeling for Power Electronics Control: A Short Review. *C Journal of CaA.rbon Research.* 2020

Thermal model

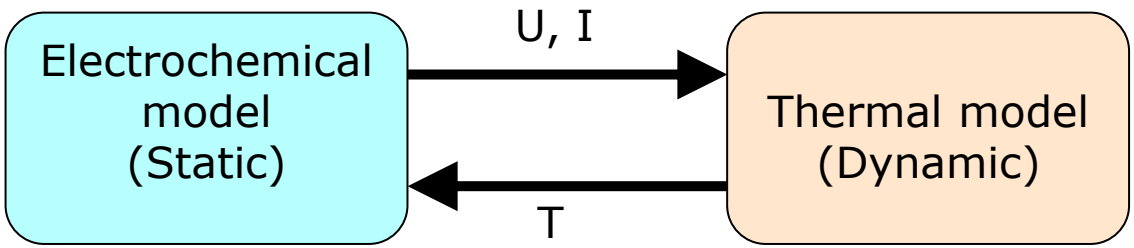
- Temperature has a beneficial impact on the global cell voltage.

- Temperature of the cell(s)/stack(s) appears in most of the electrochemical models presented before.



Thermal model

- Temperature has a beneficial impact on the global cell voltage.
- Temperature of the cell(s)/stack(s) appears in most of the electrochemical models presented before.
- Thermal dynamic is much slower than electrochemical dynamic: Model based on differential equations (ODE or PDE)
- Thermal models are coupled with electrochemical models in order to take into account the influence between electrical response and temperature in cells or stack.



Thermal model

$$C_t \frac{dT_{ez}}{dt} = \dot{Q}_{gen} - \dot{Q}_{loss} - \dot{Q}_{cool}$$

C_t Thermal capacity of the stack (J / K)

$\dot{Q}_{gen}$ Heat generated in the system due to the irreversibilities or overvoltages of the process

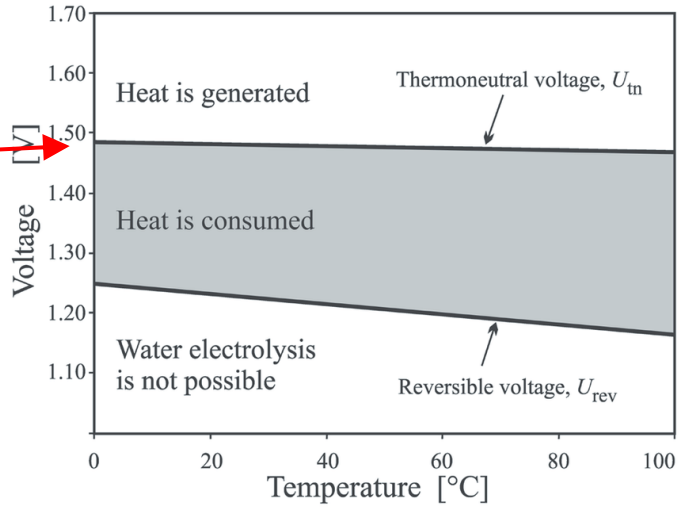
$\dot{Q}_{loss}$ *Heat that is lost by interaction with the environment by convection and radiation*

$\dot{Q}_{cool}$ *Heat that is dissipated by the cooling system*

$$\dot{Q}_{gen} = I_{el}(V_{cell} - V_{tn})n$$

$$V_{tn} \approx 1.48$$

$$\dot{Q}_{loss} = \frac{1}{R_t}(T_{el} - T_{amb})$$



C_t and R_t parameters to be adjusted

Thermoneutral voltaje: the heat generated from the electrolyser equals to the heat needed for the electrolysis to proceed,

$$V_{tn} = V_{HHV} + \frac{\Phi Y}{2F} = 1.4756 + 2.25 \cdot 10^{-4}\, t_{el} + 1.52 \cdot 10^{-8}\, t_{el}^2 + \frac{\Phi Y}{2F}$$

$$\Phi = 1.5 \frac{P_{w,sat}}{P_{el} - P_{w,sat}} \qquad P_{w,sat} = e^{\left(13.669 - \frac{8096.23}{T_{el}}\right)}$$

$$Y = 42960 + 40.762\, t - 0.06682\, t^2$$

V_{HHV} is *higher-high-value voltage*, t_{el}temperature of the electrolyser in ºC (T_{el} in Kelvin), P_{el} pressure of the electrolyser (bar), $P_{w,sat}$ partial pressure of water vapor (bar), Φ dimensionless coefficient, and Y coefficient with units J/mol.

Valverde, L. (2013). Energy *Management in Systems with Renewable Sources and Energy Storage Based on Hydrogen through Predictive Control* (Doctoral Thesis). University of Seville, Seville (Spain).

Summary

- Introduction
- Mathematical model of PEM electrolyzers
  - Static Electrochemical models
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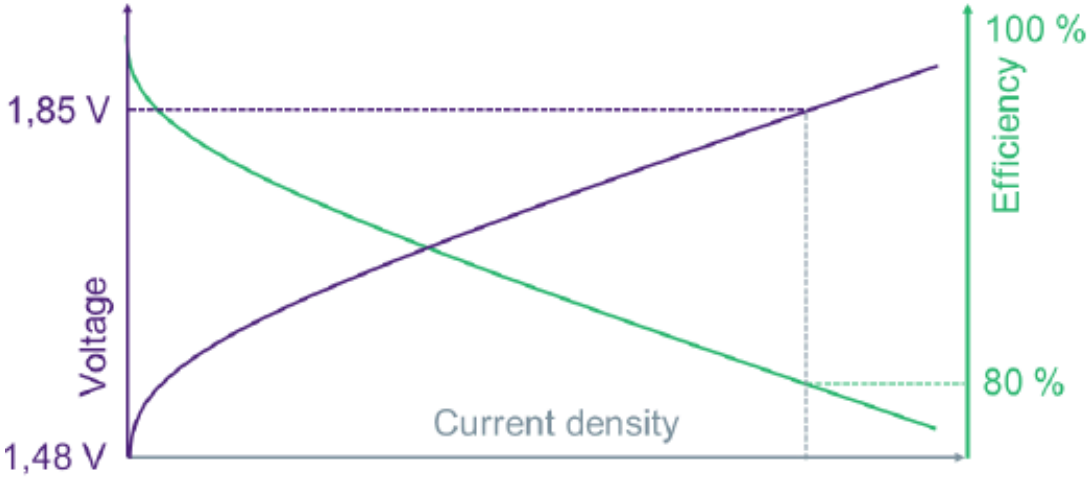
- **Efficiency**
- Degradation

