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MODELING, DEVELOPMENT AND PRELIMINARY TESTING OF A 2 MW PEM FUEL CELL PLANT FUELED WITH HYDROGEN FROM A CHLOR-ALKALI INDUSTRY

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SUMMARY

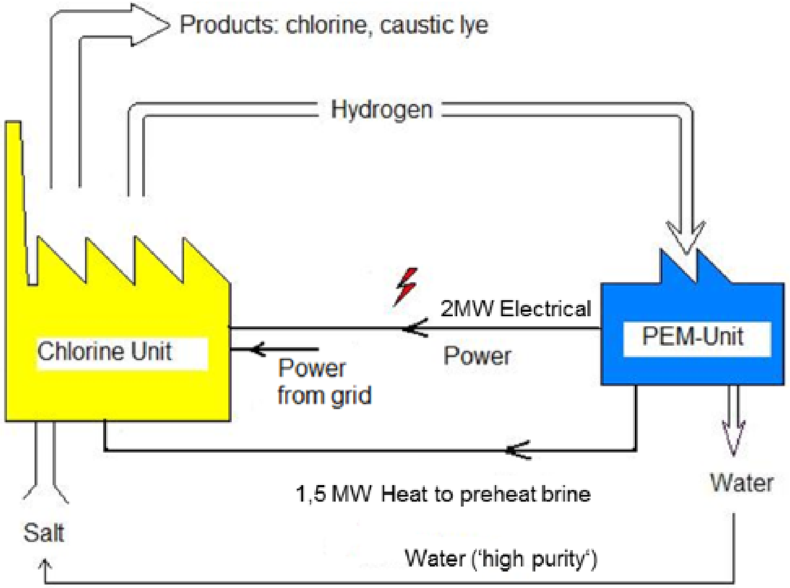
- ✓ DEMCOPEM-2MW PROJECT AND BACKGROUND
- ✓ MEA DEVELOPMENT AT JOHNSON MATTHEY
- ✓ PLANT LAYOUT, MODELING AND ENERGY BALANCES
- ✓ RESULTS OF FIRST YEAR OF OPERATION
- ✓ CONCLUSIONS AND OUTLOOK

DEMCOPEM-2MW Project outline

- Design, construction and demonstration of a combined heat and power (CHP) PEMFC power plant (2MW$_{DC\ el}$)

and

- integration into a chlor-alkali industrial plant recovering byproduct hydrogen

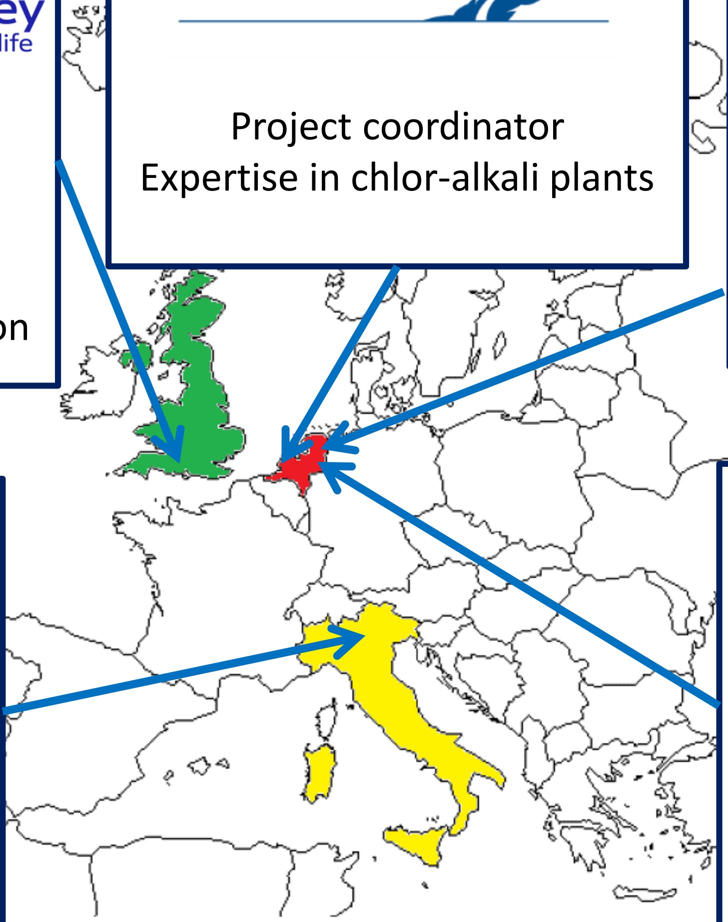


OBJECTIVES (2015-2019)

