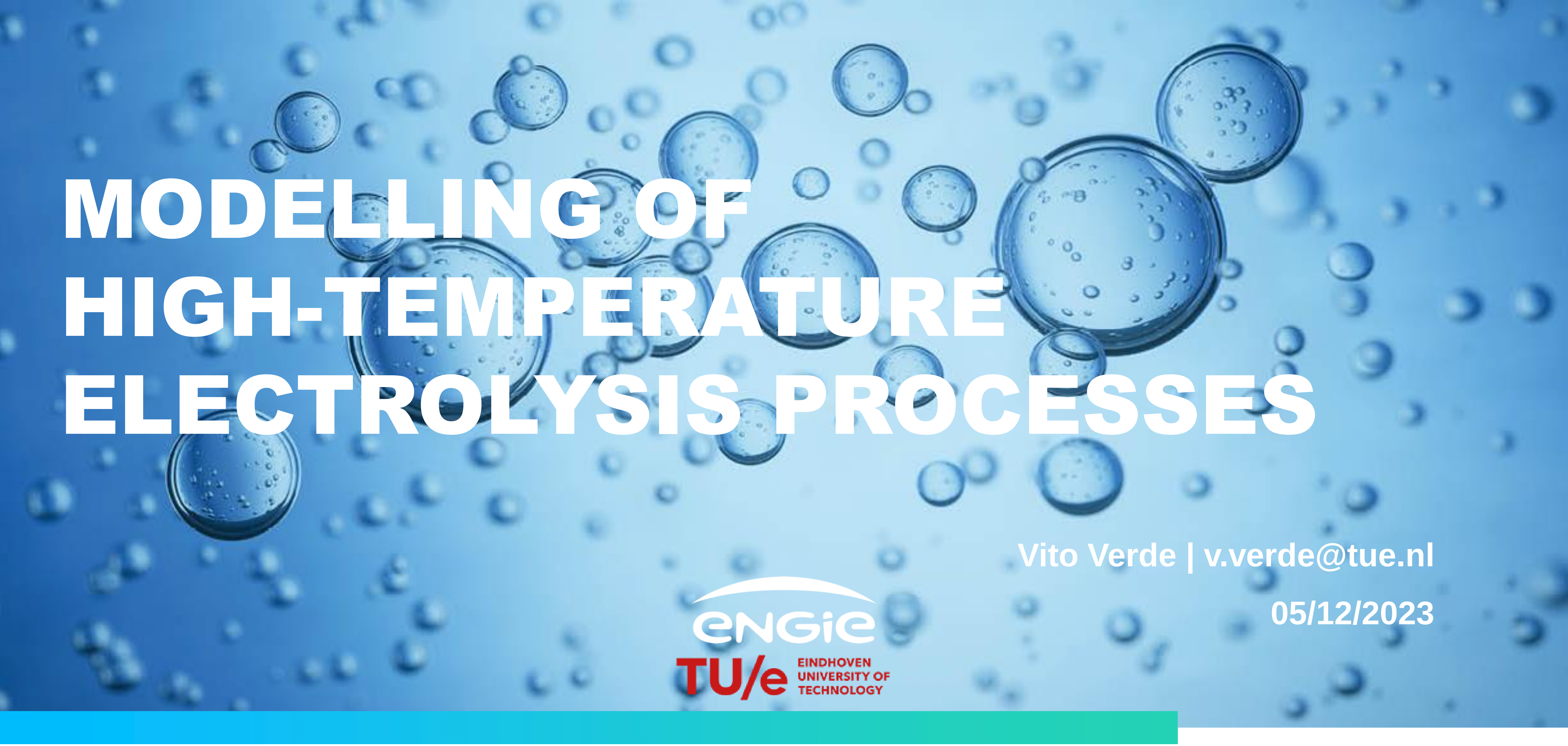

MODELLING OF HIGH-TEMPERATURE ELECTROLYSIS PROCESSES

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Contents

1

Introduction

Electrolysis thermodynamics and Solid Oxide Electrolysis Cells Fundamentals

1. Introduction

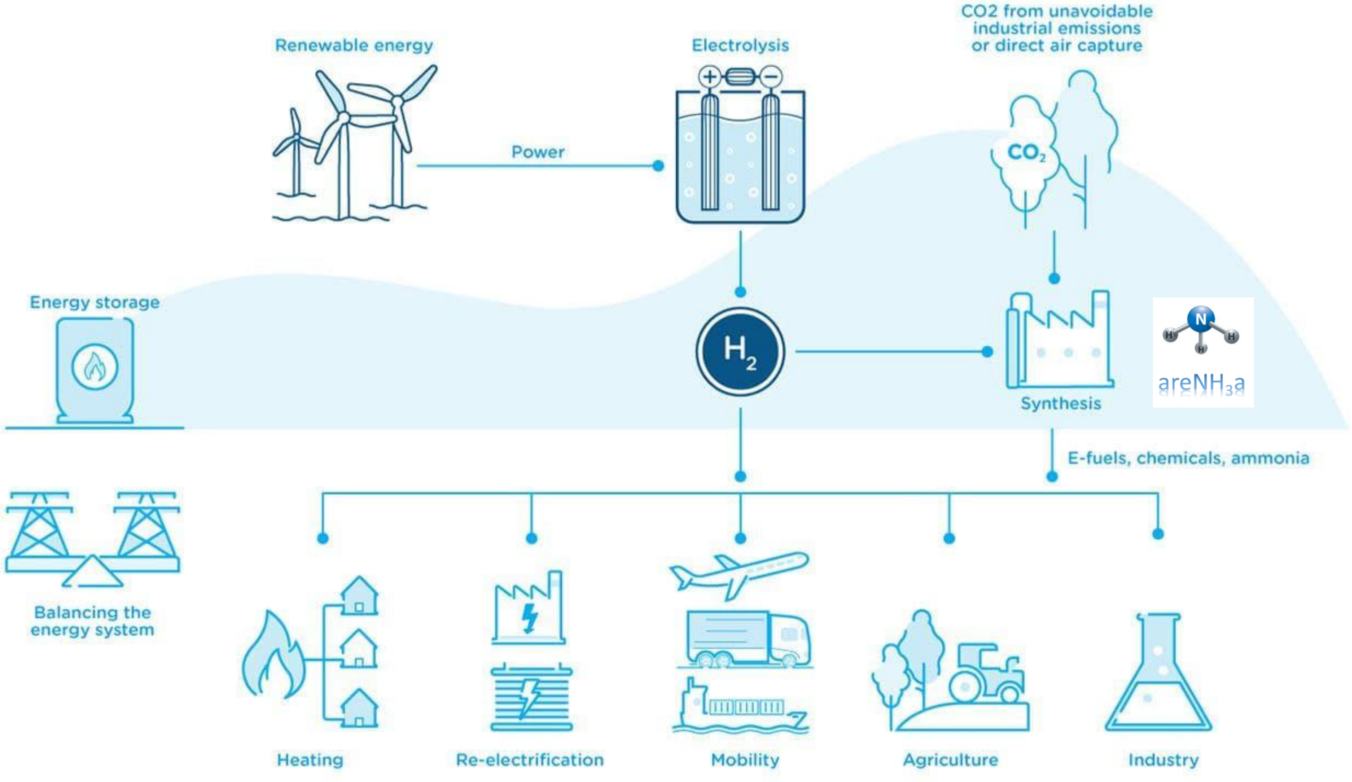
Context

EU 2030 Climate & Energy Framework:

- 55% Greenhouse Gas Emissions (compared to 1990 levels);
- 42.5% Energy produced from renewable energy;
- 36% Improvement in energy efficiency;

Hydrogen is a carbon free energy vector: only water is produced by its combustion, and it can be used for the decarbonization of several sectors

In 2022, only 0.1% of H_2 demand has been produced using electricity. We need to produce hydrogen using renewable energy and in an efficient way ⇒ **Process modelling and simulations**



