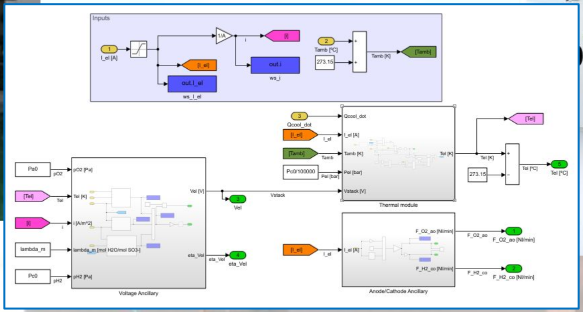
Mathematical Modeling of Electrolyzers

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



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November, 2024

Summary

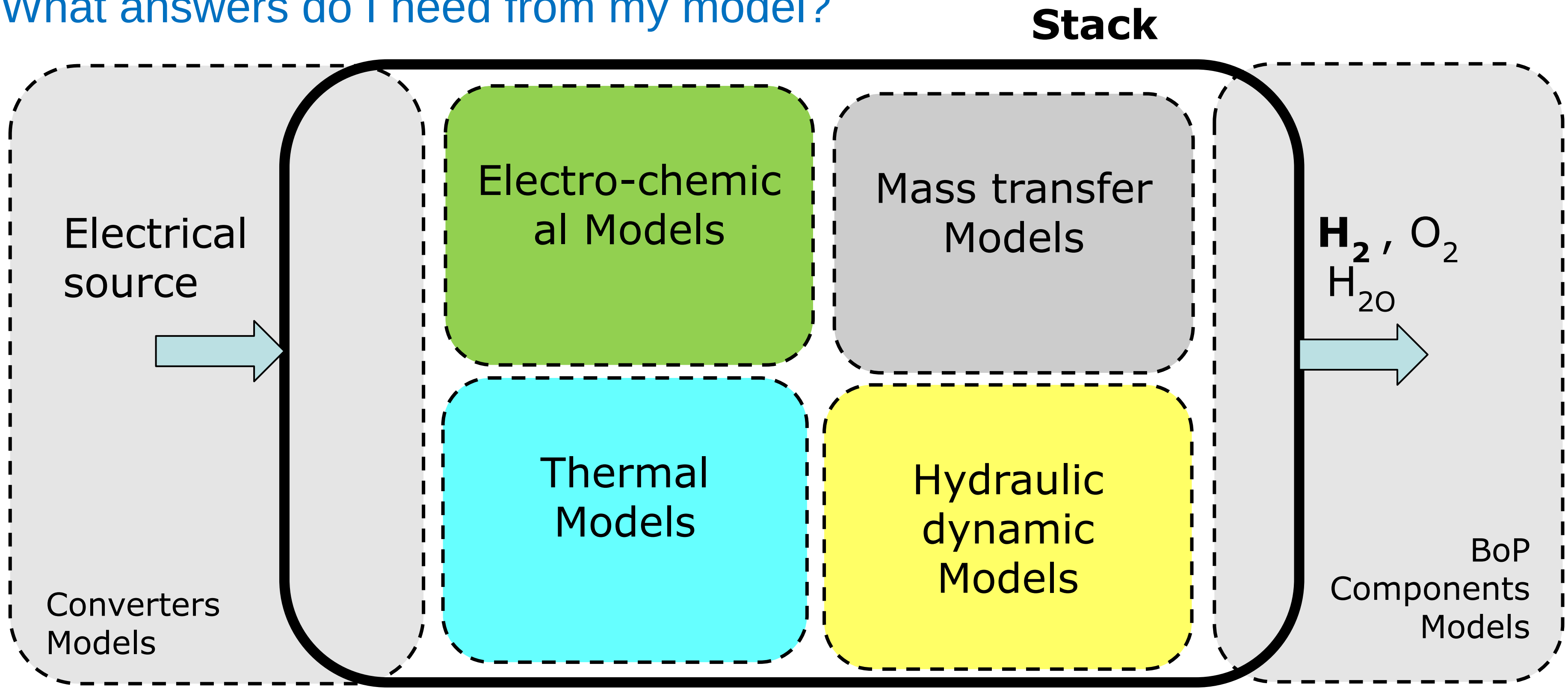
- Introduction
- Mathematical model of PEM electrolyzers
  - Electrochemical models
  - Thermal models
  - Identification
- Efficiency
- Degradation

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?



Stack

Electrical source

Converters Models

Electro-chemical Models

Mass transfer Models

Thermal Models

Hydraulic dynamic Models

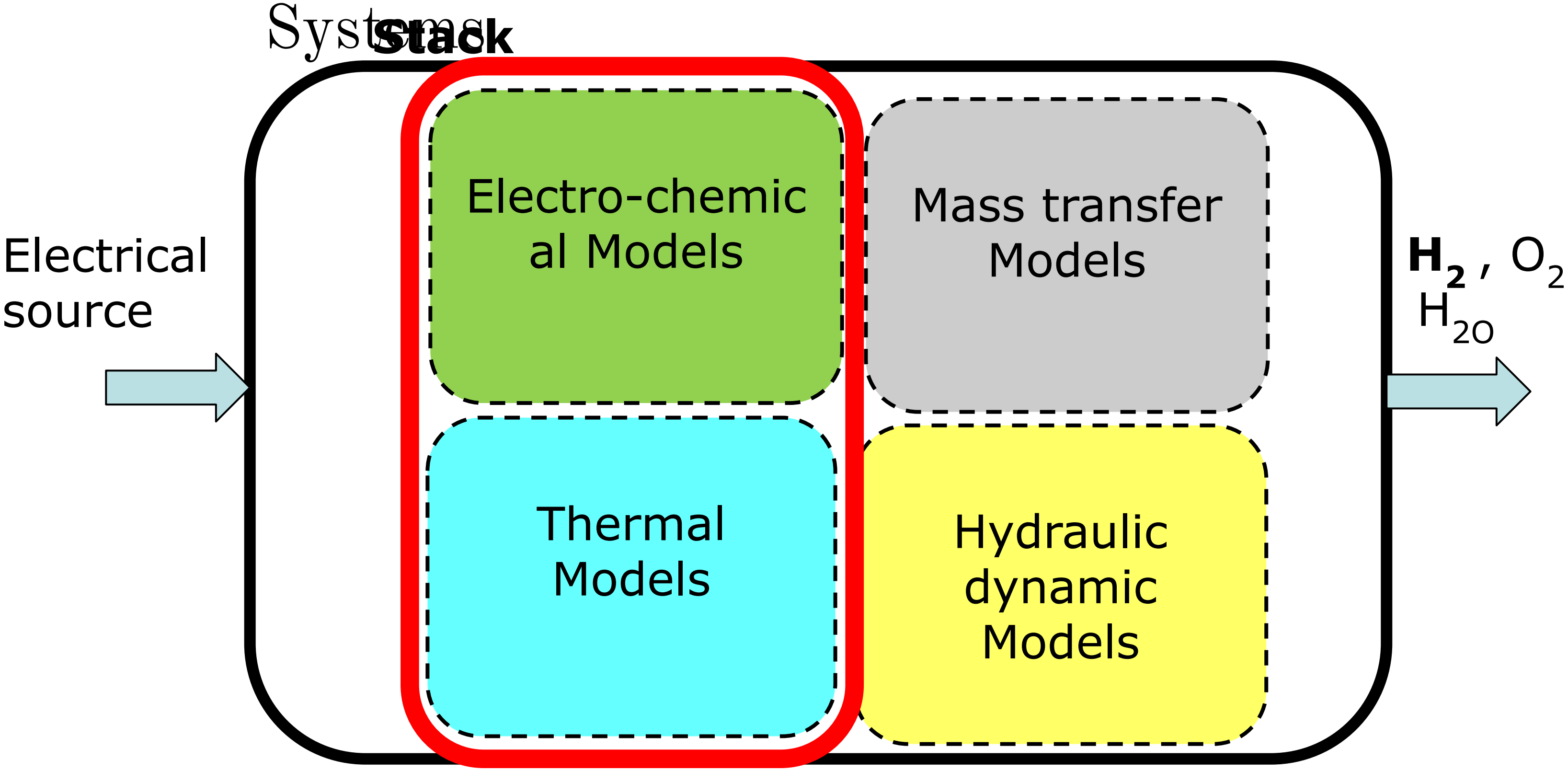
$\mathbf{H_2}$, O_2 H_{2O}

BoP Components Models

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



Stack

Electro-chemical Models

Mass transfer Models

Thermal Models

Hydraulic dynamic Models

Electrical source

H_2 , O_2 H_2O

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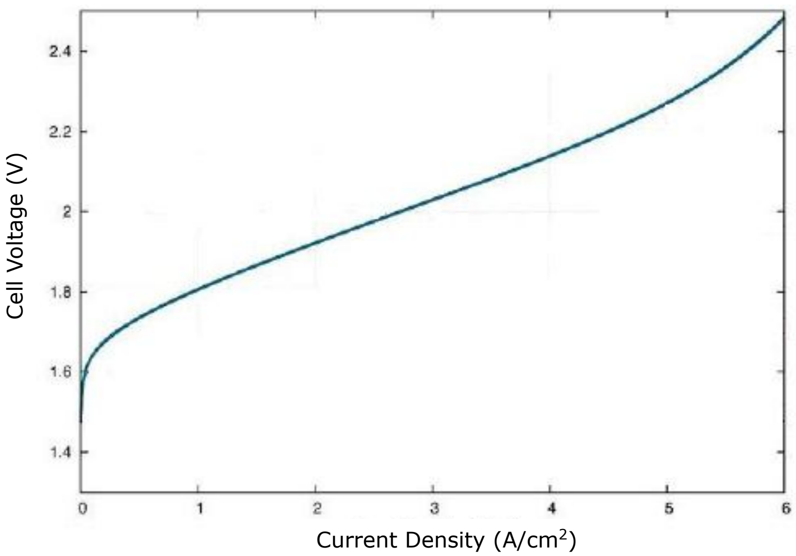
- **Mathematical model of PEM electrolyzers**
  - Static Electrochemical models
  - Thermal models
  - Identification
- Efficiency
- Degradation