- **High net conversion efficiency** (50% electric and 85% total)
- **Long lifetime** of system and fuel cells (16,000 h up to 40,000 h target)
- Development of **large-volume manufacturing process** for high-quality MEAs
- **Economical plant design** (target < 2500 €/kW$_e$)
- Fully **automated operation**
- Ensure plant reliability by developing protocols for **fuel cells monitoring and rapid replacement** of faulty stacks (on-stream availability of > 95%)
- Contribute to the general goals of the FCH-JU for installed fuel cell capacity

PROJECT PARTNERS

DEMCOPEM 2MW



Johnson Matthey
Inspiring science, enhancing life

High quality MEA assembly
Manufacturing process development
Performances, robustness, lifetime and costs optimization

AkzoNobel

Project coordinator
Expertise in chlor-alkali plants

Nedstack
PEM FUEL CELLS
To be sure.

PEM fuel cell stack development and production

POLITECNICO MILANO 1863

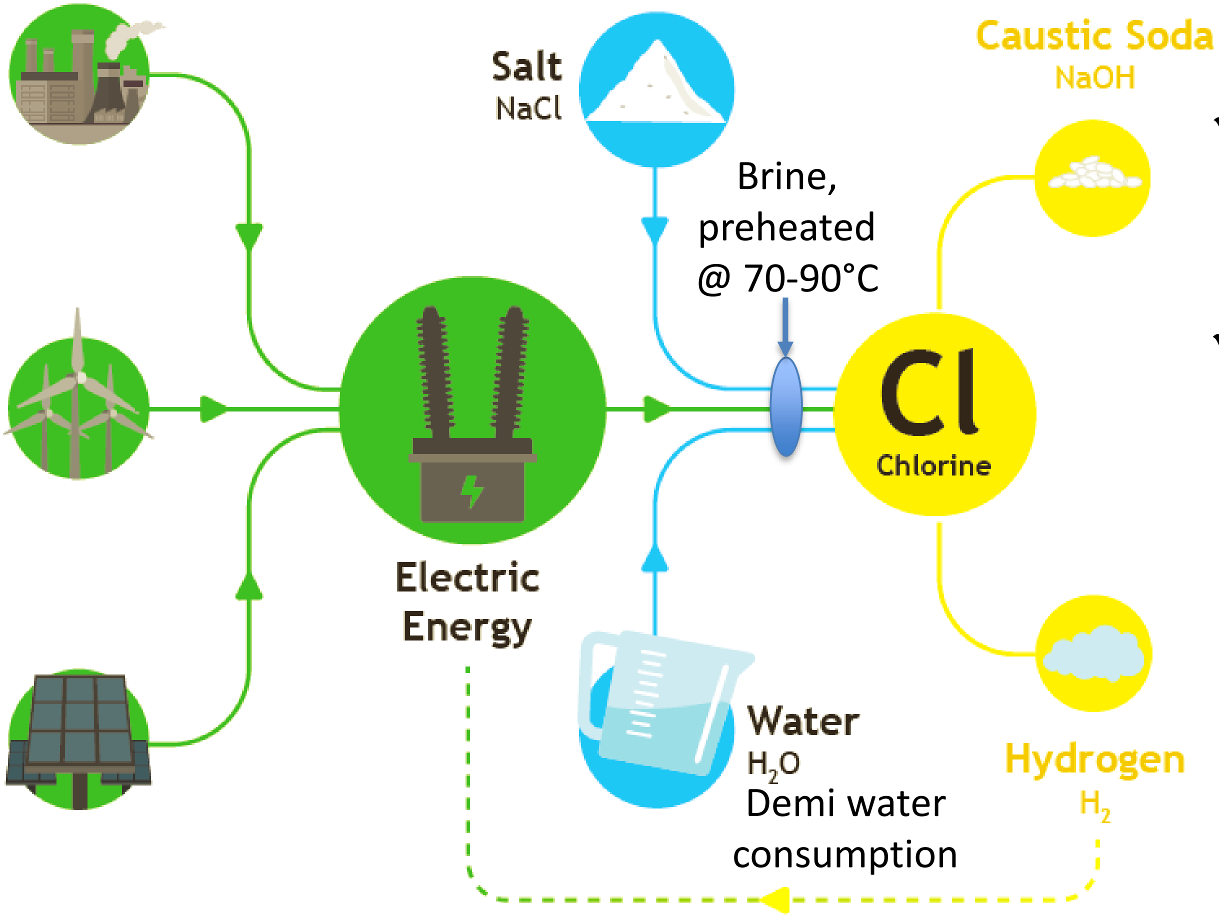
Power plant simulation model development & validation
Analysis of experimental measurements