Green Hydrogen Production Pathways and applications (Source: Ramboll)

1. Introduction

Water Electrolysis Fundamentals

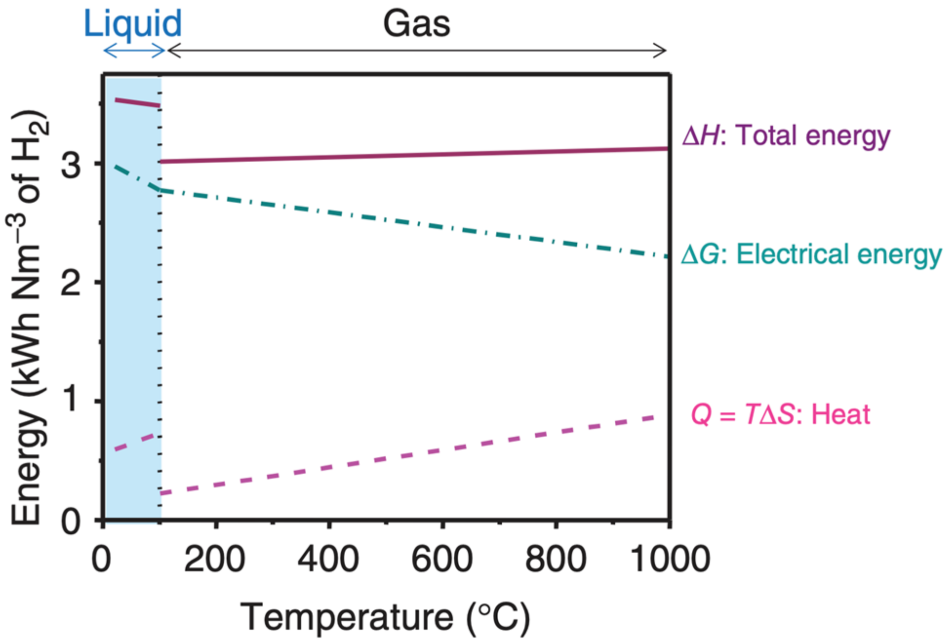
Water electrolysis is the electrochemical reaction based on the dissociation of water into hydrogen and oxygen under an induced voltage.

Water electrolysis Reaction: $H_2O \rightarrow \frac{1}{2}O_2 + \mathrm{H}_2$

Total energy required to perform electrolysis reaction: $\Delta H = \Delta \mathrm{G} + \mathrm{T} \cdot \Delta S$ $\underset{}{> 0}$

Hydrogen production:
(Faraday Law)

$$\dot{n}_{H2} = \frac{I_F}{\mathrm{z_e} \cdot F} \left\{ \begin{array}{l} I_F: Faradic\ Current\ [A] \\ F: Faraday\ Constant\ [J/mol] \\ z_e: \#\ of\ electron\ exchanged \end{array} \right.$$



Energy need for the water electrolysis reaction, as function of temperature, enthalpy (ΔH), Gibbs free energy (ΔG) and entropy (TΔS)
Source: (G. Jopek, "Hydrogen Production by Electrolysis ", 2018)

1. Introduction

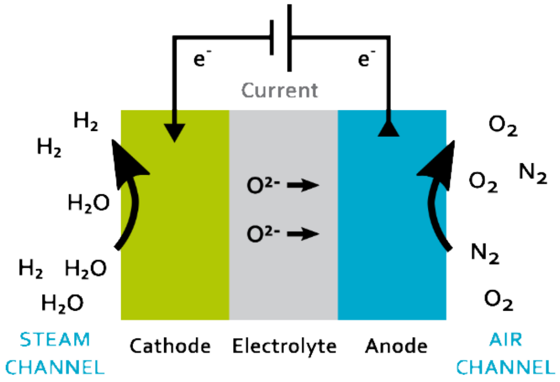
Solid Oxide Electrolysis Cells (SOECs) Fundamentals

SOECs are electrochemical devices for water electrolysis based on dense ceramic electrolytes able to conduct O2- ions.

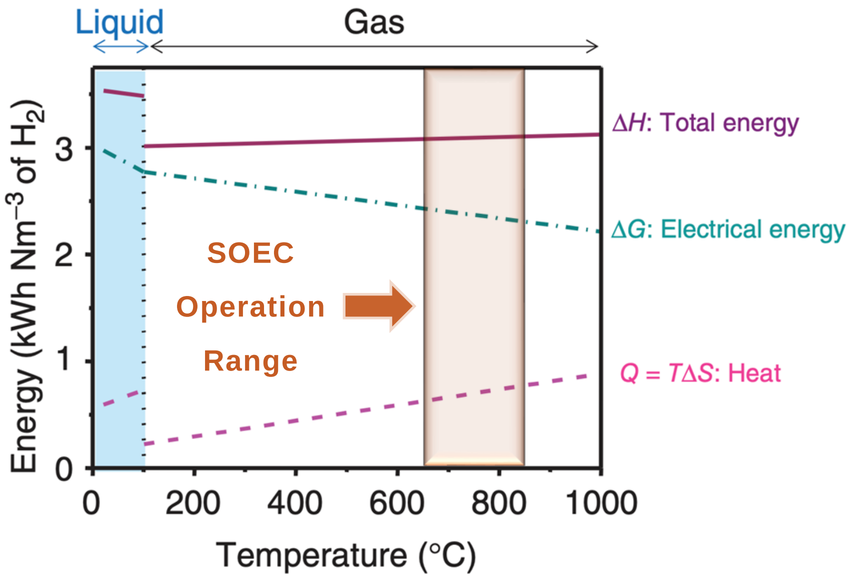
Cathode semi-reaction: $H_2O + 2e^- \rightarrow H_2 + O^{2-}$

Anode semi-reaction: $O^{2-} \rightarrow \frac{1}{2}O_2 + 2e^-$

Overall Reaction: $H_2O \rightarrow \frac{1}{2}O_2 + \mathrm{H}_2$



Source: Convion



Energy need for the water electrolysis reaction, as function of temperature, enthalpy (ΔH), Gibbs free energy (ΔG) and entropy (TΔS) (Source: G. Jopek, "Hydrogen Production by Electrolysis ", 2018)

Key advantages of high T operation:

- Higher Efficiency → Lower OPEX;
- No need for Platinum-Group Metals (PGMs) → More robust supply chain;
- Heat integration possibility (e.g. Power-to-X applications);

1. Introduction

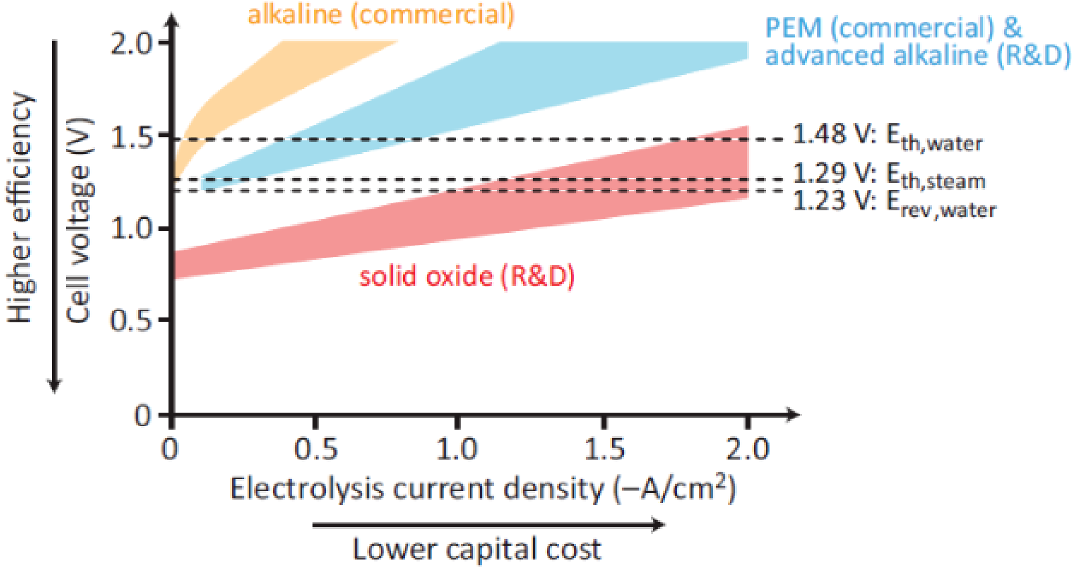
Electrolysis Technologies: Performance Comparison