Static Electrochemical Model

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

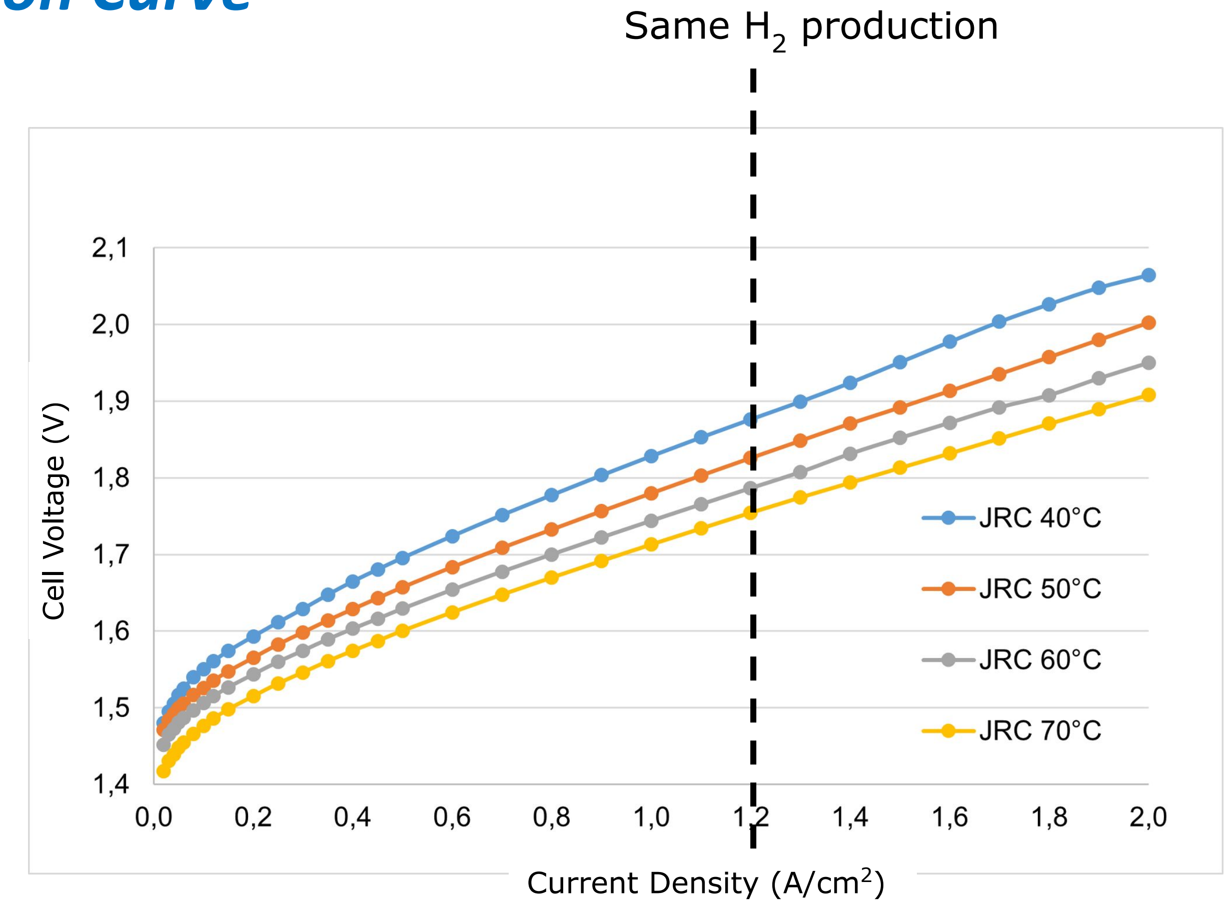
 Simplifications:
  - All the cells have the same electrical and termal behaviour
  - Temperature homogeneity across the stack
  - Oxygen and hydrogen behave as ideal gases. In addition, the gas and liquid phases are separated
  - Electrochemical dynamics can be neglected, so a static model is used (algebraic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

Polarization Curve



Electrochemical Model

Polarization Curve



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

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

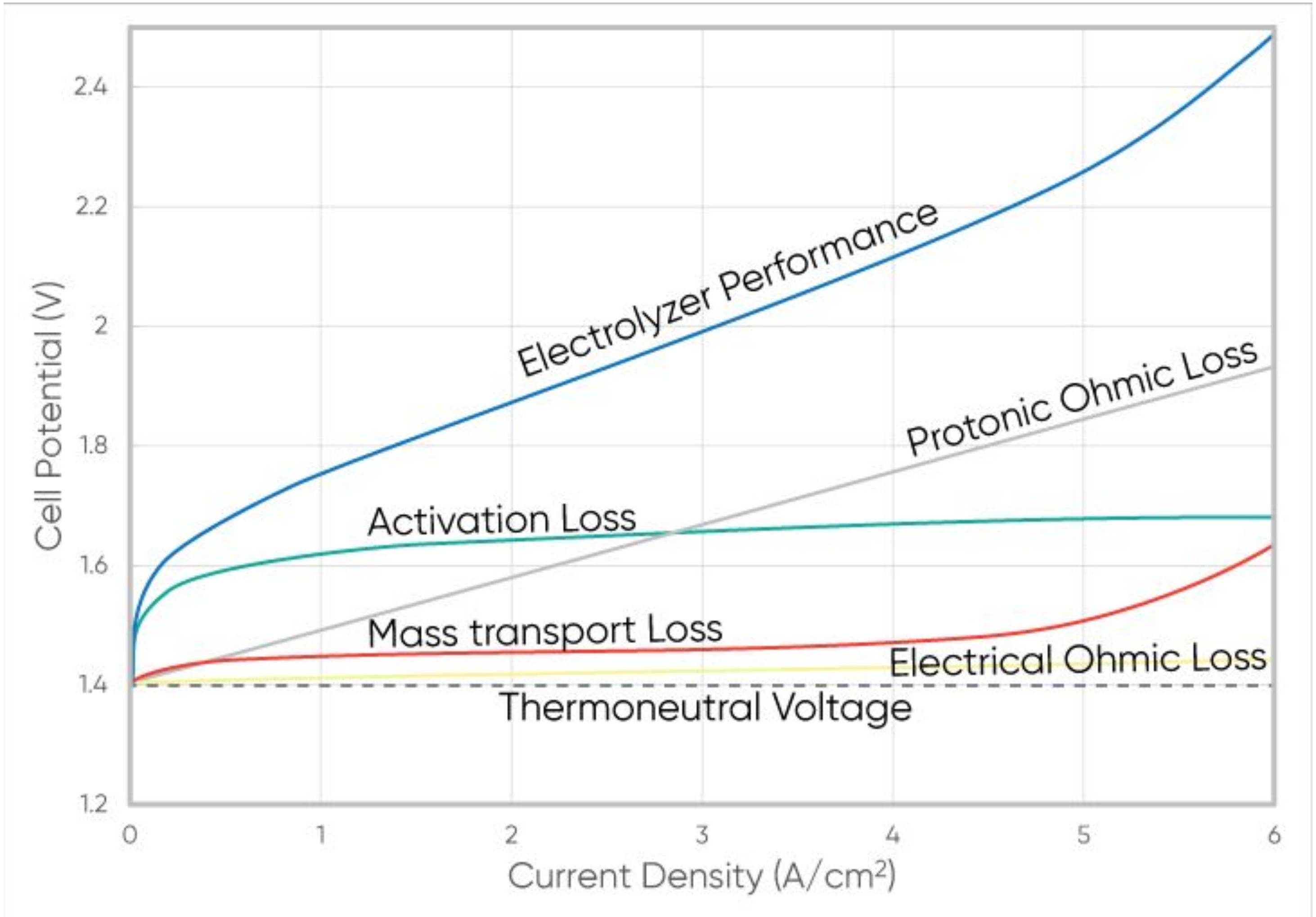
V_{ocv}	Open circuit voltage
V_{act}	Activation overvoltage
V_{ohm}	Ohmic losses overvoltage
V_{con}	Concentration overvoltage (mass transport losses)

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

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

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

Electrochemical Model



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)

Electrochemical Model

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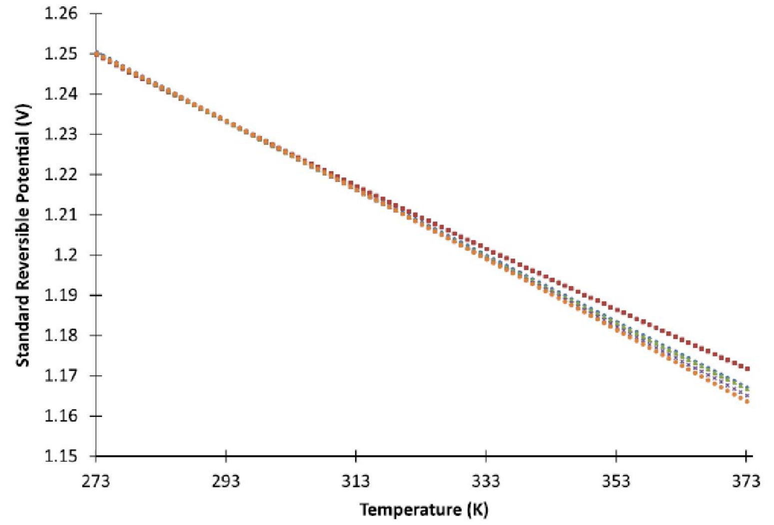