MTSA TECHNOPOWER

Plant construction
Development, production and maintenance of customer-specific equipment for energy processes

Background: the chlor-alkali process and PEMFC

The Chlor-alkali process is suitable for integration with low temperature fuel cells



Salt
NaCl

Caustic Soda
NaOH

Brine,
preheated
@ 70-90°C

Cl
Chlorine

Electric Energy

Water
H_2O
Demi water
consumption

Hydrogen
H_2

- ✓ Up to 50% of chlorine production cost is due to electricity consumption
- ✓ Excess hydrogen (340 Nm^3H_2/ton_{Cl}) can efficiently feed a fuel cell plant, generating part of electricity
- ✓ Exhaust heat can be recovered for process preheating duties

Source: EuroChlor, “Chlorine industry review 2015-2016”, Brussels, 2015

Previous projects and PEMFC scale-up

Scale-up based on previous experiences (Nedstack & MTSA)

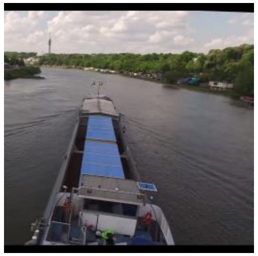
- **70 kW_{el}** PEM Power Plant at AkzoNobel (Delfzijl, NL, 2007)
- **1 MW_{el}** PEM Power Plant at Solvay (Antwerp, BE, 2011)

The new 2 MW plant installation is located in **China:**

- large chlor-alkali plants market - ca. 180 plants → 1000 MW_{el} PEM potential
- high electricity prices
- issues with electricity supply shortages and reliability

Plant construction at MTSA, shipment and startup

- **Construction and shipment** of the plant in mid 2016 @ MTSA factory (NL)



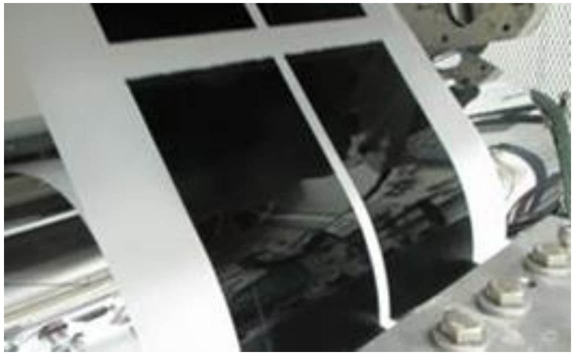
https://www.youtube.com/watch?v=W8QE8iEXAyM

- **Opening ceremony** on Oct. 14, 2016 at plant location of Ynnovate Ltd in Yingkou, China