Electrolysis Technology	Alkaline (AEC)	Proton Exchange Membrane (PEMEC)	Solid Oxide (SOEC)
Nominal current density	0.2-0.8 A/cm2	0.2-2 A/cm2	0.3-1 A/cm2
Voltage Range (Cell)	1.4-3 V	1.4-2.0 V	1.0-1.5 V
Operating Temperature	60-90°C	50-80°C	700-850°C
Efficiency (%HHV)	60%-84% (HHV)	64-84% (HHV)	75-85% (LHV)
Electrical Efficiency (Stack)	47-66 kWh/kgH2	47-61 kWh/kgH2	35-45 kWh/kgH2
Electrical Efficiency (System)	50-78 kWh/kgH2	50-83 kWh/kgH2	44-50 kWh/kgH2

Typical operating ranges of different electrolysis technologies (Source: Chatenetet al., Chemical Society Reviews, 2022, 51, 4583.)

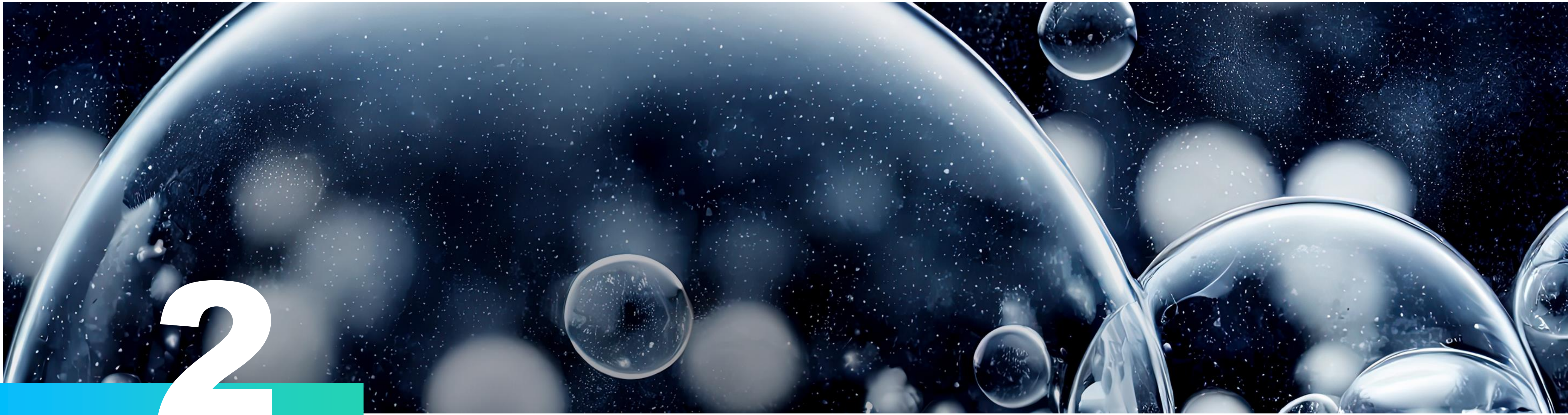
70-75% SOEC System electrical efficiency (LHV) possible
(Depending on hydrogen delivery pressure)

Further improvements possibles with external heat integration!



Typical operating zones of different electrolysis technologies (Source: Graves et al., 2021)

More than 70% of Hydrogen production cost (LCOH) is related to electricity cost (>50 €/MWh), having high electrolysis efficiencies and high productivity is crucial!



2

SOECs Modelling

Methodology & Tools

2. SOEC Modelling

SOEC Modelling overview

High-temperature electrolysis process based on SOEC involves several multiphysics processes that can be studied ad different levels:

Electrochemistry

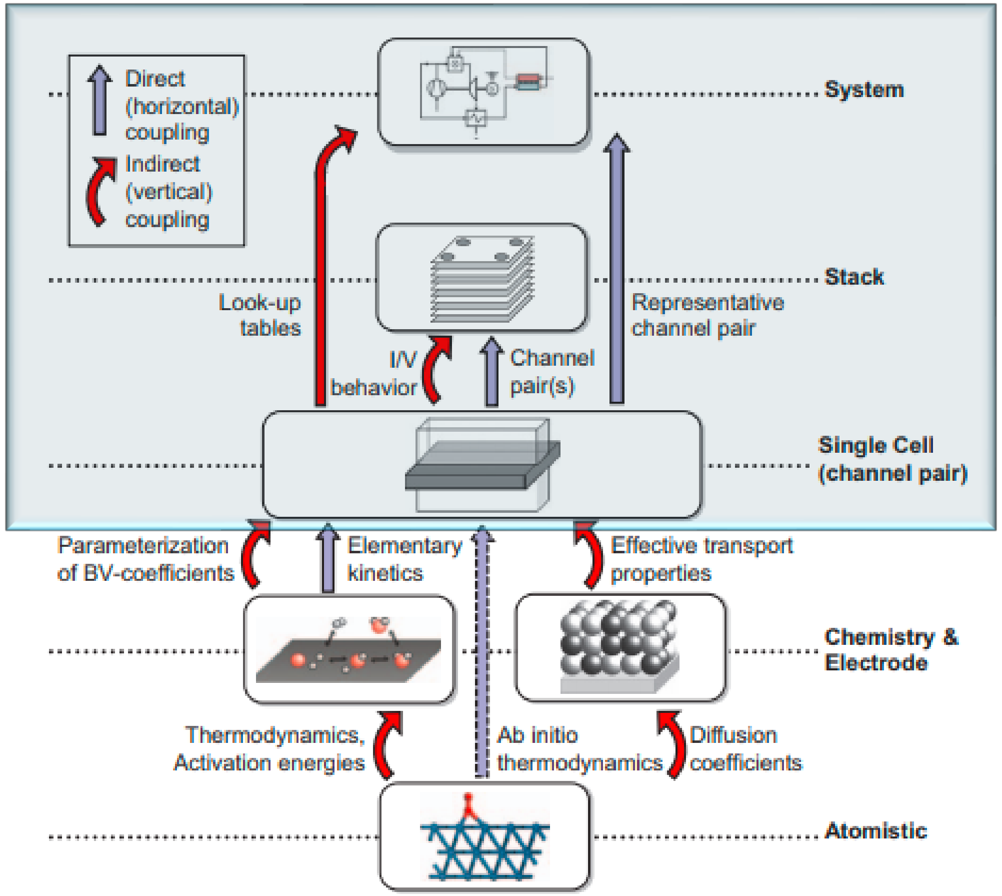
Mass Transport

Heat Exchange

Electrical

Fluid-dynamics

Different model state (Steady, Dynamic) and dimension depending on the application