P. Olivier *et al*. Low-Temperatore electrolysis system modelling: A Review. Renewable and Sustainable Energy Reviews 78 (2017)

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

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

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

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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

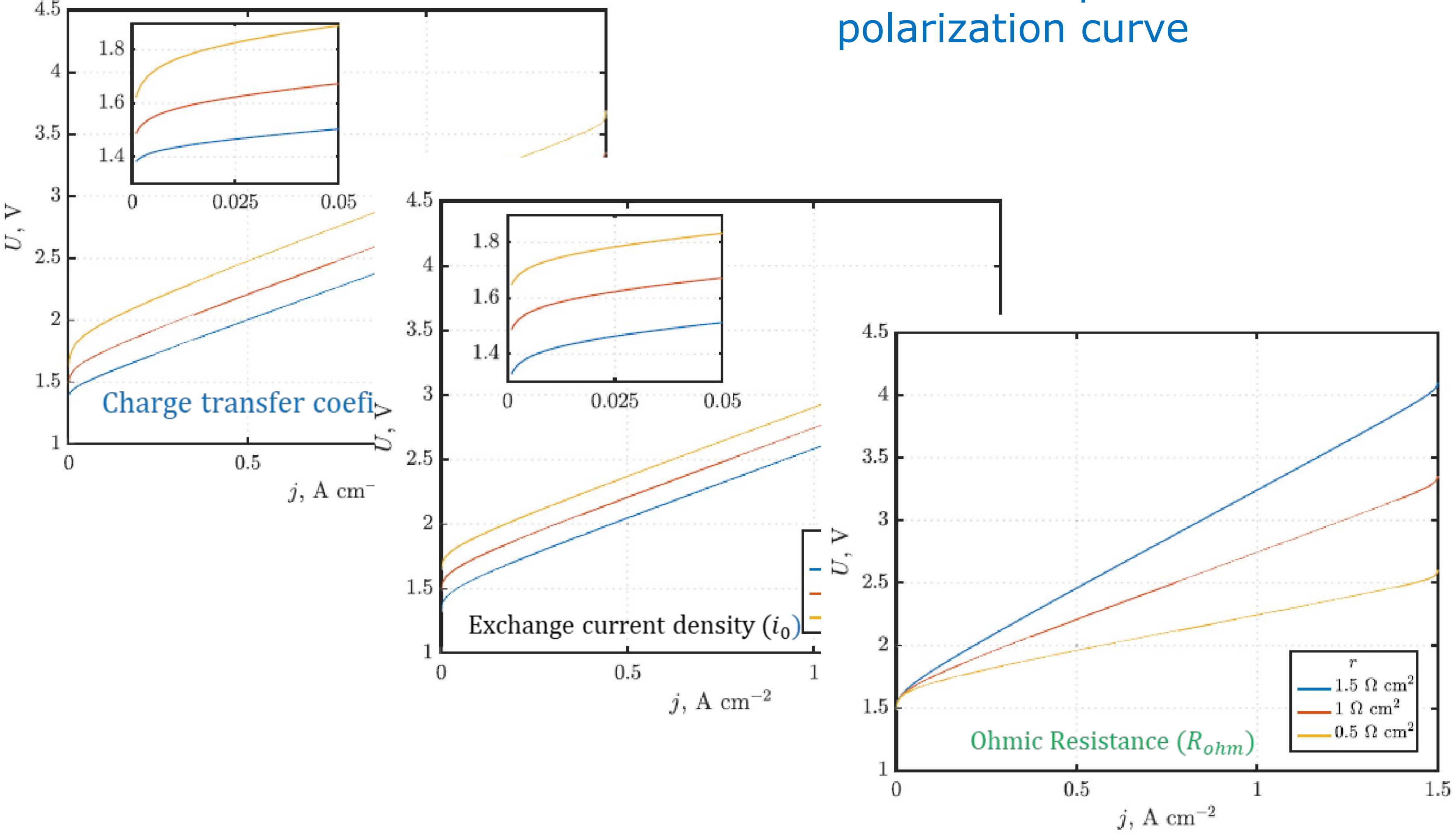
$$\sigma_m = (0.005139\,\lambda_m - 0.00326)\,e^{1268\left(\frac{1}{303} - \frac{1}{T_{el}}\right)}$$

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

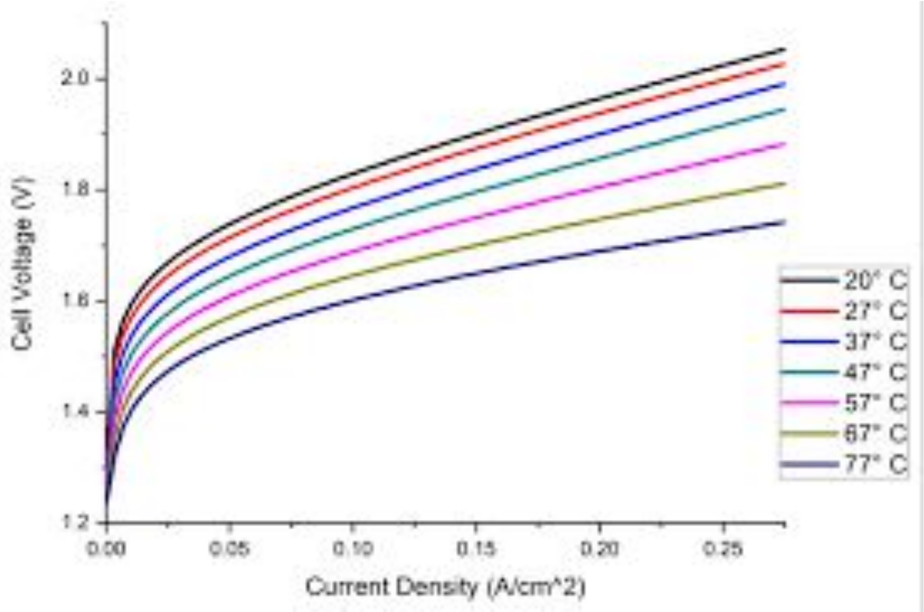
Static Electrochemical Model

Efect of the parameters in the polarization curve



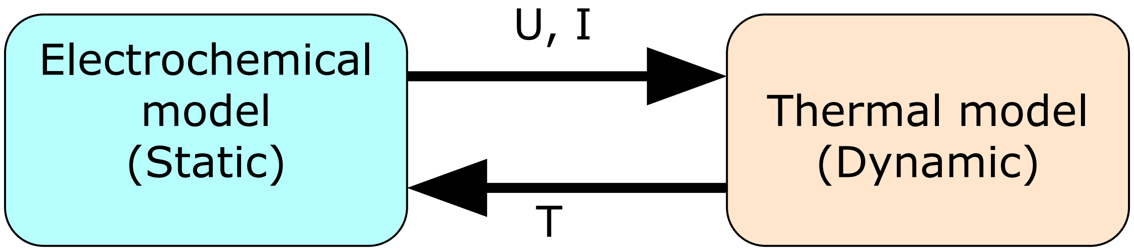
Thermal model

- 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

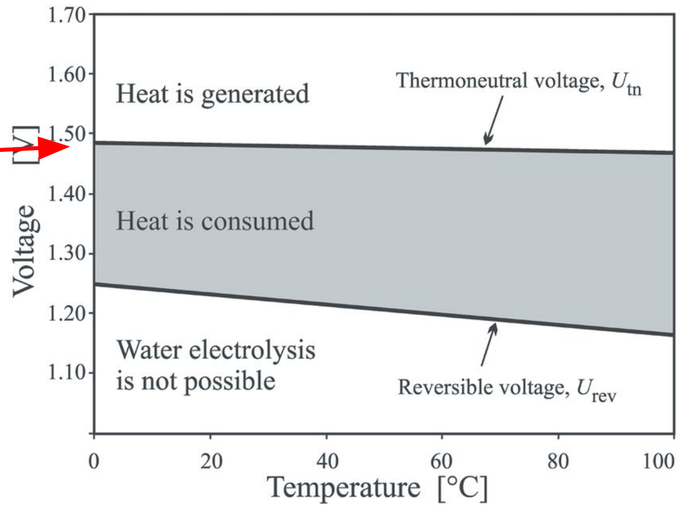
$\dot{Q}_{loss}$ *Heat that is lost by interaction with the environment by convection and radiation*

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

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

$$\approx 1.48$$

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



C_t and R_t parameters to be adjusted

Experimental data for identification & validation

PEM Stack 1.4 kW

Feature	Value
Active electrode area	28.3 cm² (ø 60 mm)
Number of cells	10
Max. H_2 production	4.4 Nl/min (0.26 Nm³/h)
Max. O_2 production	2.2 Nl/min (0.13 Nm³/h)
Operation temperature	65 - 80 °C
Stack voltage (40 bar, 70 °C)	approx. 16.3 - 22.3 DCV @ Beginning of Life (BOL)
Stack current (40 bar, 70 °C)	2.8 - 62.2 A
Connected load (40 bar, 70 °C)	approx. 0.05 - 1.39 kW @ BOL
H_2 output pressure	max. 40 bar
O_2 output pressure	near ambient
H_2O-flow	min. 2 l/min @BOL
H_2O-input pressure	max. 1.5 bar