Efficiency

Voltage efficiency:
Quotient of thermo-neutral voltage and the measured cell voltage

$$\eta_V = \frac{V_{th}}{V_{cell}}$$



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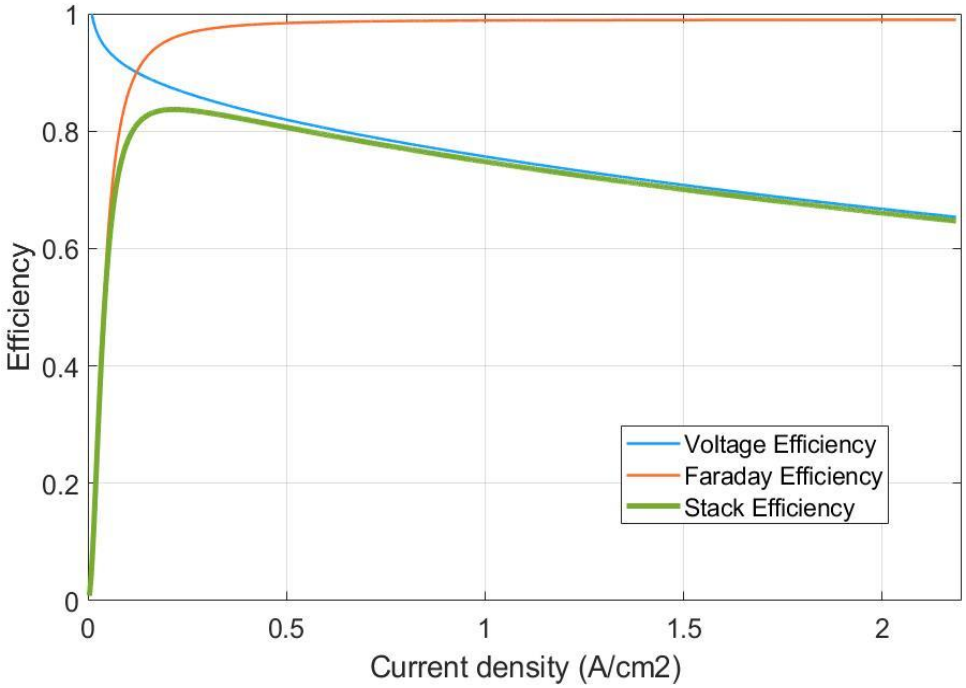


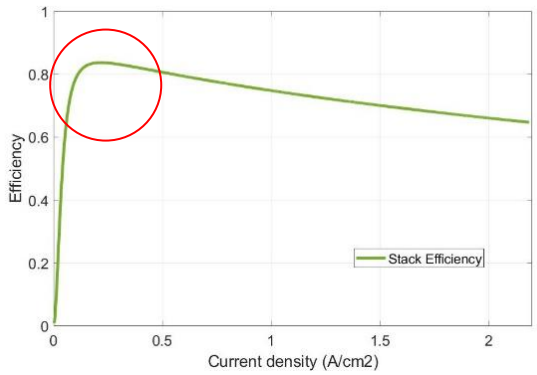
Faraday efficiency:
Ratio between the theoretical hydrogen quantity and the generated quantity of H_2

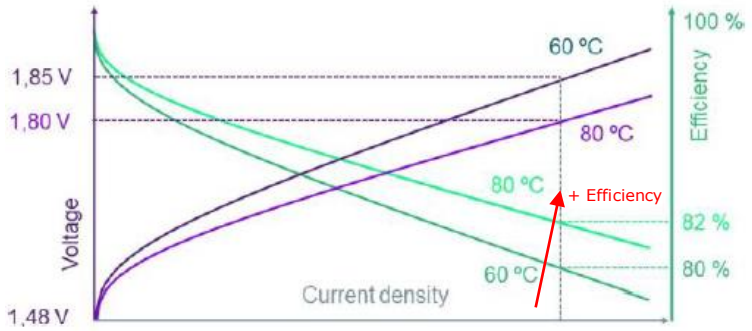
Due to H2 diffusion losses through the membrane,…

Stack efficiency:

$$\eta_{stack} = \eta_V \, \eta_F$$

Efficiency





Why not simply operate at low current densities?