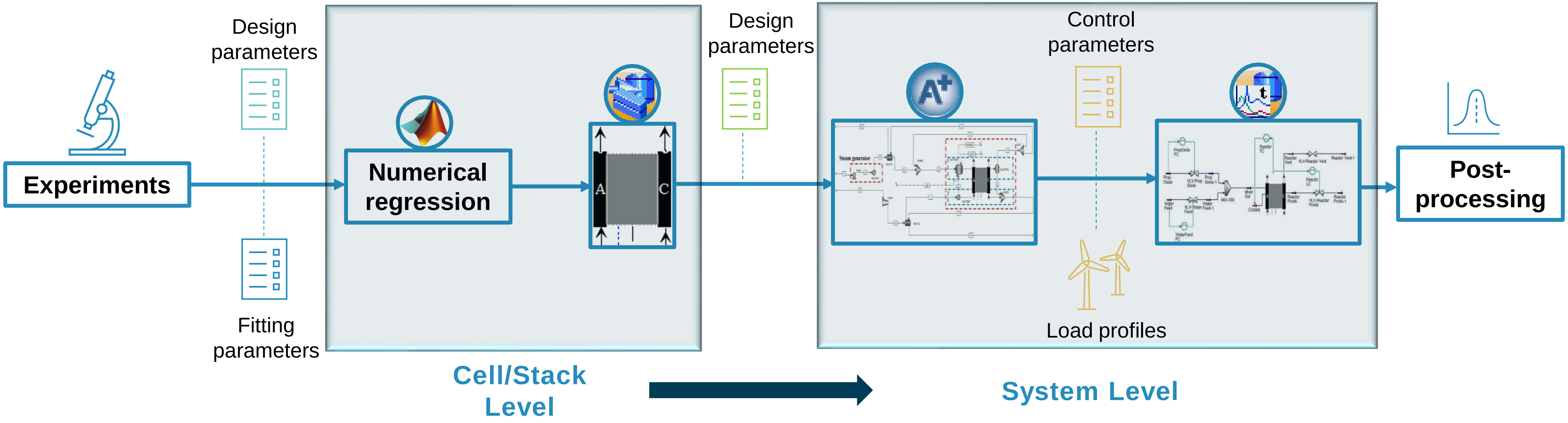


2. SOEC Modelling

SOEC System Modelling Approach

Modelling tools:

- MATALB/Aspen Custom Modeler (Cell/Stack level);
- Aspen Plus/ Aspen Plus Dynamics (System Level);



Design parameters

Experiments

Numerical regression

Fitting parameters

A

C

Design parameters

Control parameters

Load profiles

Post-processing

Cell/Stack Level

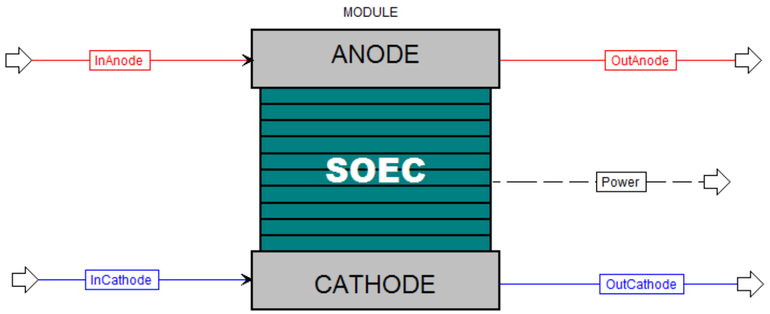
System Level

2. SOEC Modelling

Cell/Stack Model

SOEC Stack Lumped parameter model based on several assumptions:

- Peng-Robinson state equation;
- Constant stack pressure drop ;
- Negligible effects related to mass transport dynamics;
- Average values (T, P, V, i) representative of the entire unit.

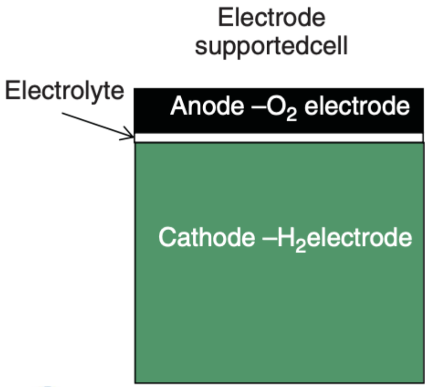


- ✓ Suitable for simple water electrolysis
- ✓ Lower computational times for long term simulations!

2 Models developed in the context of ARENHA EU project:

Model 1:

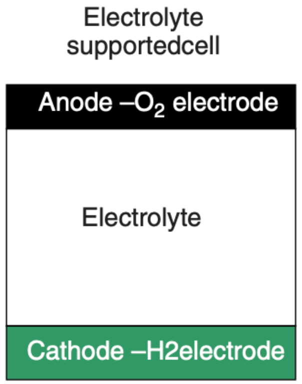
Cathode Supported



elcogen

Model 2:

Electrolyte supported



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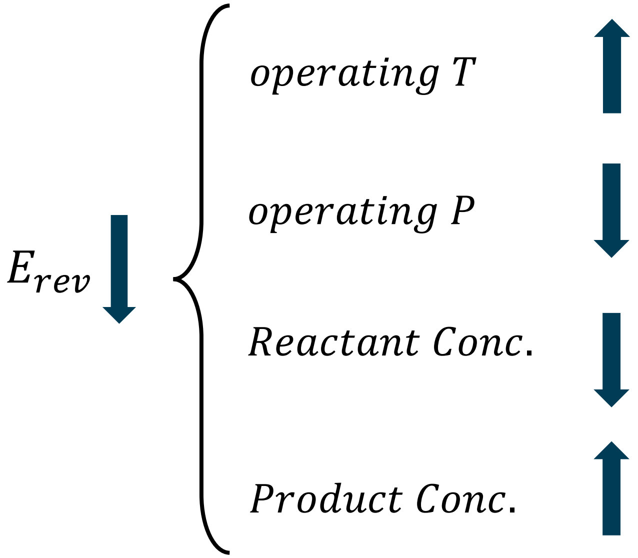
2. SOEC Modelling

Cell Polarization: Open Circuit Voltage (OCV)

$$V_{cell} = \boxed{E_{rev}} + \eta_{an}^{act} + \eta_{cat}^{act} + \eta_{Ohm} + \eta_{an}^{conc} + \eta_{cat}^{conc}$$

- Voltage in no-current operating condition (Ideal Voltage);
- Derived from the combination of Faraday equation with 1st and 2nd principles of thermodynamics for open systems with no irreversibility;

Potential	Symbol	Law	Equation
Reversible potential (OCV)	E_{rev}	Nernst Equation	$E_{rev} = \frac{\Delta G^0}{z_e F} + \frac{RT}{z_e F} \, ln \frac{P_{O_2}^{1/2} \cdot P_{H_2}}{P_{H_2O}}$ $\Delta G^0 = 244{,}800 - 49.18 \cdot T - 2.72 \cdot T^2$ ΔG^0: *gibbs free energy in standard conditions*



E_{rev} ↓

operating T ↑

operating P ↓

Reactant Conc. ↓

Product Conc. ↑

2. SOEC Modelling

Cell Polarization: Activation Overvoltage

$$V_{cell} = E_{rev} + \boxed{\eta_{an}^{act} + \eta_{cat}^{act}} + \eta_{Ohm} + \eta_{an}^{conc} + \eta_{cat}^{conc}$$

- Voltage spent to activate the electrochemical reaction at the electrode → **Charge Transfer**

Potential	Symbol	Law	Equation
Activation overpotential	$\eta_{a/c}^{act}$	Butler-Volmer equation	$\eta_{a/c}^{act} = \frac{RT}{z_e F} \sinh^{-1}\left(\frac{i}{2i_{0,a/c}}\right)$

i_0: Exchange Current density. Dependent on operating conditions, catalyst and its distribution in the electrode

$$i_{0,an} = B \cdot \left(\frac{p_{O_2}}{p_{ref}}\right)^{n} \cdot \exp\left(-\frac{Eact_{an}}{RT}\right)$$