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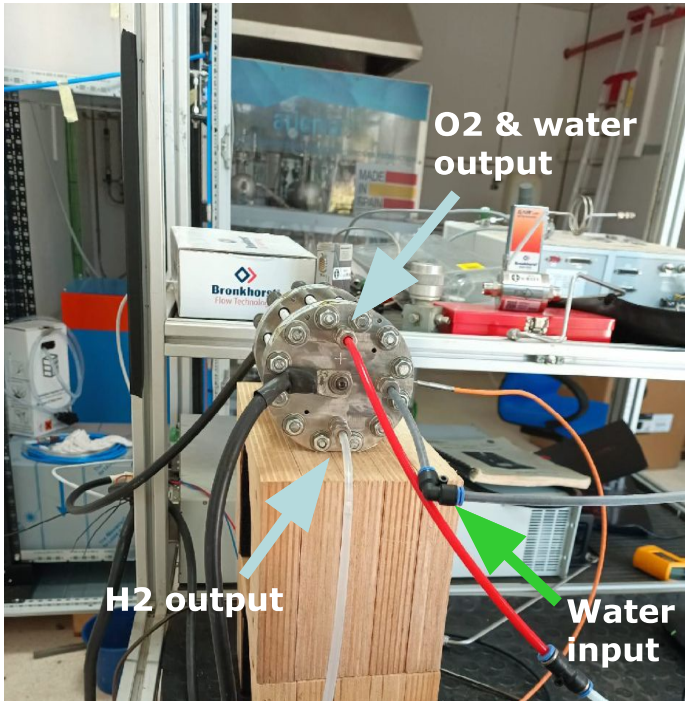
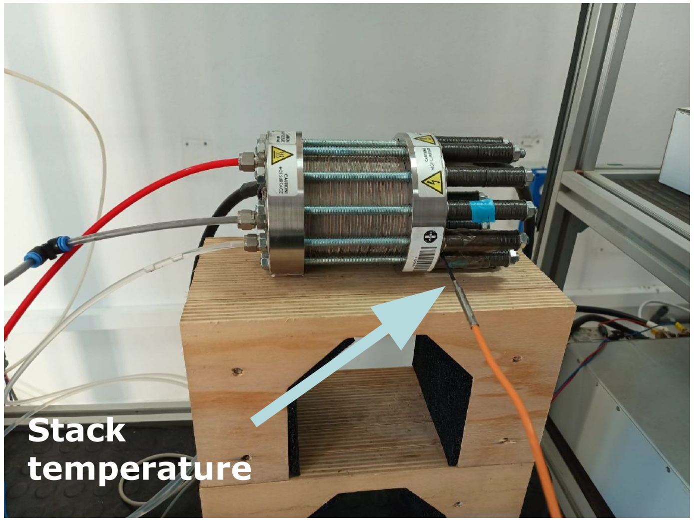
Experimental data for identification & validation

Time (s)	H2 Pressure (bar)	H2 Flow (Nl/min)	O2 Pressure (bar)	Water Temperature (ºC)	Enviromental Temperature (ºC)	Stack Temperature (ºC)	Stack Voltage (V)	Stack Current (A)
0	2,551657	0,01762486	-0,0516974	31,993471	24,825102	28,478231	0,11534744	0,00823628
1	2,5519857	0,01758067	-0,05601	32,072838	24,749264	28,445021	0,11937767	0,00812791
…	…	…	…	…	…	…	…	…
8725	6,1429033	0,03864089	0,01937729	47,402832	26,190796	43,021027	3,6212292	-0,0039556



PEM Stack
1.4 kW



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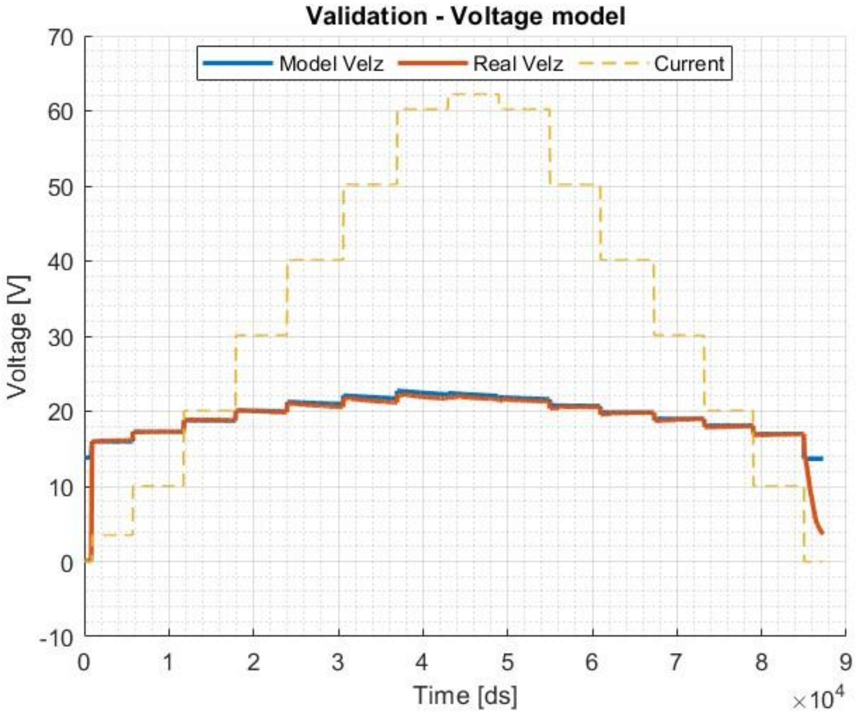
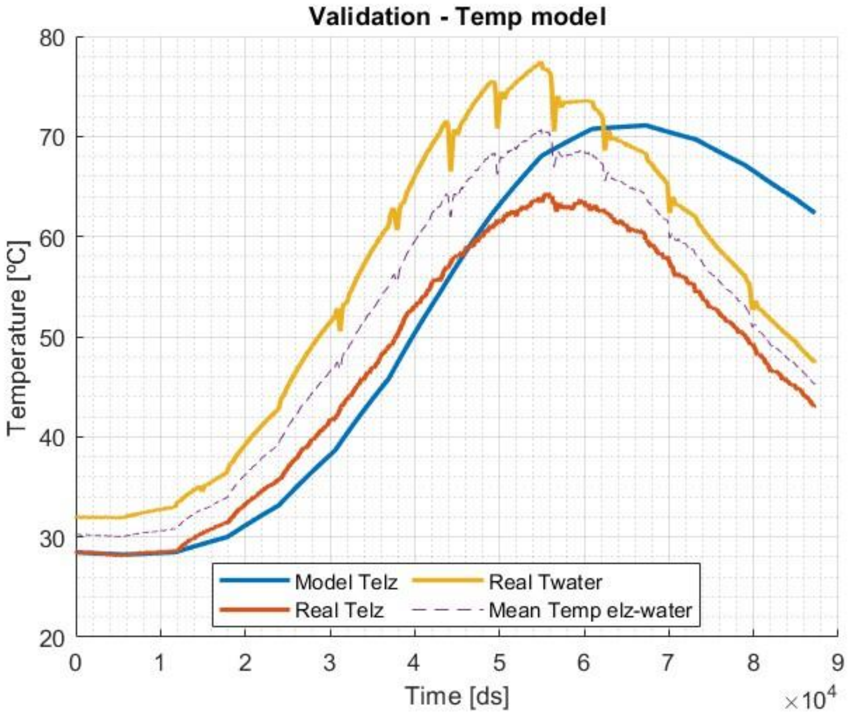
PEM Stack experimental tests