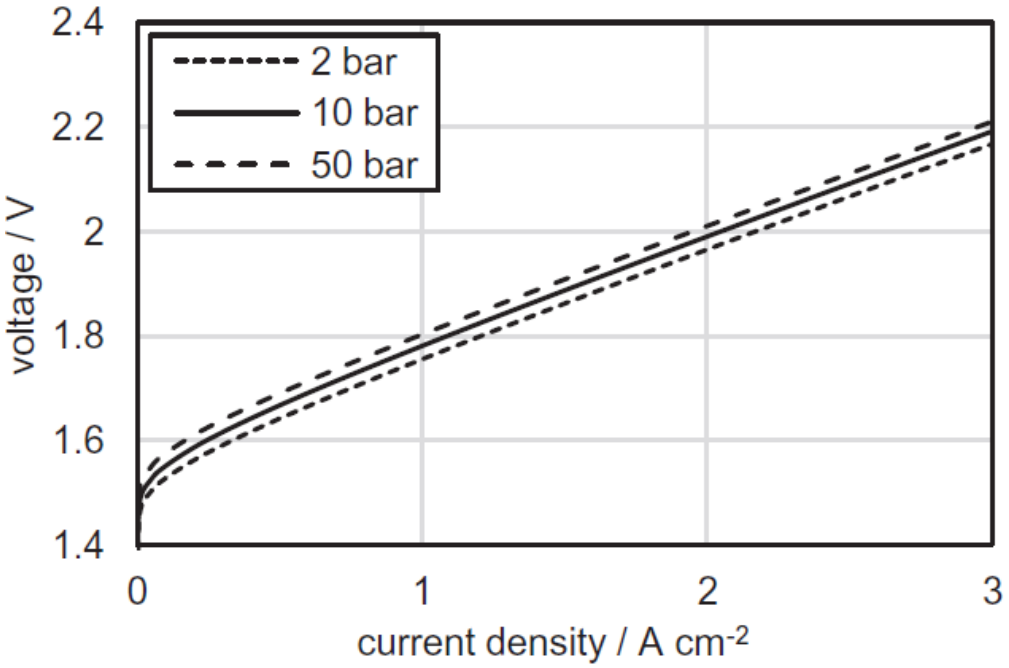
- ✓ The higher the current density, the higher the rate of hydrogen production.
- ✓ Specific costs for an electrolyzer increase at lower current density.
- ✓ The current density should be obtained with the objective of minimizing hydrogen production costs (the optimum between high-efficiency and low specific CAPEX)

Why not simply operate at higher temperatures?

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

P. Lettenmeier . White paper l Efficiency – Electrolysis. Siemens-energy

Efficiency vs. operating conditions



Pressure has no significative effect on polarization curve (voltaje efficiency)

G. Tjarks *et al.* Energetically-optimal PEM electrolyzer pressure in power-to-gas plants,Applied Energy, Volume 218, 2018.
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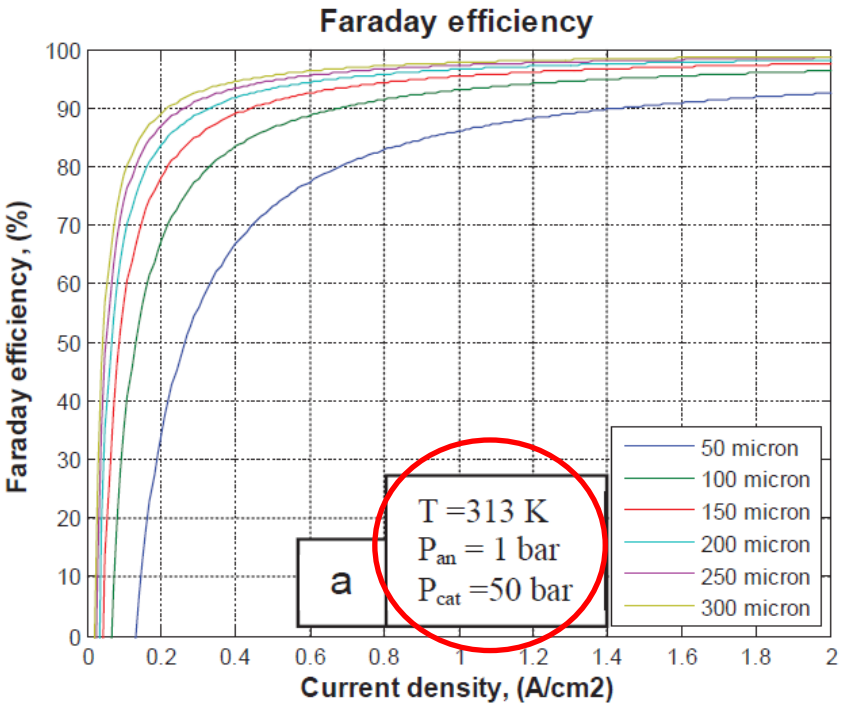
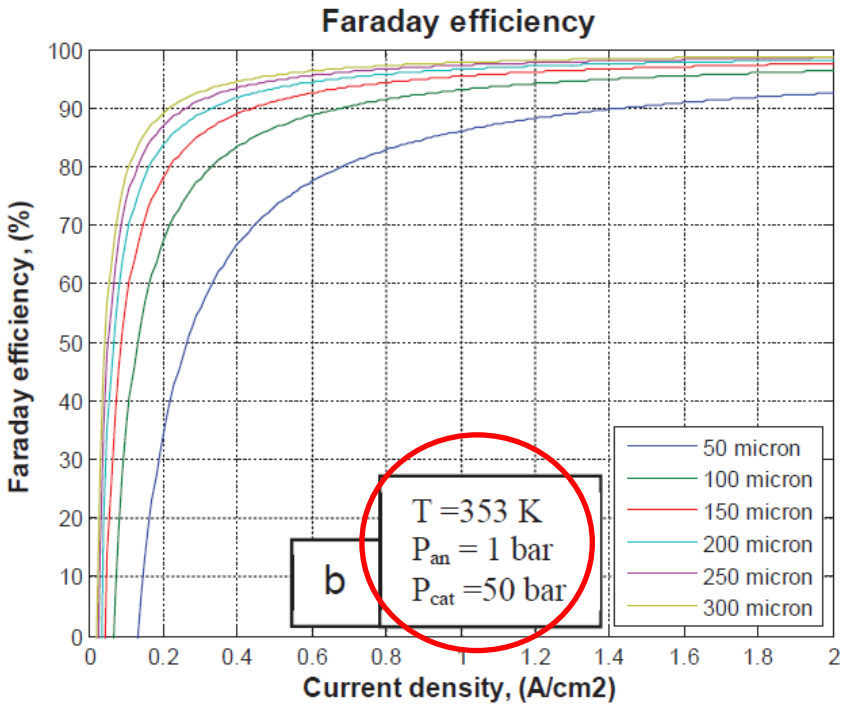
Efficiency vs. operating conditions