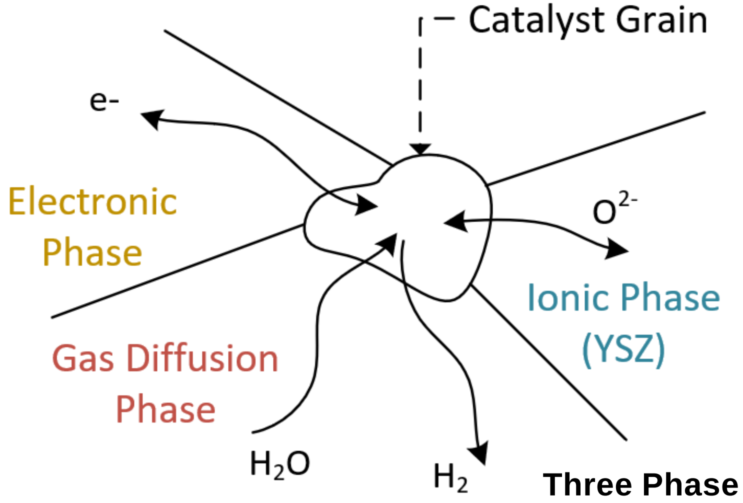
$$i_{0,cat} = A \cdot \left(\frac{p_{H_2}}{p_{ref}}\right)^{m} \cdot \left(\frac{p_{H_2O}}{p_{ref}}\right)^{p} \cdot \exp\left(-\frac{Eact_{cat}}{RT}\right)$$

Fitting Parameters

$Electrode\ at\ Open\ Circuit$:

$$H_2O + 2e^- \leftrightharpoons H_2 + O^{2-}$$

$$r_{FW} = r_{BW}$$



Three Phase Boundary

2. SOEC Modelling

Cell Polarization: Ohmic Overvoltage

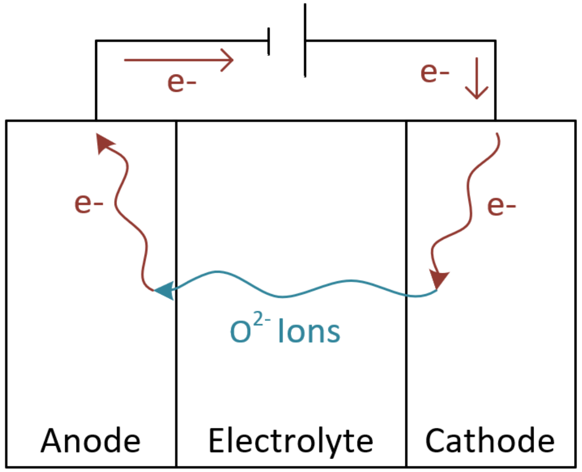
$$V_{cell} = E_{rev} + \eta_{an}^{act} + \eta_{cat}^{act} + \boxed{\eta_{Ohm}} + \eta_{an}^{conc} + \eta_{cat}^{conc}$$

- Voltage increase due to ionic conduction in the electrolyte and e- conduction in the interconnector/electrodes;
  → **Charge transport**

Potential	Symbol	Law	Equation
Ohmic Overvoltage	η_{Ohm}	Ohm's Law	$\eta_{Ohm} = i\left(\frac{\tau_a}{\sigma_a(T)} + \frac{\tau_e}{\sigma_e(T)} + \frac{\tau_c}{\sigma_c(T)} + \boxed{R_{cc}}\right)$ Correlation for material conductivities $\sigma(T)$

Fitting Parameter

$$\eta_{Ohm} \downarrow \left\{ \begin{array}{ll} Material & \\ Operating\ T \\ \text{(Mostly Ionic behaviour)} & \uparrow \\ Material\ \ thickness\ \tau & \downarrow \end{array} \right.$$



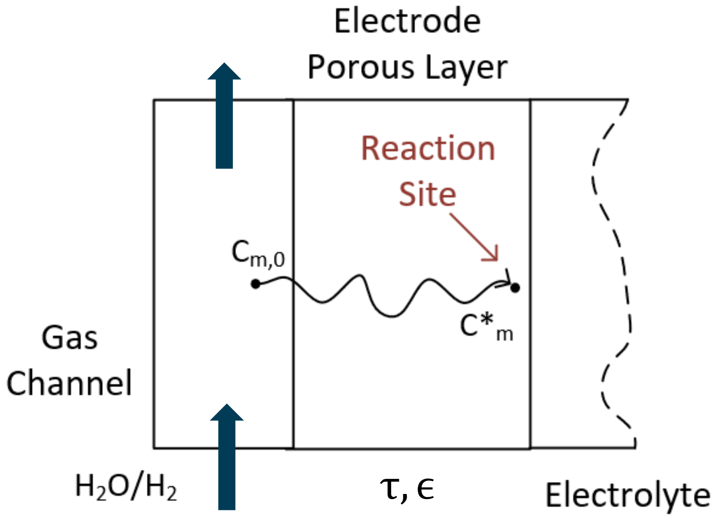
2. SOEC Modelling

Cell Polarization: Concentration Overvoltage

$$V_{cell} = E_{rev} + \eta_{an}^{act} + \eta_{cat}^{act} + \eta_{Ohm} \boxed{+ \eta_{an}^{conc} + \eta_{cat}^{conc}}$$

- Concentration overvoltage is the voltage increase related to diffusion of chemical species inside electrodes
  → **Mass Transport**

Potential	Symbol	Law	Equation
Concentration overpotential	$\eta_{a/c}^{conc}$	Knudsen and molecular diffusion	$\eta_{a/c}^{conc} = \frac{RT}{z_e F} ln \prod_m \left(\frac{c_m^*}{c_{m,0}}\right)^v$



$c_{m,0}$: *calculated from Fick's law using an effective Diffusion coefficient*

$$D_{eff} = \frac{1}{\frac{1}{D_k} + \frac{1}{D_{1,2}}}$$

$$\eta_{a/c}^{conc} \left\{ \begin{array}{l} Operating\ T \\ Bulk\ Concentrations \\ Electrode\ structure\ (\tau, \epsilon) \end{array} \right.$$

c_m^*: m^{th} *specie concenctration at reaction site*

$c_{m,0}$: m^{th} *specie bulk concenctration*

τ: *electrode tortuosity*

ϵ: *electrode porosity*

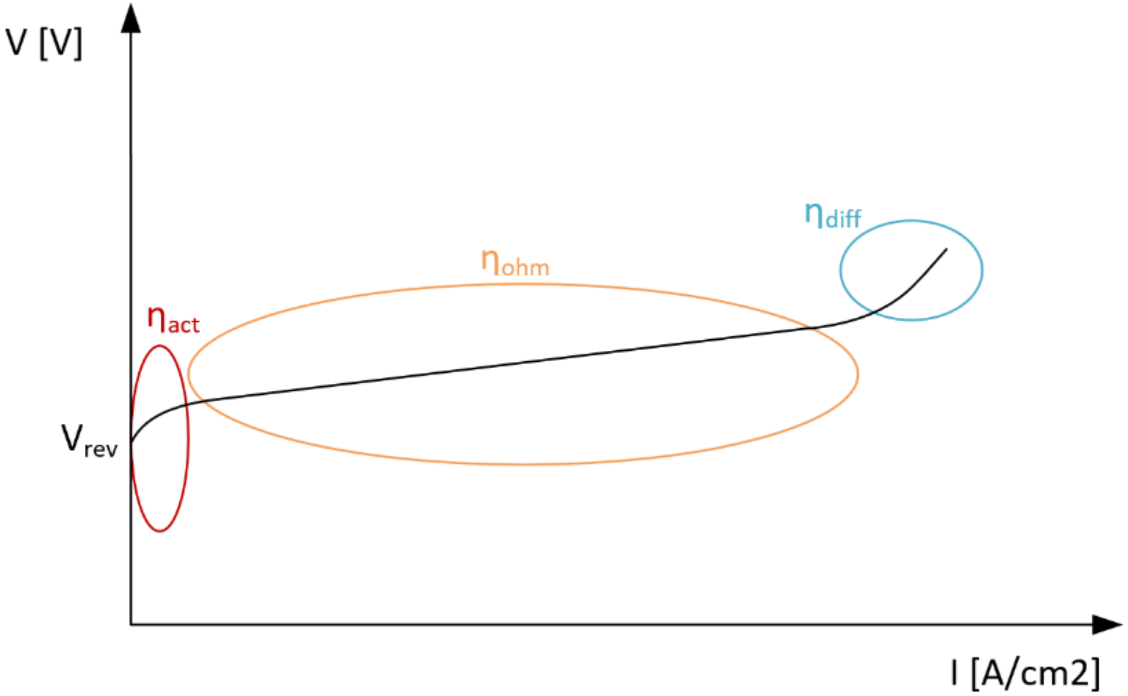
2. SOEC Modelling

Cell Polarization

$$\boxed{V_{cell}} = E_{rev} + \eta_{an}^{act} + \eta_{cat}^{act} + \eta_{Ohm} + \eta_{an}^{conc} + \eta_{cat}^{conc}$$