- 2016-2018: more than one year of plant operation: **data analysis**

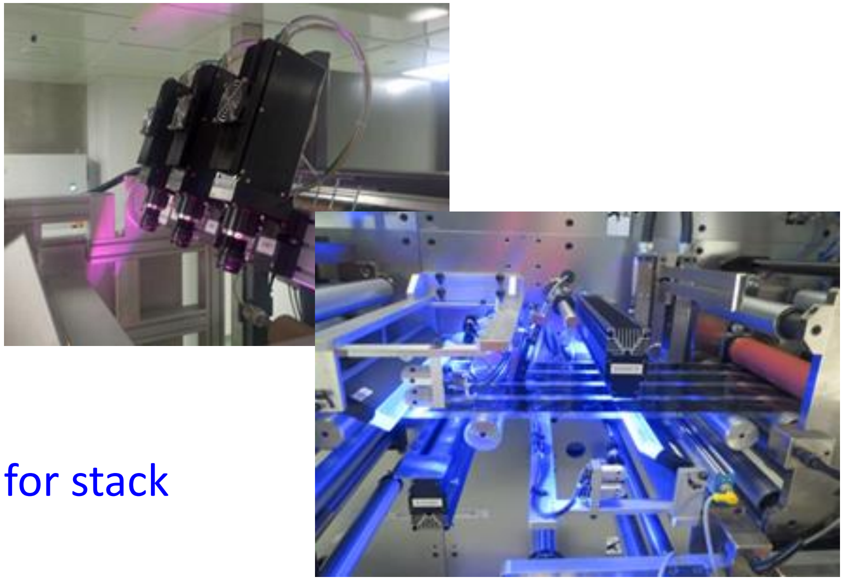
MEA DEVELOPMENT AT JOHNSON MATTHEY - I

- ✓ JM committed to developing a capable volume manufacturing process to produce MEAs whilst maintaining quality and performance
- ✓ The DEMCOPEM-2MW long life MEA is created with a high volume manufacturing process:
  - special gas-diffusion layers were coated with catalyst layers and dried in line, then cut to size in a semi-automated process.
  - Further reduction in the number of manual operations was achieved by sourcing and testing a single-layer edgeprotection/seal heat-stabilised material, meeting the demands of Nedstack’s accelerated stress test.



MEA DEVELOPMENT AT JOHNSON MATTHEY - II

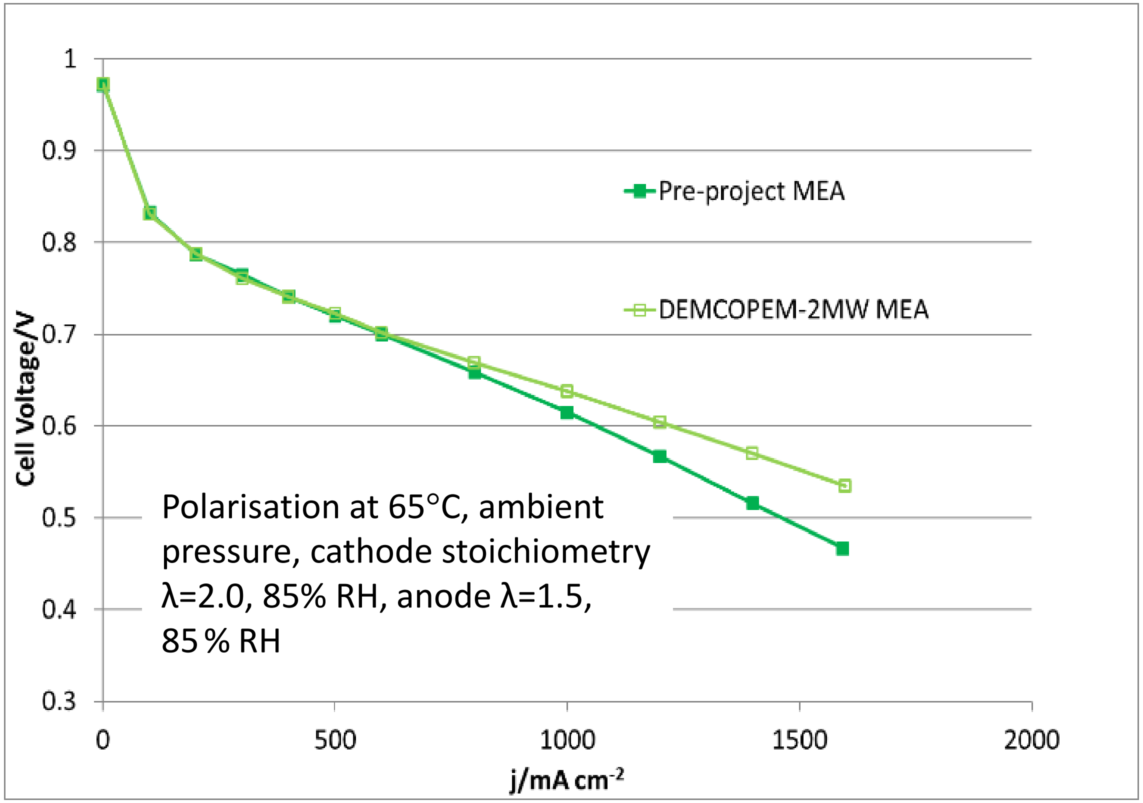
- ✓ The DEMCOPEM-2MW long life MEA is created with a high volume manufacturing process:
  - The single layer seal was bonded to the polymer-electrolyte membrane in a continuous roll-to-roll cutting and converting process, producing high quality membrane seal assemblies (MSAs).
  - The MSAs were collated with the electrodes in a semi-automated process involving an automated hot melt glue bead, then laminated, inspected and packed for shipping