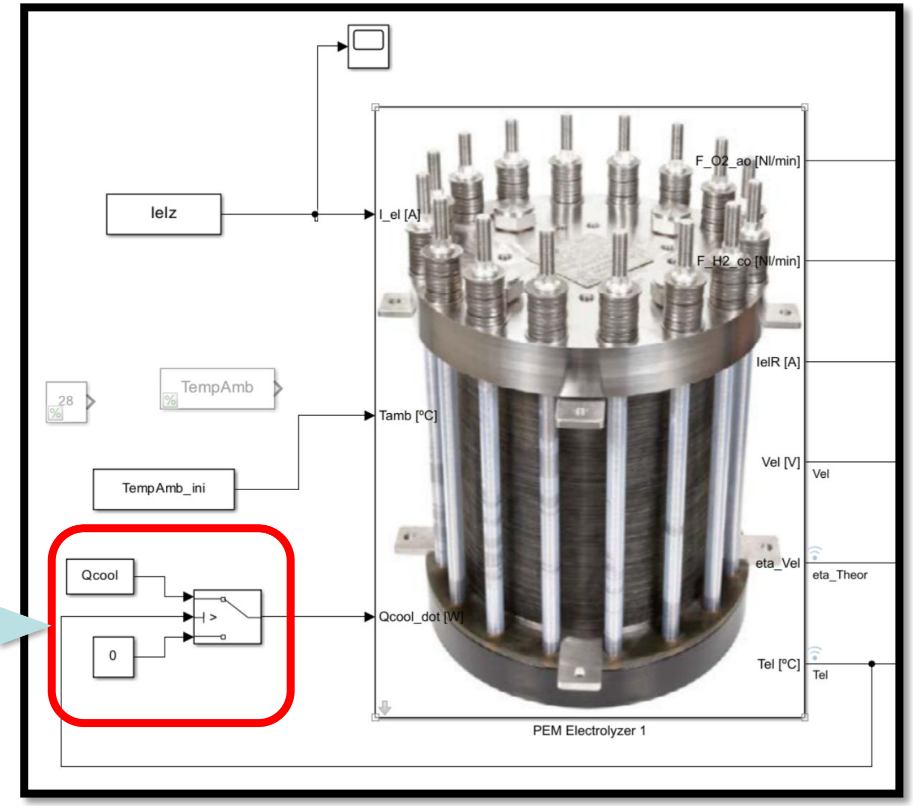




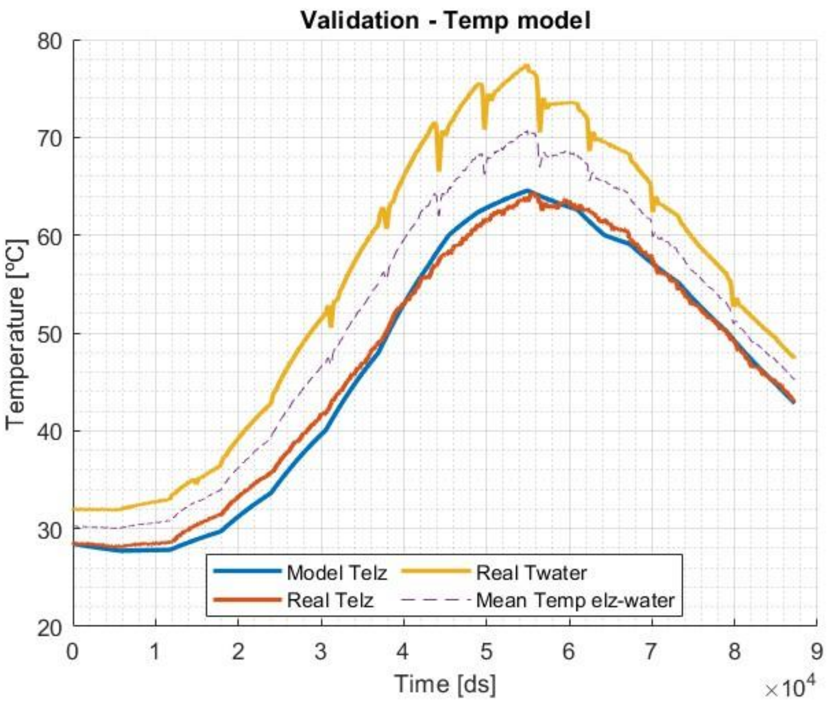
Thermal identification

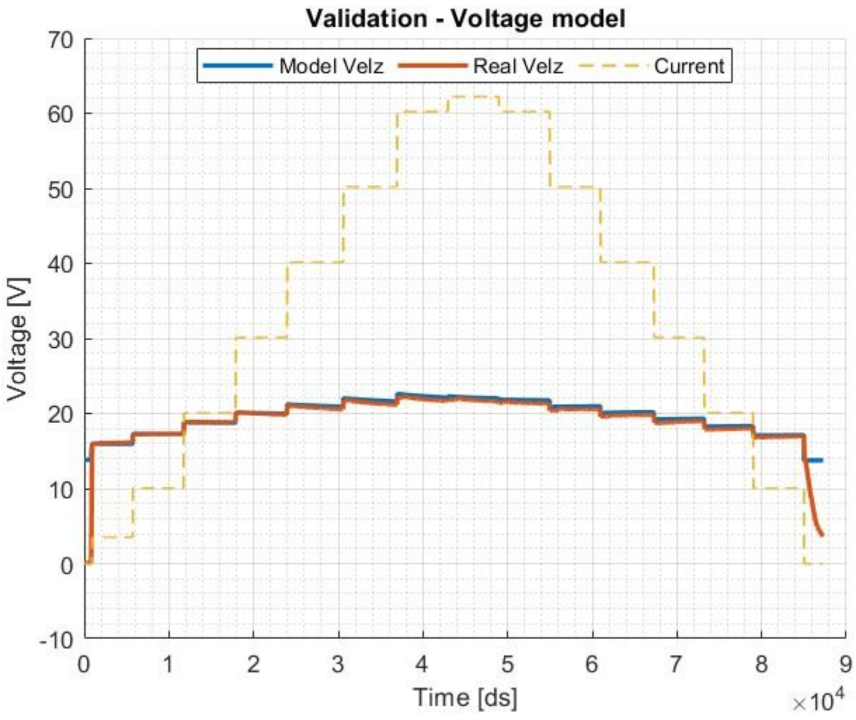
When the experimental data was obtained, a fan was activated which serves to cool the stack temperature. However, it is not stated how much heat is cooled by this fan, nor at what stack temperature it is activated. Therefore, a series of tests have been carried out in which two variables, Tcontrol and Qcontrol, have been created to optimise the temperature at which the fan is activated and the heat it cools.

Boundaries: Tcontrol (ºC): 50 – 70; Qcool (W): 50 – 100



Validation of the models





Summary

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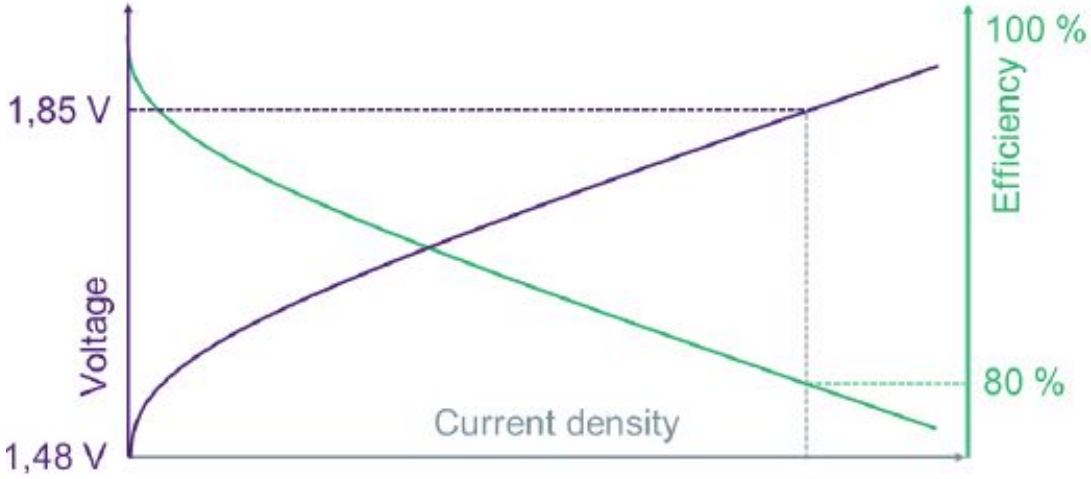
  - Static Electrochemical models
  - Thermal models
  - Identification
- **Efficiency**
- Degradation

Efficiency

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

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



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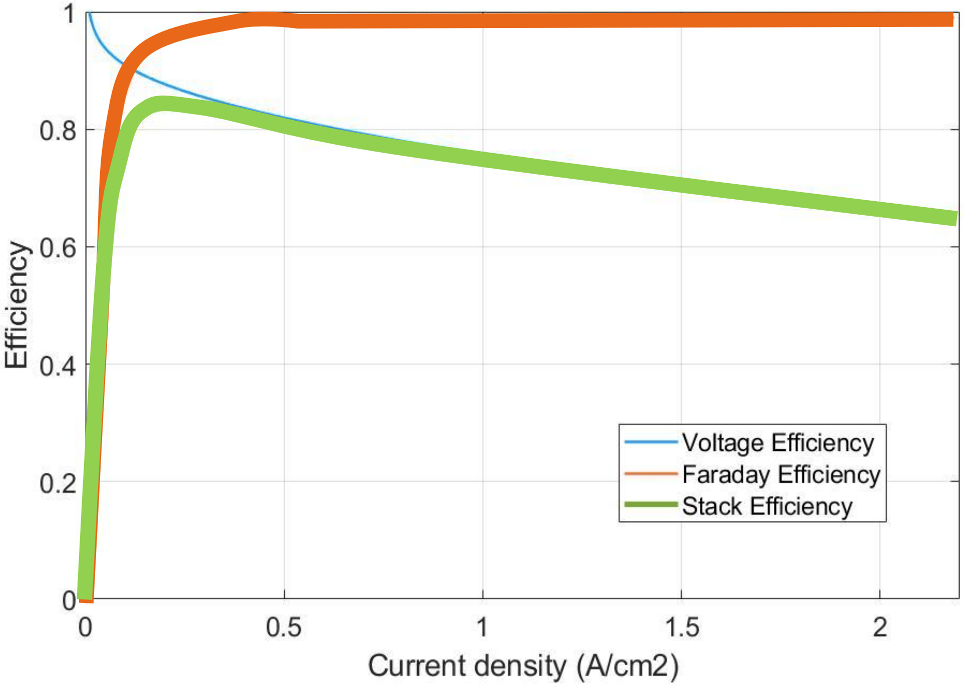


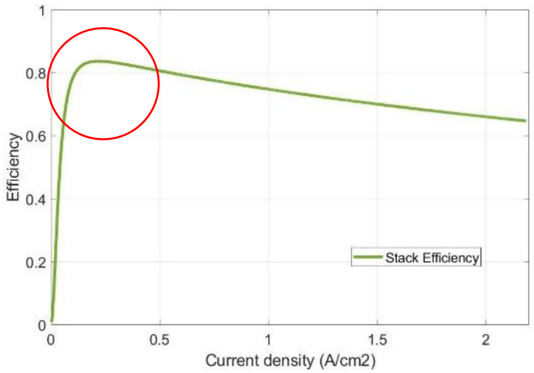
Faraday efficiency:
Ratio between the theoretical hydrogen quantity and the generated quantity of H_2

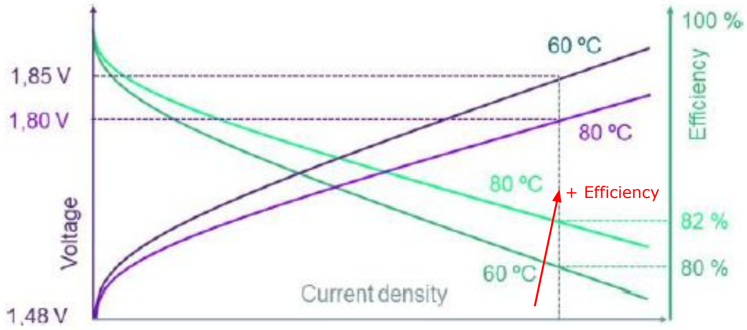
Due to H2 diffusion losses through the membrane,…

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.