Potential	Symbol	Law	Equation
Reversible potential (OCV)	E_{rev}	Nernst Equation	$E_{rev} = \frac{\Delta G^0}{z_e F} + \frac{RT}{z_e F} \ln \frac{{P_{O_2}^{g}}^{1/2} P_{H_2}^{g}}{P_{H_2O}^{g}}$
Activation overpotential	$\eta_{a/c}^{act}$	Butler-Volmer equation	$\eta_{a/c}^{act} = \frac{RT}{z_e F} arcsinh\left(\frac{i}{2 i_{0,a/c}}\right)$
Ohmic resistance	η_{Ohm}	Ohm's Law	$\eta_{Ohm} = i\left(\frac{\tau_a}{\sigma_a(T)} + \frac{\tau_e}{\sigma_e(T)} + \frac{\tau_c}{\sigma_c(T)} + R_{cc}\right)$
Concentration overpotential	$\eta_{a/c}^{conc}$	Knudsen and molecular diffusion	$\eta_{a/c}^{conc} = \frac{RT}{z_e F} \ln \prod_{m} \left(\frac{c_m^*}{c_{m,0}}\right)^{v}$

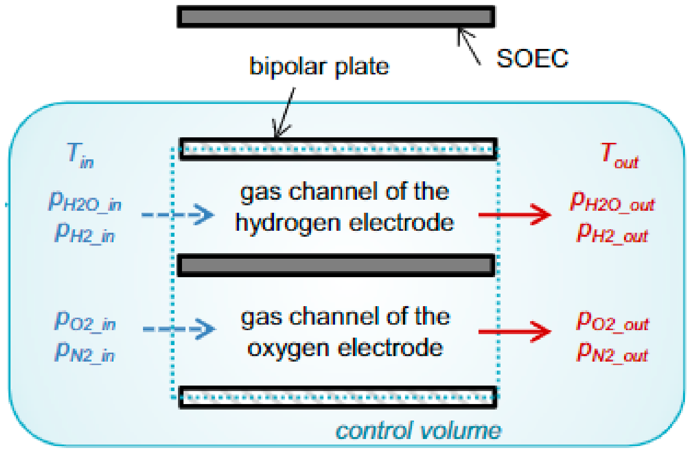
- Polarization curve is obtained with the combination of ideal and all overvoltages: each one has a visible trend in a range of polarization curve;



2. SOEC Modelling

Stack Heat Balance

Electrolysis Cell 0D Sub Model



Schematic representation of cell sub-model (Source: F. Petipas et al. 2013)

$$T_{stack} = \frac{T_{out} + T_{in}}{2}$$

Fuel and Air Channels Enthalpy Balance

$$P_{an} = \bar{h}_{in,an} \cdot \dot{n}_{in,an} - \bar{h}_{out,an} \cdot \dot{n}_{out,an}$$

$$P_{cat} = \bar{h}_{in,cat} \cdot \dot{n}_{in,cat} - \bar{h}_{out,cat} \cdot \dot{n}_{out,cat}$$

Stack Heat Losses:

$$\dot{Q}_{loss,mod} = \frac{\lambda_{ins\left(\frac{T_{env}+T_{stack}}{2}\right)}}{l_{ins}} \cdot A_{unit} \cdot (T_{stack} - T_{env})$$

Stack Heat Balance:

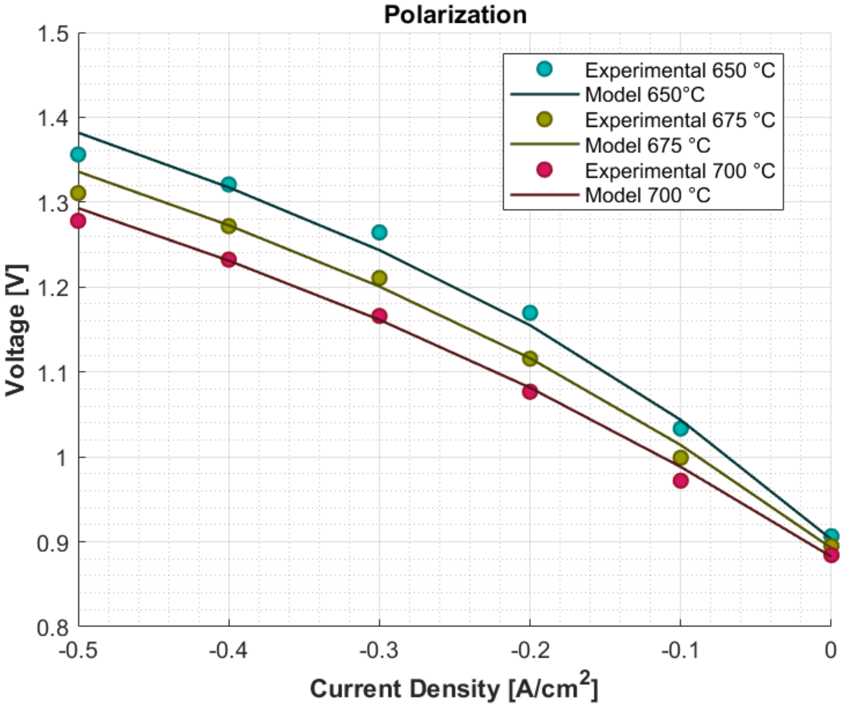
$$\boldsymbol{Cap \cdot \frac{dT_{stack}}{dt} = P_{an} + P_{cat} + W_{el} - \dot{Q}_{loss,mod}}$$

Stack thermal capacity, influences system dynamics!

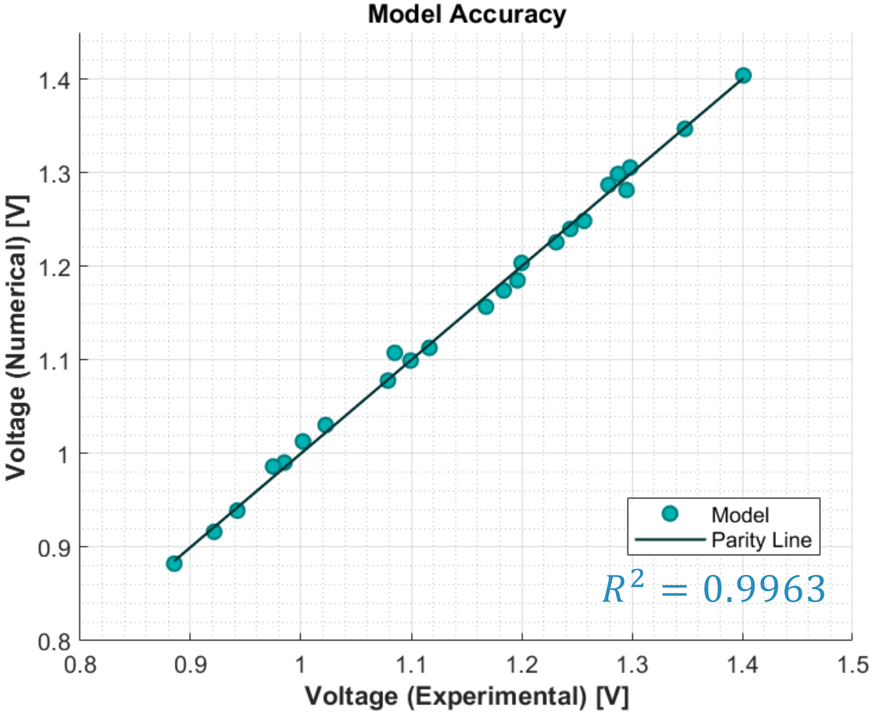
2. SOEC Modelling

Cell Model Validation

- Experimental polarization curves with different temperatures, composition and Reactant Utilisation (RU) can be used for model calibration. Activation energies, pre-exponentials (i_0), additional resistance R_{cc} and exchange current exponents are used as fitting parameters.