- ✓ A total of 25,200 MEAs (plus spare) was delivered for stack manufacturing

MEA DEVELOPMENT AT JOHNSON MATTHEY - III

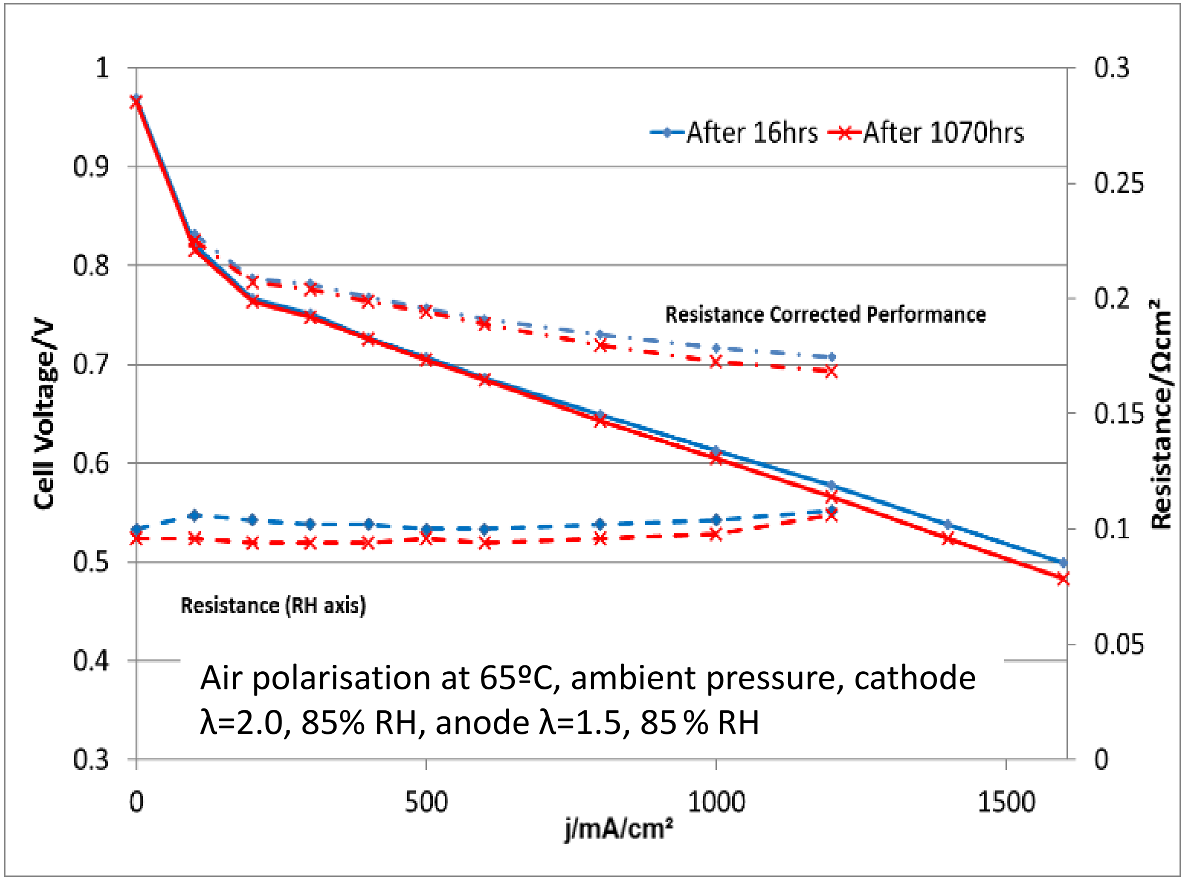
- ✓ The new MEAs matched the performance of the pre-project long life MEA at lower current densities, and exceeded it at higher current densities.
- ✓ This reflects the probable enhanced gas access to the catalyst-electrolyte interface due to the more open gas diffusion media structure, and possibly also an increased porosity of the catalyst layer.