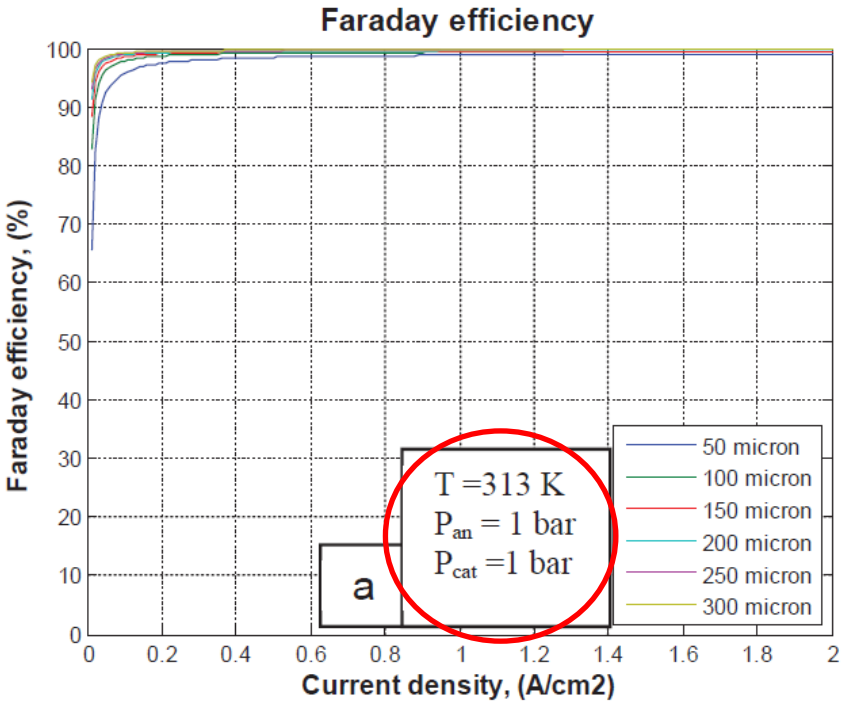


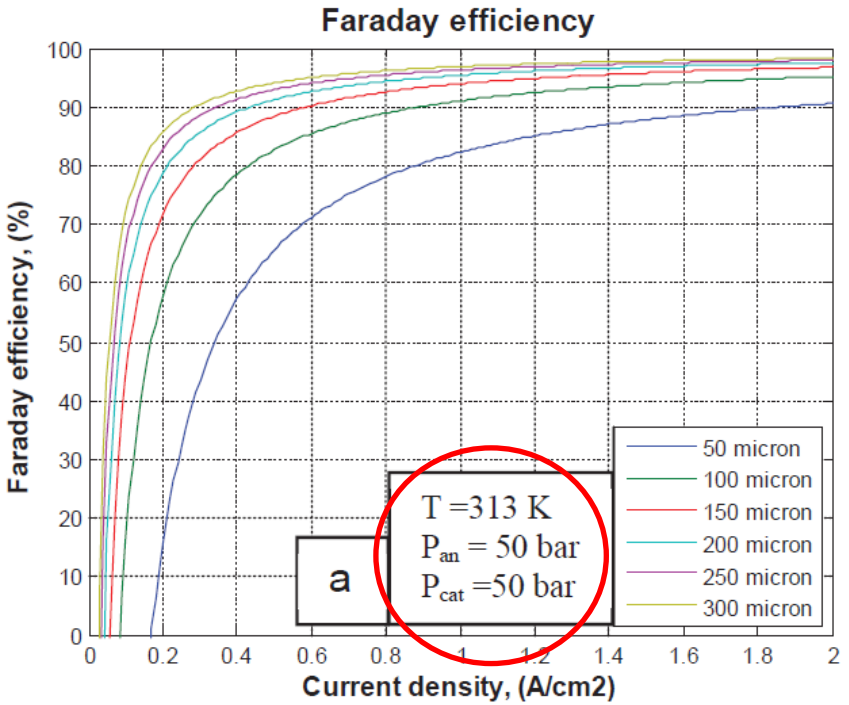


Temperature has no significative effect on Faraday efficiency

A. Salami et al. Numerical Modeling the Effect of Operating Variables on Faraday Efficiency in PEM Electrolyzer, Procedia Technology, Volume 26, 2016,