Polarization curve for a cathode supported SOEC at 700 °C, 4.3 air to steam ratio. Fuel inlet: 21.08 l_N/min H_2O and 2.34 l_N/min H_2 (10% Hydrogen to steam ratio)



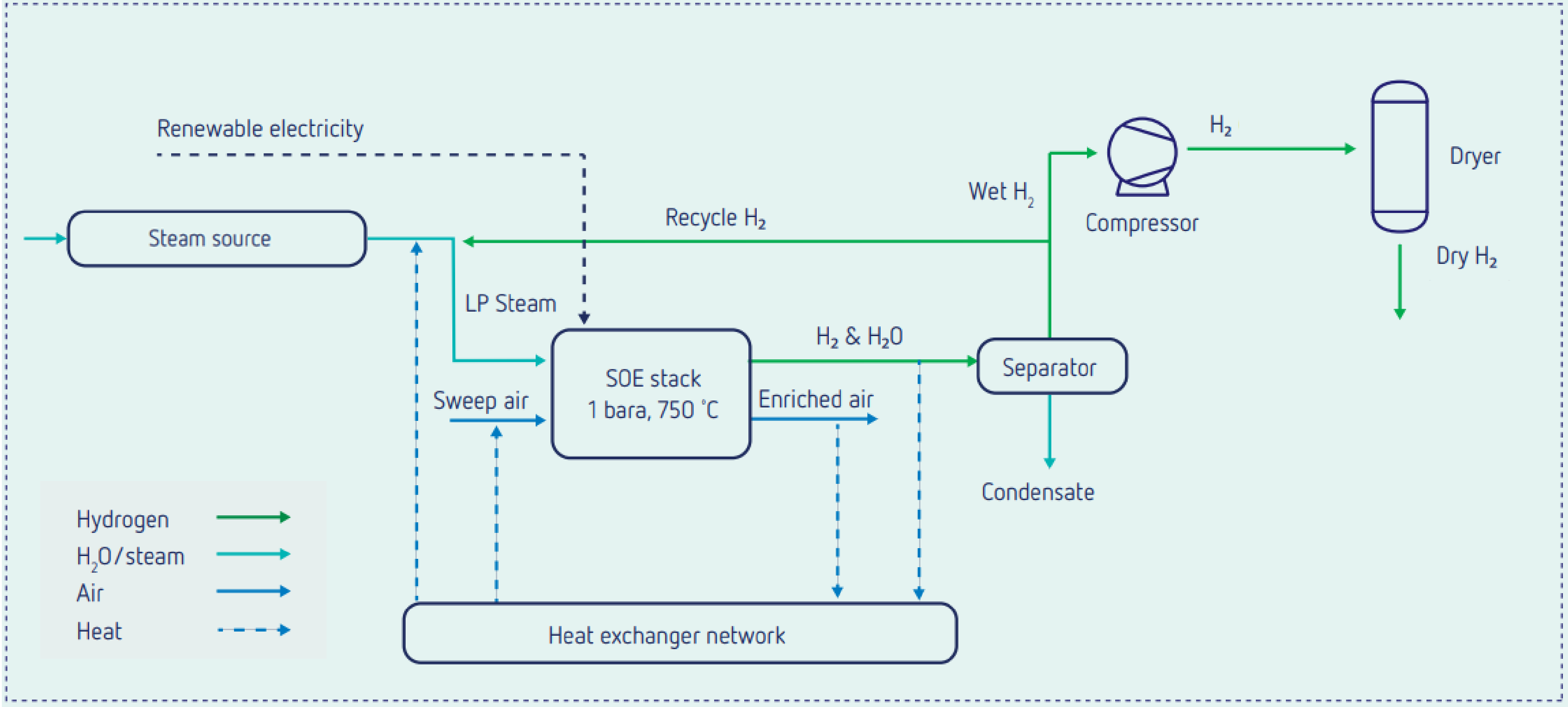
Parity plot for Cathode Supported Cell Model

2. SOEC Modelling

SOEC System Process Overview: Passing From Stack to System Level

High-temperature electrolysis process at systems level is based on few steps:

1. Steam Generation
2. Cathodic/anodic streams pre-heating
3. Electrolysis
4. Water Separation
5. Compression & Drying

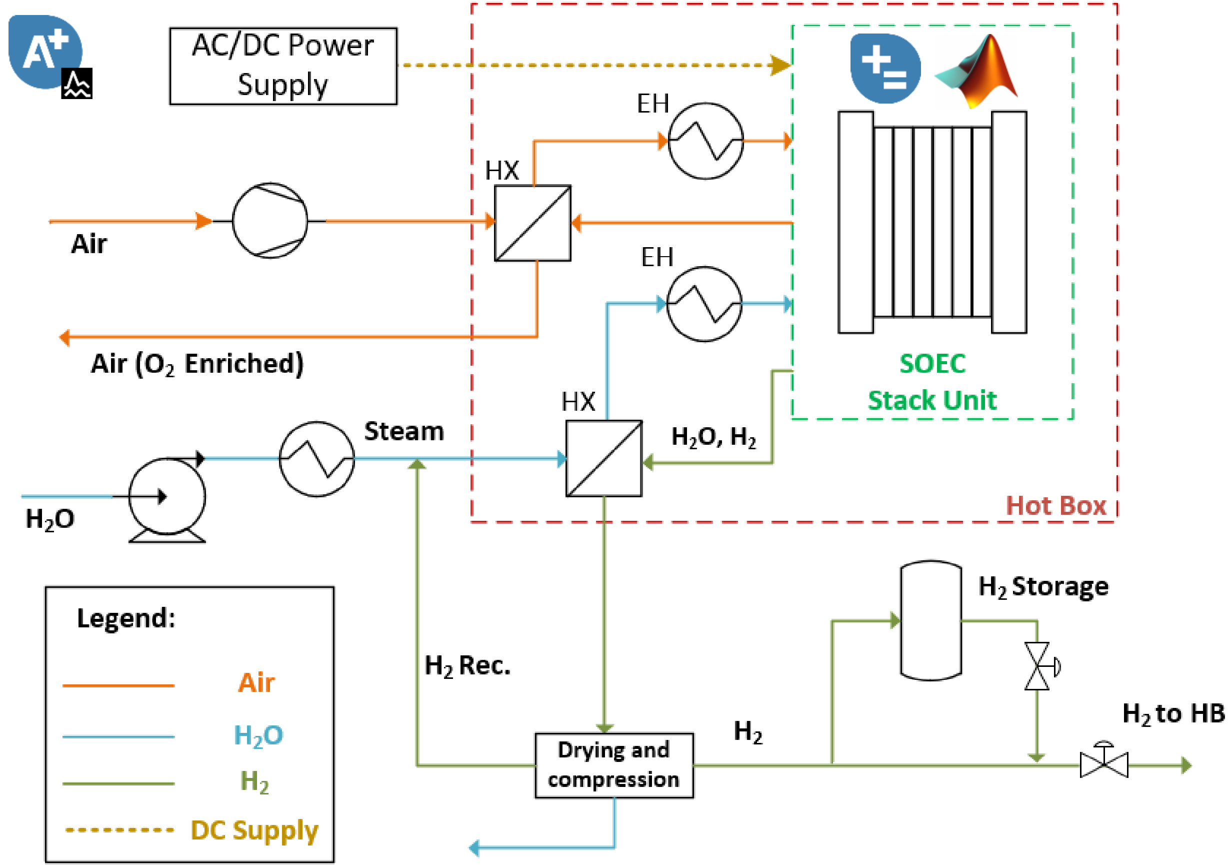


Green Hydrogen Production Process Based on SOEC (Source: ISPT, "Next Level Solid Oxide Electrolysis", 2023)