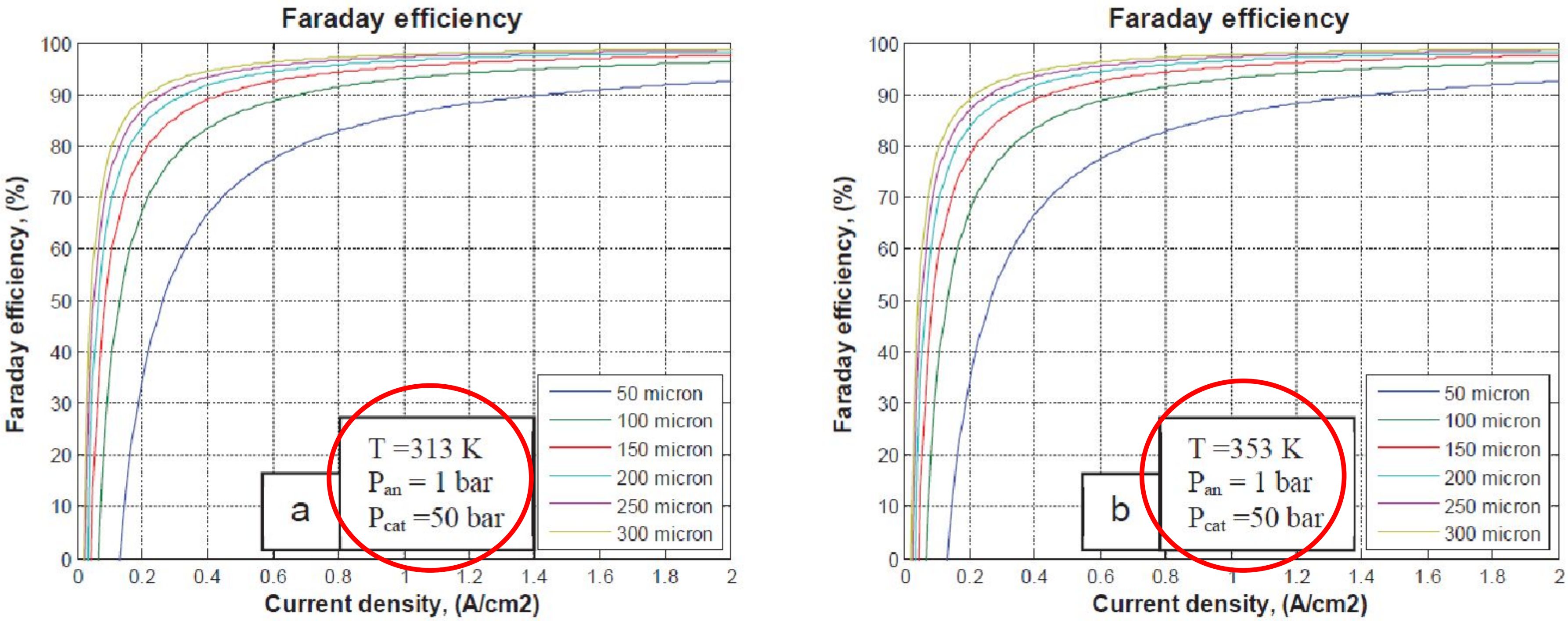
✔ The correct operating temperature should be optimized with the objective of minimizing hydrogen production costs.

✔ The objective is to obtain an optimum balance between high efficiency and service life

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

Efficiency

Efficiency vs. operating conditions

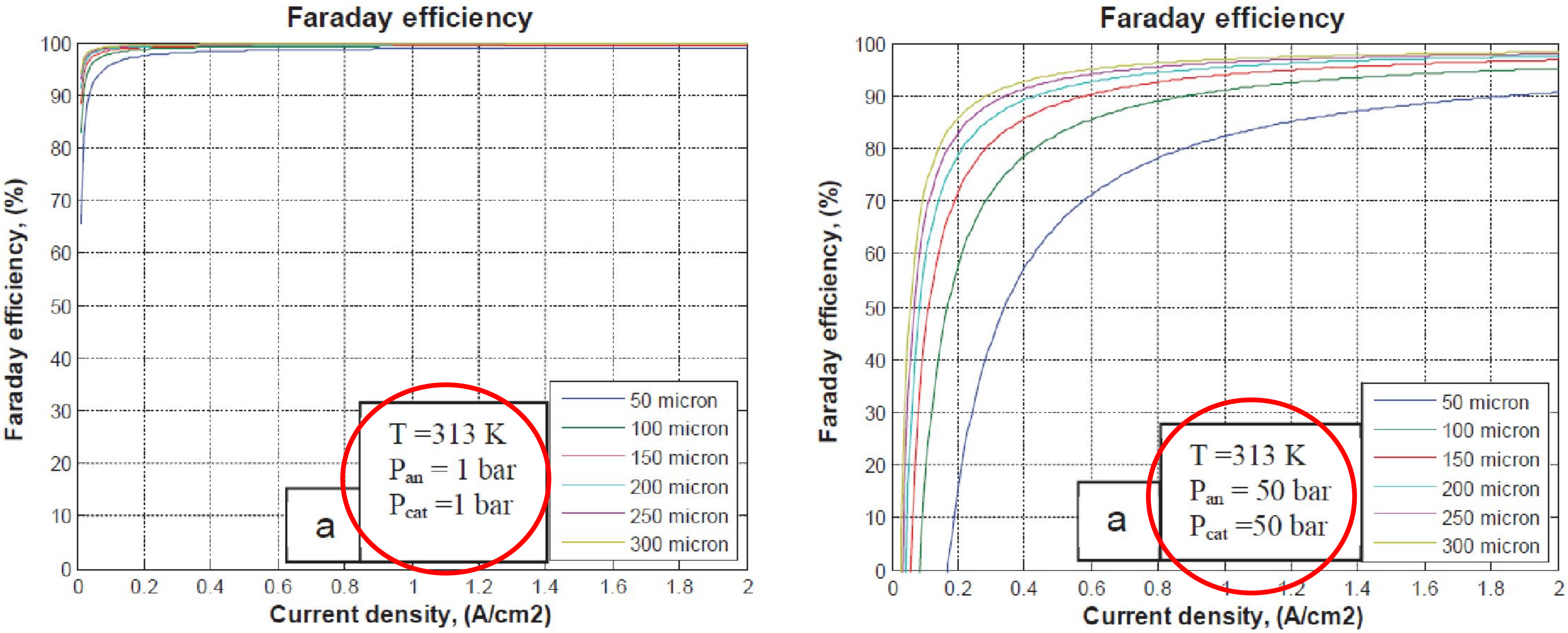


Temperature has no significative effect on Faraday efficiency

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

Efficiency

Efficiency vs. operating conditions

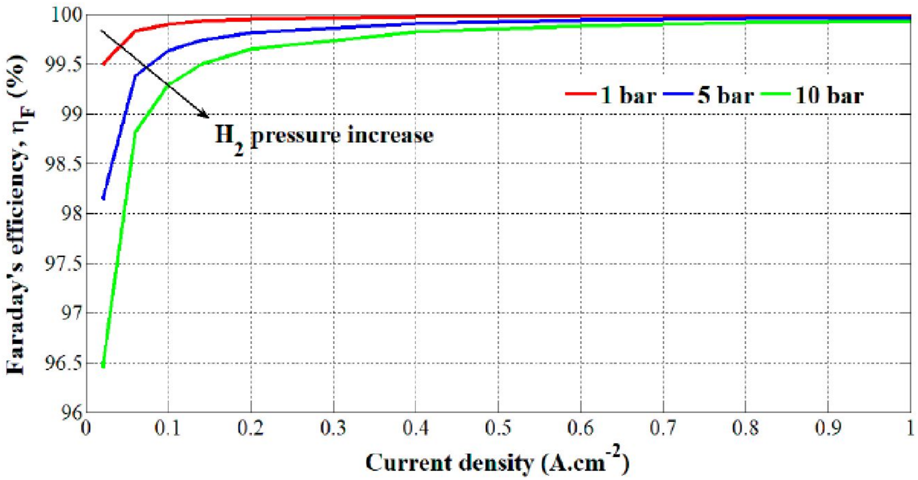


Faraday efficiency increase at low pressure…, but an external compressor is needed. Efficiency of the complete system need to be studied