Efficiency vs. operating conditions

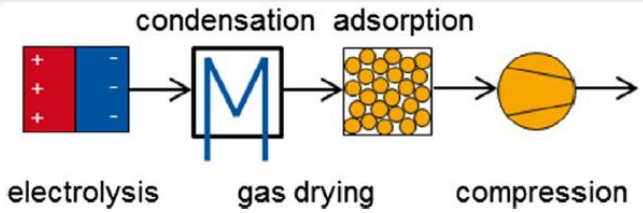




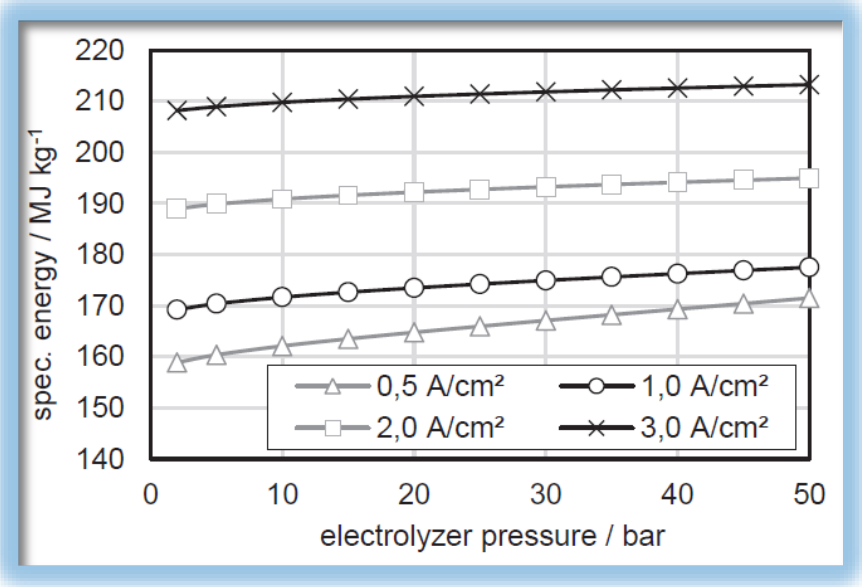
Faraday efficiency increase at low pressure…, but an external compressor is needed. Efficiency of the complete system need to be studied

A. Salami et al. Numerical Modeling the Effect of Operating Variables on Faraday Efficiency in PEM Electrolyzer, Procedia Technology, Volume 26, 2016,

Efficiency of the complete system



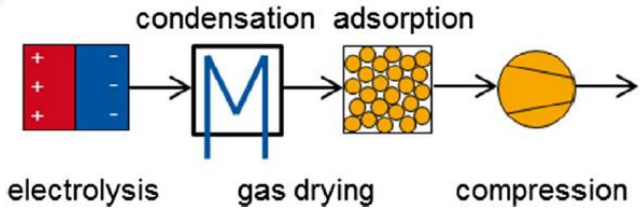
Specific energy demand is defined as energy demand per amount of produced hydrogen



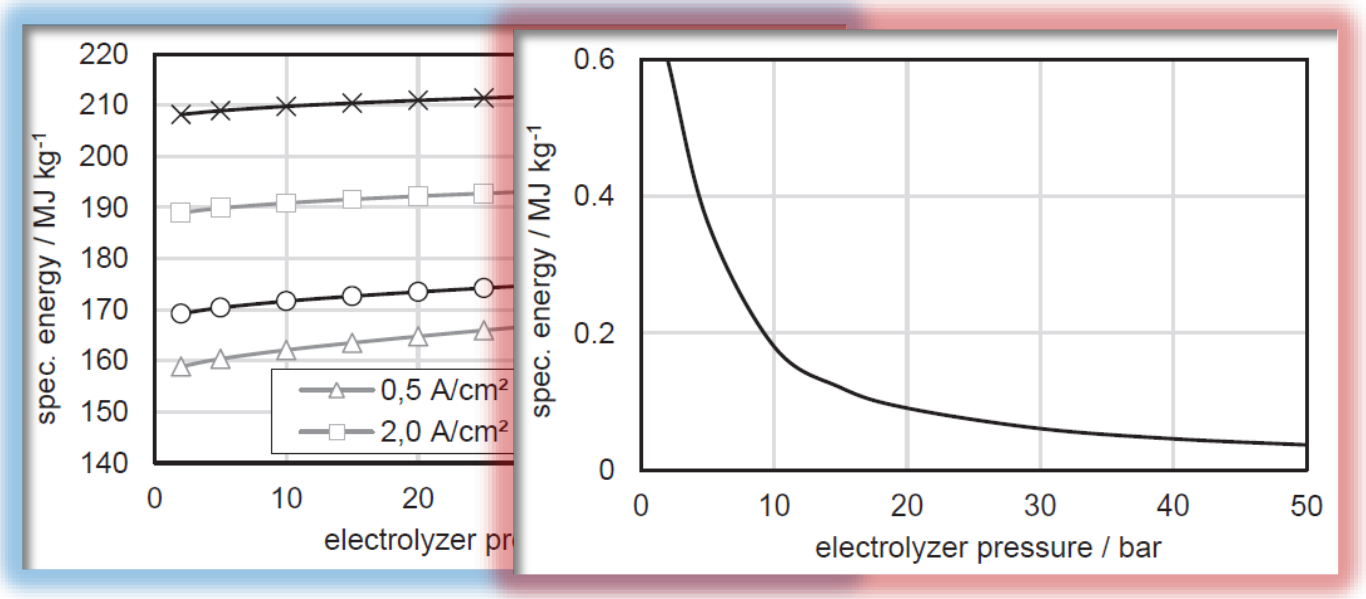
- ✓ Overvoltages increase with the current density, efficiency of production decreases.
- ✓ Faraday efficiency decrease with pressure, specific energy demand increases with pressure

G. Tjarks *et al.* Energetically-optimal PEM electrolyzer pressure in power-to-gas plants,Applied Energy, Volume 218, 2018.

Efficiency of the complete system



Specific energy demand is defined as energy demand per amount of produced hydrogen



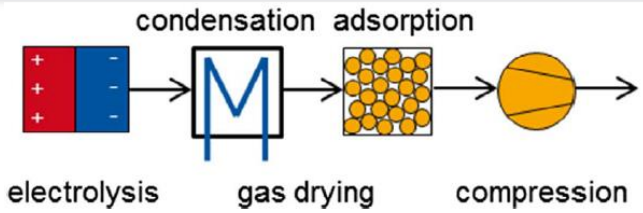
Electrolyzer

Drying process

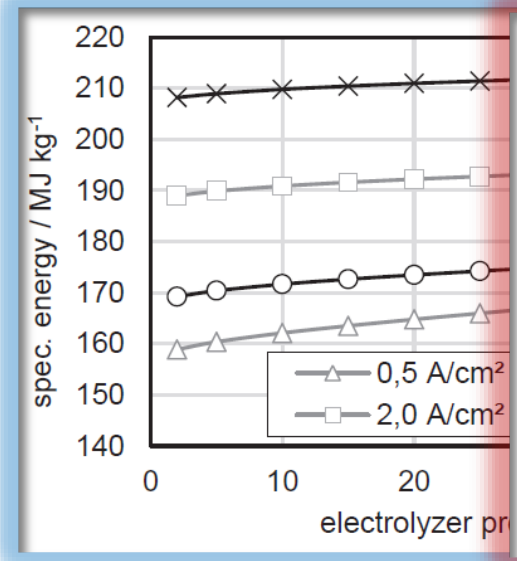
✓ Water content of produced hydrogen decrease with electrolyzer pressure