Polarisation at 65°C, ambient pressure, cathode stoichiometry λ=2.0, 85% RH, anode λ=1.5, 85 % RH

MEA DEVELOPMENT AT JOHNSON MATTHEY – IV

- ✓ In order to assess the early stability of the MEA to corrosion, the MEA was tested for 1000 h at the assumed operating point. Figure shows the polarisation performance before and after the 1000 h stability testing

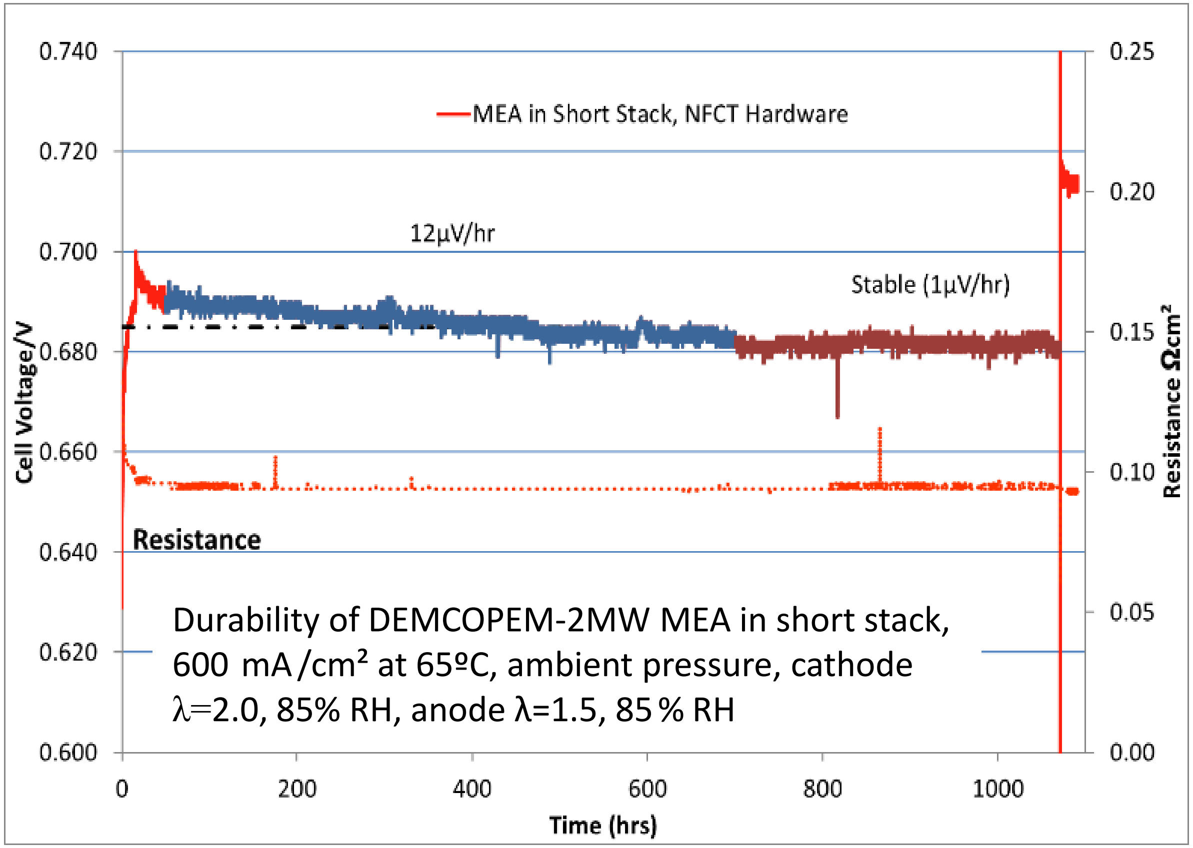


Air polarisation at 65ºC, ambient pressure, cathode λ=2.0, 85% RH, anode λ=1.5, 85 % RH