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

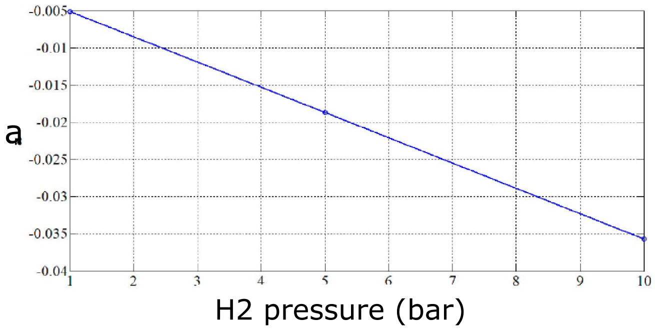
Efficiency modelling

Typically, empirical approaches are used



$$\eta_F = a\left(\frac{i_{el}}{A}\right)^b + c$$

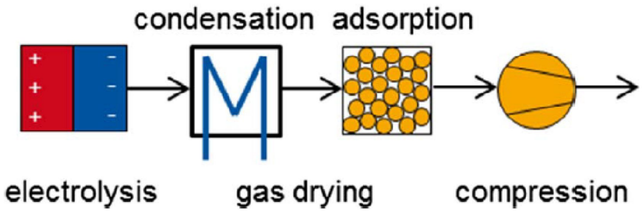
p (Bar)	a	b	c
1	−0.005103	−1	1
5	−0.01871	−1	1
10	−0.03572	−1	1



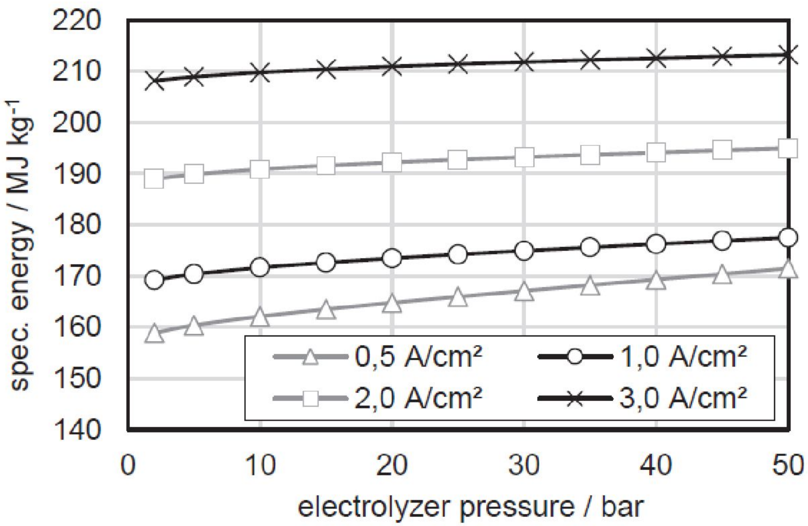
$$\eta_F = (a_1 p + a_2)\left(\frac{i_{el}}{A}\right)^b + c$$

Yodwong, B.; Guilbert, D.; Phattanasak, M.; Kaewmanee, W.; Hinaje, M.; Vitale, G. Faraday's Efficiency Modeling of a Proton Exchange Membrane Electrolyzer Based on Experimental Data. Energies 2020, 13.

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.

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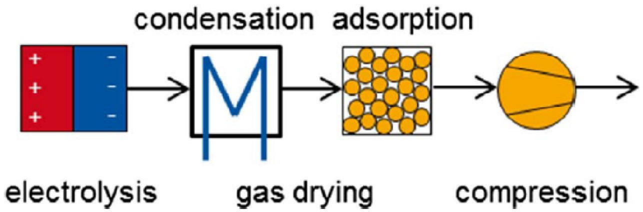
Efficiency of the complete system



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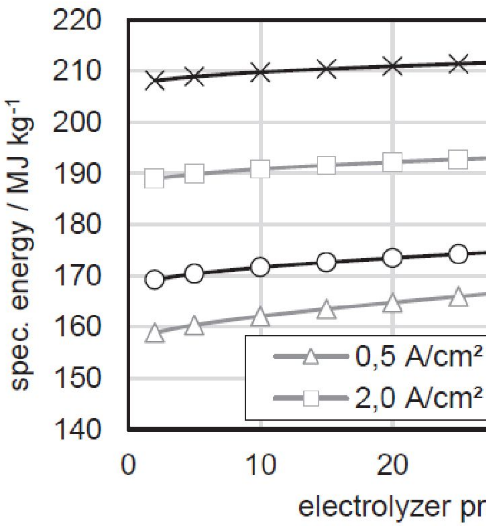

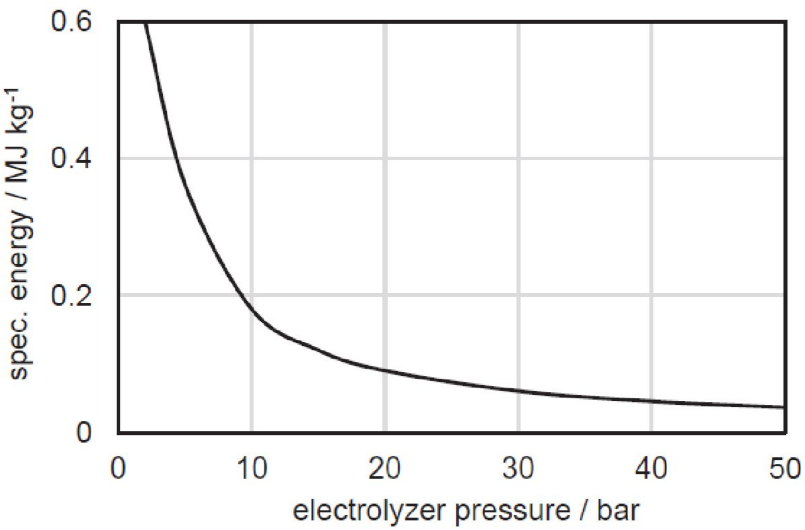

Electrolyzer

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.
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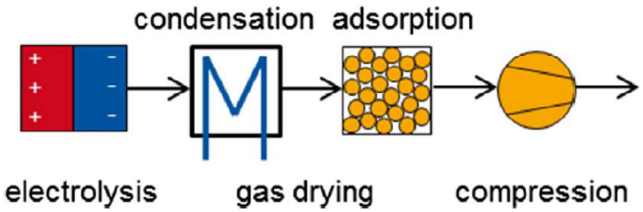
Efficiency of the complete system



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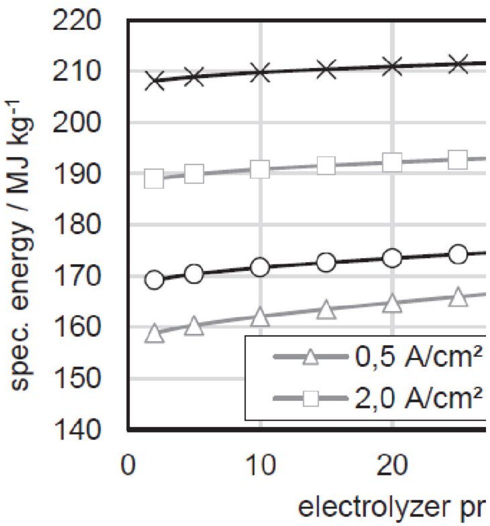
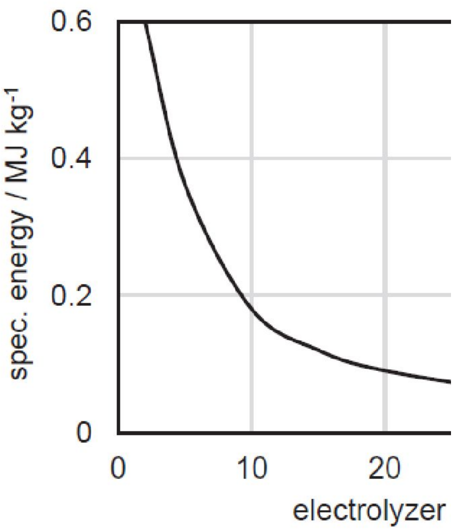
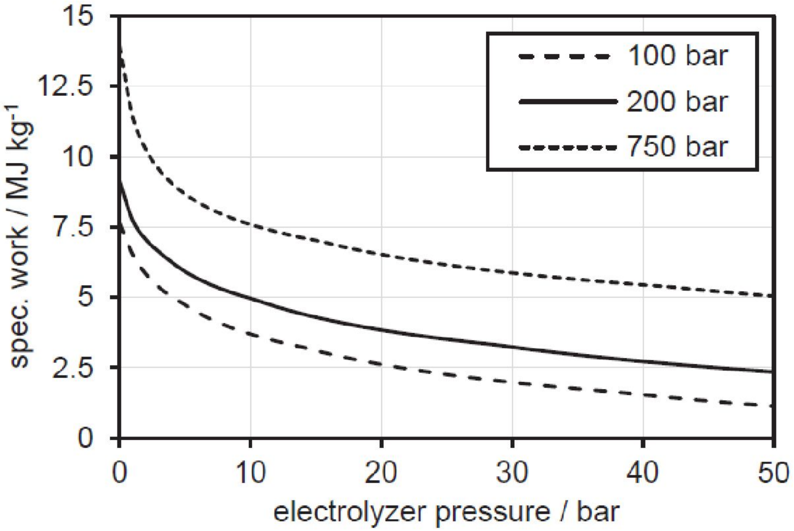


Electrolyzer



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.