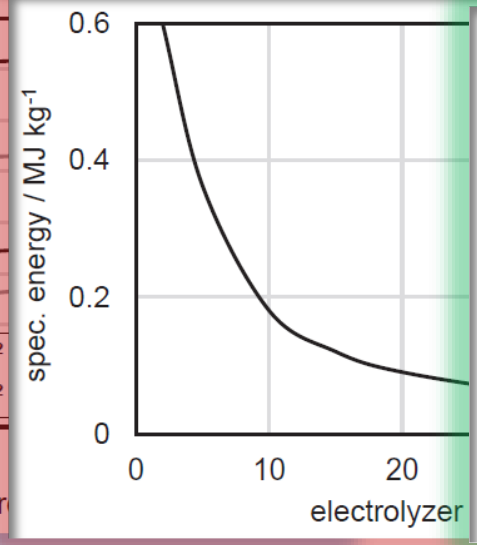
G. Tjarks *et al.* Energetically-optimal PEM electrolyzer pressure in power-to-gas plants,Applied Energy, Volume 218, 2018.

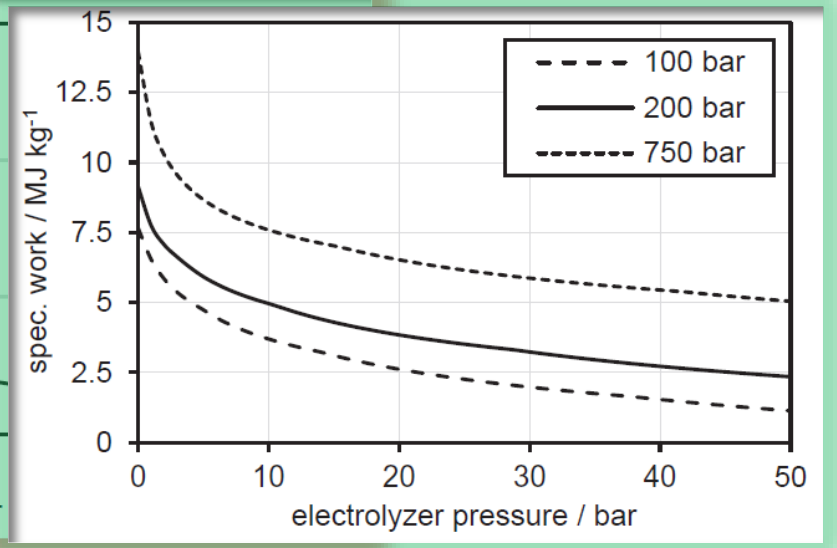
Efficiency of the complete system



Specific energy demand is defined as energy demand per amount of produced hydrogen







Electrolyzer Drying process Compression

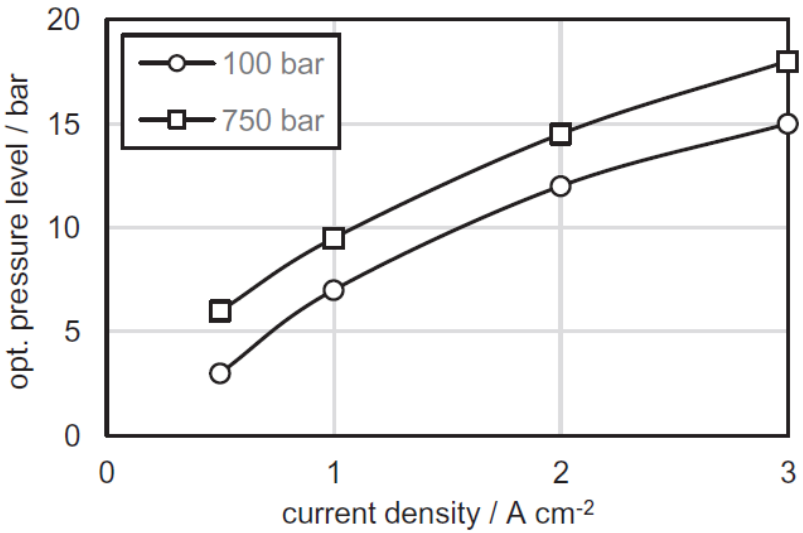
In several work, only electrolyzer and compression is considered for efficiency

G. Tjarks *et al.* Energetically-optimal PEM electrolyzer pressure in power-to-gas plants,Applied Energy, Volume 218, 2018.

Efficiency of the complete system

- The pressure operation of the electrolyzer can reduce the total energy demand of the overall process

- Several works propose to **select the operation pressure** of electrolyzer, **maximizing the efficiency of the system** as a function of the operation point:
  - Current density
  - Storage pressure



G. Tjarks *et al.* Energetically-optimal PEM electrolyzer pressure in power-to-gas plants,Applied Energy, Volume 218, 2018.

J. Koponen et al. Control and energy efficiency of PEM water electrolyzers in renewable energy systems, International Journal of Hydrogen Energy, Volume 42, Issue 50, 2017.