Polarization performance before and after the 1000 h stability testing

MEA DEVELOPMENT AT JOHNSON MATTHEY - V

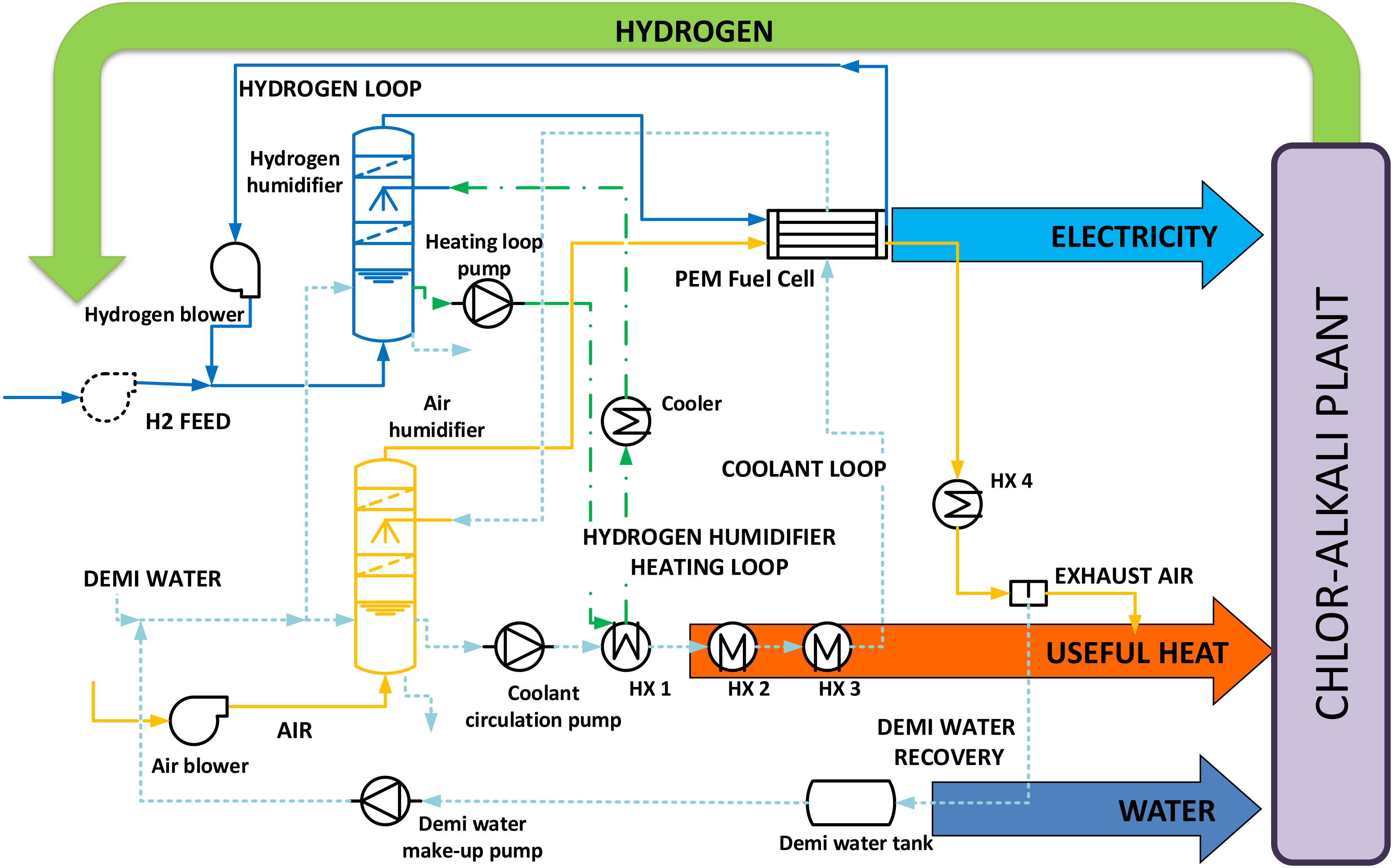
- ✓ During stability testing, after an initial 700 h of decay at 12 µV/hr, the rate of decay levels off to create highly stable performance.
- ✓ Following an interruption for diagnostic testing at 1050 hr, the voltage at 600 mA/cm^2 climbed by around 34 mV



Durability of DEMCOPEM-2MW MEA in short stack, 600 mA/cm² at 65ºC, ambient pressure, cathode λ=2.0, 85% RH, anode λ=1.5, 85 % RH

- ➢ This regeneration in performance may be due to reduction of oxides or other surface contaminants caused by the rapid drop in the cathode potential when the air supply is interrupted and hydrogen crosses the membrane