2. SOEC Modelling

Solid Oxide Electrolyser: Dynamic Model Overview

- Development of a dynamic model for the evaluation of system operation and performances under intermittent operation;



Controlled Variables:

- SOEC Stack Temperature
- SOEC Stack load range
- SOEC Stack heating rate
- SOEC Stack Reactant Utilisation
- SOEC Reactant Composition
- Hydrogen Storage Level

Main system Constraints:

- Heating rates
- SOEC load range
- SOEC ramp rate
- Compressor suction pressure

3

Activities Related

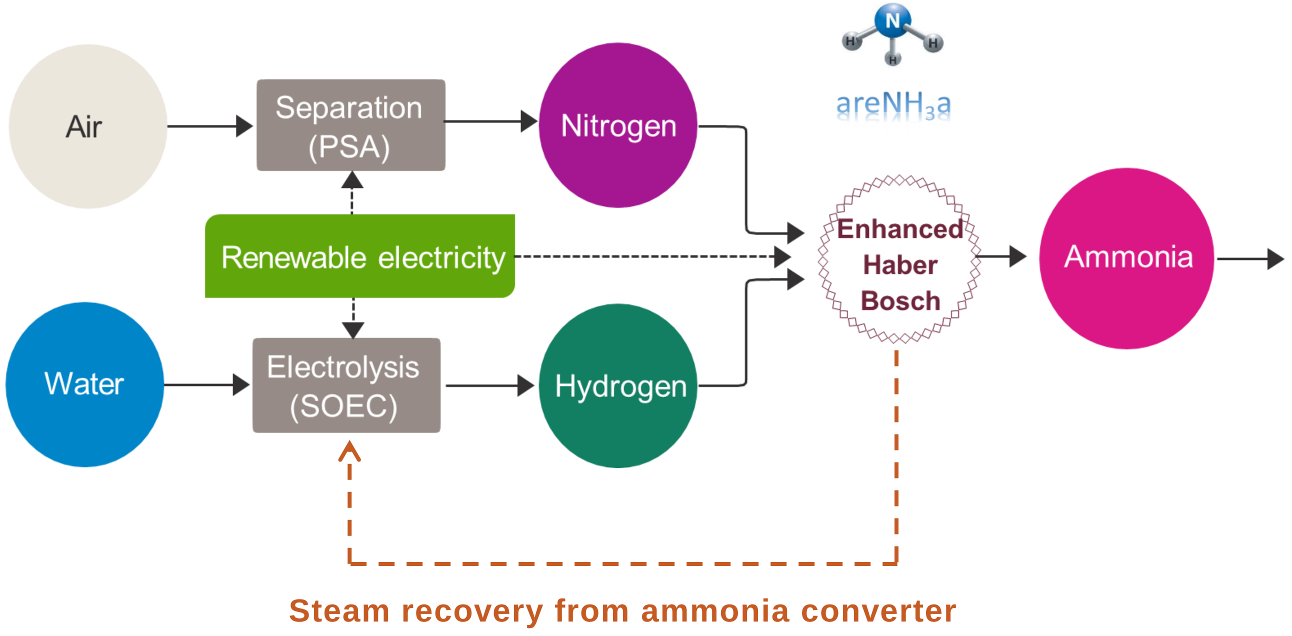
Integration of high-temperature electrolysis with enhanced ammonia synthesis processes

3. Activities Related

ARENHA: Integration of high-temperature electrolysis with enhanced ammonia synthesis processes

Challenge:

- Integration of electrolysis for green hydrogen production with ammonia synthesis processes dealing with renewable energy intermittency;



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Air

Separation (PSA)

Nitrogen

Renewable electricity

Water

Electrolysis (SOEC)

Hydrogen

Enhanced Haber Bosch

Ammonia

Steam recovery from ammonia converter

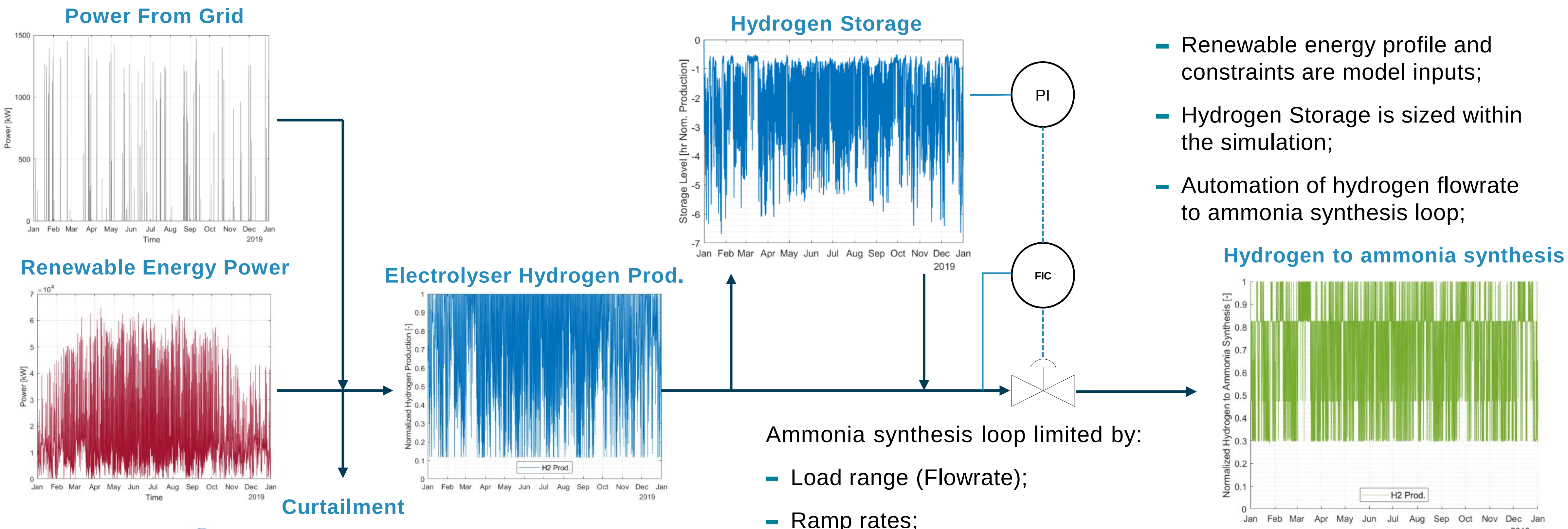
Objectives:

- Evaluate the potential of the integration of ammonia and high-temperature electrolysis processes considering both performances and operation strategies;
- Demonstrate the economic viability of Power-to-Ammonia systems based on Solid Oxide Electrolytic cells (SOECs) and new ammonia separation technologies;

3. Activities Related

Solid Oxide Electrolyser Dynamic Model: Integration with Ammonia Synthesis

- Solid oxide electrolyser dynamic model for system performances evaluation (Aspen Dynamics);



- Renewable energy profile and constraints are model inputs;
- Hydrogen Storage is sized within the simulation;
- Automation of hydrogen flowrate to ammonia synthesis loop;

Ammonia synthesis loop limited by:

- Load range (Flowrate);
- Ramp rates;

Conclusions and Key Takeaways

- Solid Oxide Electrolysis technology benefits of many advantages in comparison to traditional electrolysis technologies allowing for high efficiency hydrogen production;
- Dynamic 0D Lumped parameter modelling for high-temperature electrolysis processes allow for the evaluation of system performances and economics using long term intermittent renewable energy power profiles as well as the development of strategies for the operation of downstream processes (Power-to-X);

Thank you for your attention!
Any question?

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