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Summary

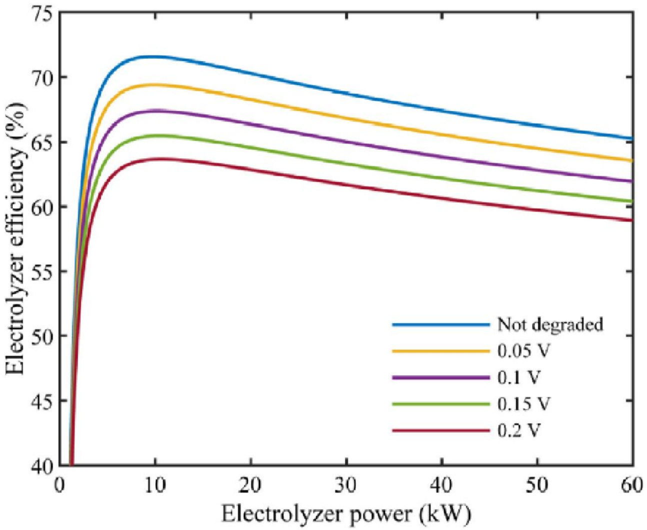
- Introduction
- Mathematical model of PEM electrolyzers
  - Static Electrochemical models
  - Thermal models
  - Identification
- Efficiency
- **Degradation**

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.

Degradation

Conclusions of studies (power)

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

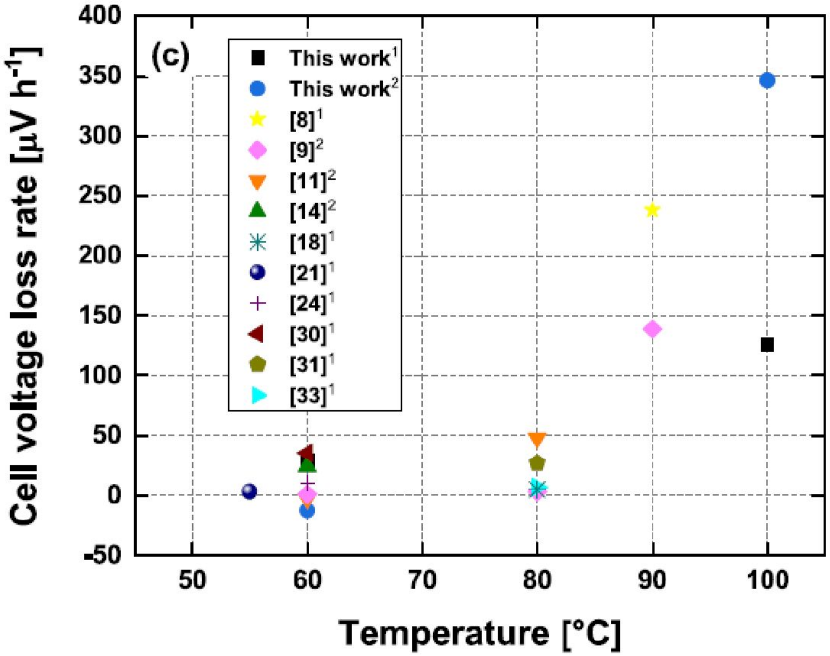
Mode	
Maintaining operation (very low power)	1.5
Low power fluctuation (600 W – P_t)	50
Constant P_t	20
High power fluctuation (P_t - P_{el})	66
Constant high power (P_{el})	196

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

Degradation

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*

Muchas gracias!!

Muito obrigado!!

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PROGRAMA IBEROAMERICANO DE CIENCIA
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INVESTIGACIÓN

OPAL
H2

Identification algorithm

Boundaries (lb and ub)

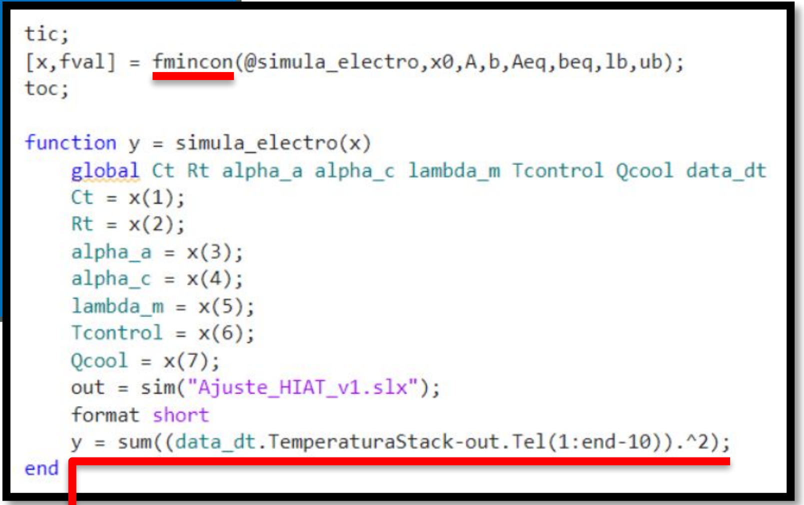
Ct (J/K): 9000 [1] – 400000 [2]

Rt (K/W): 0.014 [3] – 0.14 [2]

Alpha_a: 0.24 – 2.1 [4]

Alpha_c: 0.1 – 0.9 [2]

Lambda_m: 0 – 24 [2]



```
tic;
[x,fval] = fmincon(@simula_electro,x0,A,b,Aeq,beq,lb,ub);
toc;

function y = simula_electro(x)
    global Ct Rt alpha_a alpha_c lambda_m Tcontrol Qcool data_dt
    Ct = x(1);
    Rt = x(2);
    alpha_a = x(3);
    alpha_c = x(4);
    lambda_m = x(5);
    Tcontrol = x(6);
    Qcool = x(7);
    out = sim("Ajuste_HIAT_v1.slx");
    format short
    y = sum((data_dt.TemperaturaStack-out.Tel(1:end-10)).^2);
end
```

Minimize Squared Error

Identification tests

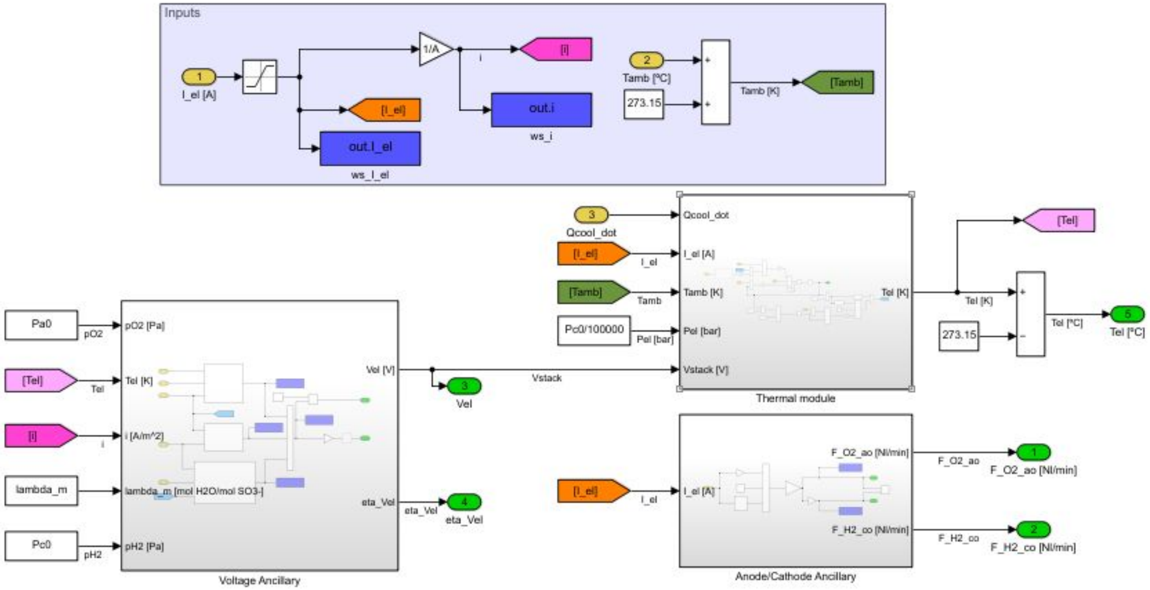
	Initial	1a	1b	2	3a	3b
Ct (J/K)	25000	16079	15231	16079	15701	16218
Rt (K/W)	0.25	0.1203	0.1156	0.1203	0.14	0.1339
Tcontrol (ºC)	-	-	-	-	60	60
Qcool (W)	-	-	-	-	99.9686	65.536
Alpha_a	2	2	0.93025	0.93025	0.93025	2
Alpha_c	0.7	0.7	0.9	0.9	0.9	0.7
Lambda_m	9	9	13.7385	13.7385	13.7385	9
Time (s)	-	495.63	513.56	1519.46	623.42	1668.22

Time that fmincon expends to achive the optimal values of the parameters identified

Validation of the models

	Initial	1a	1b	2	3a	3b
	Error mean					
Temp	-4.1201	0.5606	0.3962	0.0197	-0.2452	0.4074
Voltage	-0.46173	-0.5212	-0.9876	-0.9870	-0.9799	-0.5153
	RMSE					
Temp	8.5824	1.3456	0.9930	1.2375	1.1679	1.1261
Voltage	1.779	1.7907	2.1057	2.1049	2.1055	1.7894

Simulink model



OPALH2 and ODYELH2 Projects