F. Scheepers et al. Improving the Efficiency of PEM Electrolyzers through Membrane-Specific Pressure Optimization. Energies 2020,

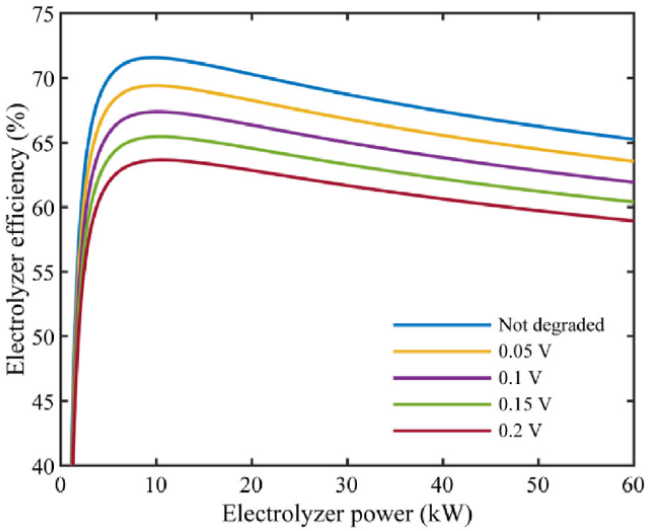
F. Scheepers et al. Temperature optimization for improving polymer electrolyte membrane-water electrolysis system efficiency, Applied Energy, Volume 283, 2021.

Summary

- Introduction
- Mathematical model of PEM electrolyzers
  - Static Electrochemical models
  - Dynamic Electrochemical models
  - Thermal models
- Efficiency
- **Degradation**

Degradation

- One of the biggest challenges of PEM technologies is the high cost of production, which has to be addressed both by lowering material cost and by **extending its lifetime**.
- There are not significative mathematical models of the degradation
- There are several works where degradation is studied under different operation conditions.



- Effect of degradation is observed as a voltage increment in the polarization curve.
- Typically, is measured in $\mu V/h$
- Degradation is highly dependent on operation conditions.

Conclusions of studies (current density)

- Constant operation:
  - At 2 A/cm^2 degradation is high (mode B)
  - At 1 A/cm^2 there is no degradation (mode A)
- Dynamic operation:
  - Degradation rates at high current densities of 2 A/cm2 are reduced if repetitive periods of lower current density (1 A/cm^2) are used (mode C)
  - Degradation rates are reduced even more with repetitive current interruptions (modes D, E).
- A smaller number of longer current interruptions are preferred to a higher number of shorter interruptions

Mode	$\mu V/h$
A - Const. 2 A/cm^2	196
B - Const. 1 A/cm^2	0
C – 2 – 1 A/cm^2	65
D – 2 – 0 A/cm^2 (6 hours cycles)	16
D – 2 – 0 A/cm^2 (10 min. cycles)	50

C. Rakousky *et al*, Polymer electrolyte membrane water electrolysis: Restraining degradation in the presence of fluctuating power, Journal of Power Sources, Volume 342,2017

Conclusions of studies (power)

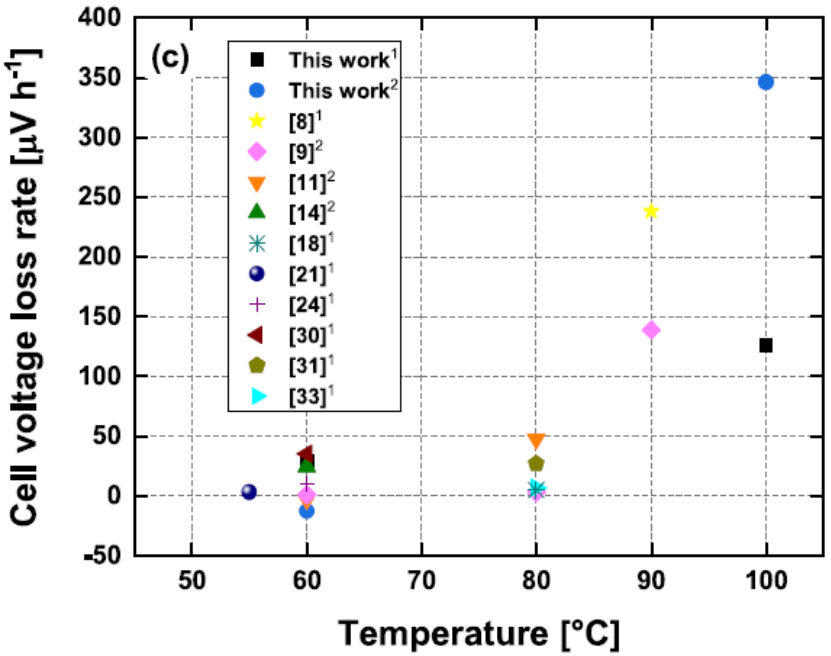
- In this study a P_{el} =60 kW is considered
- Maintaining operation: 600 W
- P_t=40 kW

Mode	$\mu V/h$
Maintaining operation (very low power)	1.5
Low power fluctuation (600 W – P_t)	50
Constant P_t	20
High power fluctuation (P_t - P_{el})	66
Constant high power (P_{el})	196

Xinyu Lu, *et al.* Optimization of power allocation for wind-hydrogen system multi-stack PEM water electrolyzer considering degradation conditions, International Journal of Hydrogen Energy, Volume 48, Issue 15, 2023

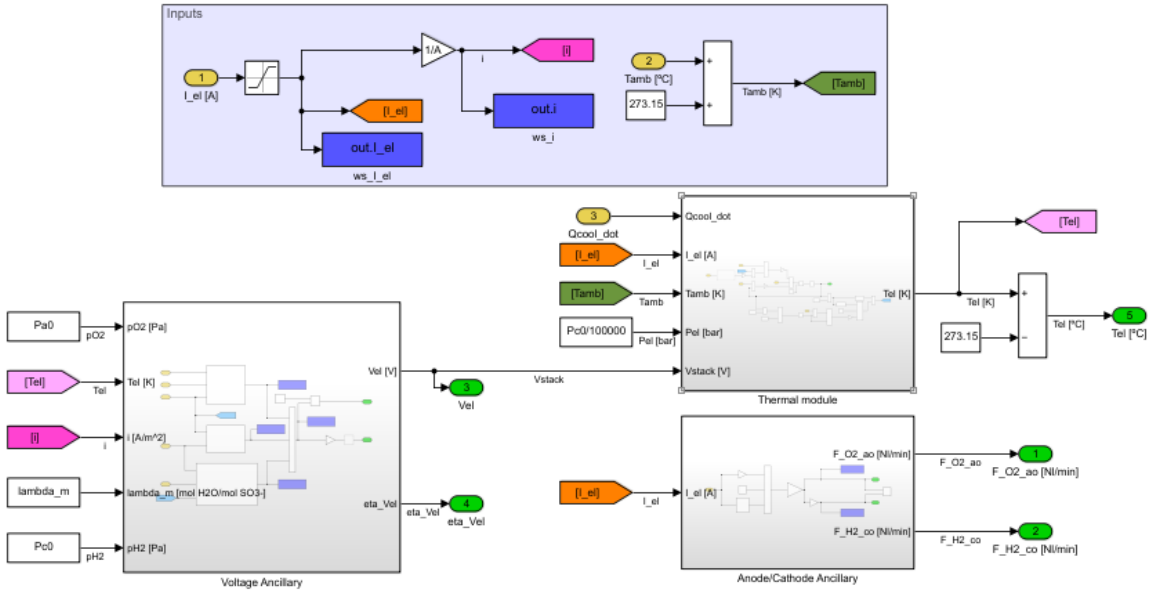
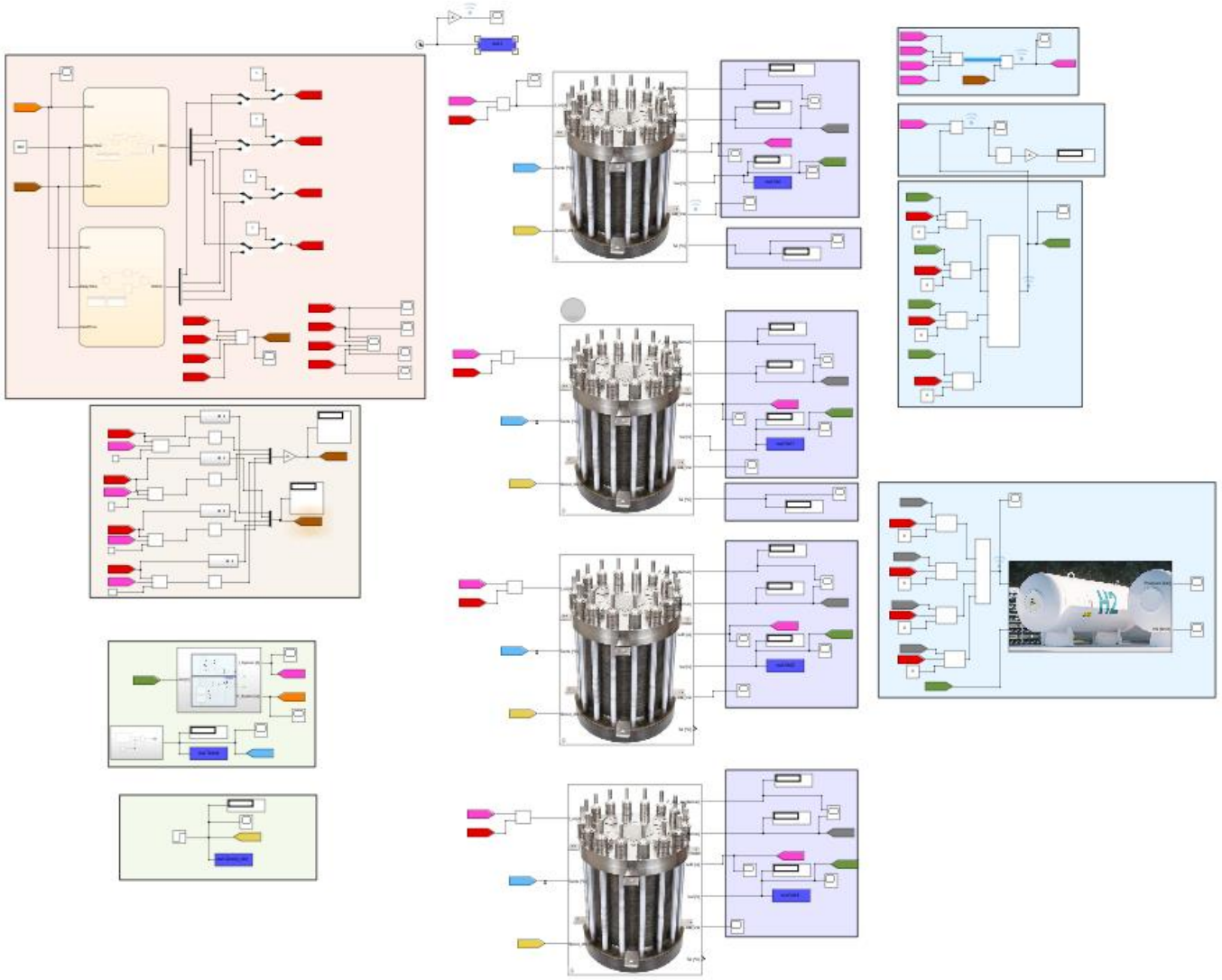
Conclusions of studies (temperature)

- Many experiment in literature, but no conclusive results



Steffen Garbe *et al.* Understanding Degradation Effects of Elevated Temperature Operating Conditions in Polymer Electrolyte Water Electrolyzers *Journal of The Electrochemical Society, Volume 168, Number 4, 2021*

Simulink model



OPALH2 and ODYELH2 Projects