Plant conceptual layout

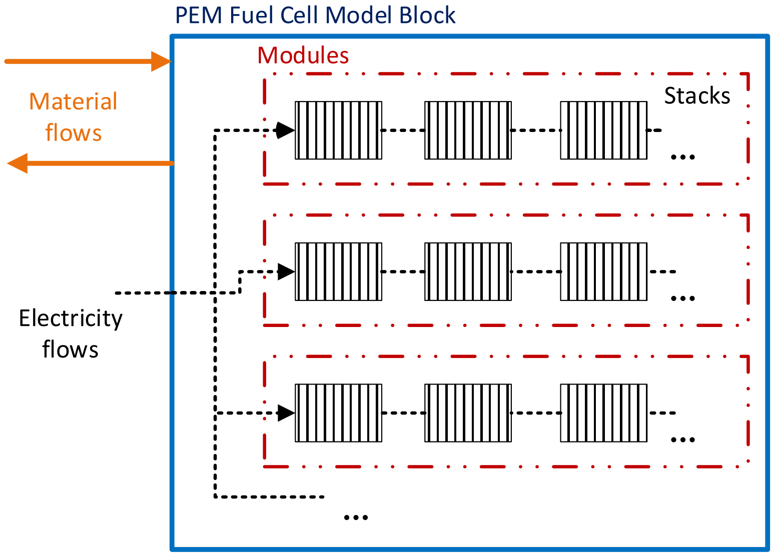


Plant installation @ Ynnovate Ltd

- The plant is arranged in three containers units:
  - Fuel Cell and control room
  - mechanical and thermal BOP
  - main inverters and electric BOP

- It is currently *the world largest stationary PEM fuel cell system in operation* (2 MW_{el}).

PEM FUEL CELL MODEL - I



- ✓ Lumped model developed in Aspen Custom Modeler®, for integration with the balance of plant in Aspen Plus.
- ✓ Modular modelling approach reproducing the plant layout:

STACKS ➡ MODULES ➡ 6 GROUPS (each connected to one inverter @360 kW max)

Semi-empirical formulation of the V-i curve, validated against experimental data

- Considers reactants stoichiometry (x_{H2}, x_{O2}), exchange and limit current density (i_0, i_L)
- Neglects RH effects: stacks at constant RH thanks to circuit humidifiers

$$V(i, x_{H2}, x_{O2}, T) = A_T + B_T \ln\left(\frac{x_{H2}}{x_{H2,st}}\right) + C_T \ln\left(\frac{x_{O2}}{x_{O2,st}}\right) + D_T i + E_T \ln\left(\frac{i}{i_0} + 1\right) + F_T \ln\left(1 - \frac{i}{i_L(x_{H2}, x_{O2})}\right)$$

- Further correction is added to take into account voltage decay effect vs. time

PEM FUEL CELL MODEL - II

$$V(i,x_{H2},x_{O2},T) = A_T + B_T \ln\left(\frac{x_{H2}}{x_{H2,st}}\right) + C_T \ln\left(\frac{x_{O2}}{x_{O2,st}}\right) + D_T i + E_T \ln\left(\frac{i}{i_0}+1\right) + F_T \ln\left(1-\frac{i}{i_L(x_{H2},x_{O2})}\right)$$

$$E_0 = -\frac{\Delta G}{nF} = -\left(\frac{\Delta H - T\Delta S}{nF}\right)$$

$$A_T = E_{0,T} - (E_0 - A)\frac{T}{T_{ref}}$$

$$B_T = B\frac{T}{T_{ref}},\ C_T = C\frac{T}{T_{ref}},\ E_T = E\frac{T}{T_{ref}},\ F_T = F\frac{T}{T_{ref}}$$

$$D_T = D\,exp\left(1268\left(\frac{1}{T}-\frac{1}{T_{ref}}\right)\right)$$

$$i_0 = i_0^{ref}\exp\left[-\frac{E_c}{RT}\left(1-\frac{T}{T_{ref}}\right)\right]$$

$$\frac{x_{H2}}{x_{H2,st}} = 1 + \frac{S_H - 1}{S_H - 1 - x_{sat}(T_{an})\cdot RH_H}$$

$$\frac{x_{O2}}{x_{O2,st}} = 1 + \frac{S_O - 1}{S_O + 0.21(1 - x_{sat}(T_{cat})\cdot RH_O)}$$

$$I_L(x_{H_2},x_{O_2}) = I_{L,1} + I_{L,2}\left(\frac{x_{H_2}}{x_{H_{2,ref}}}\right) + I_{L,3}\left(\frac{x_{O_2}}{x_{O_{2,ref}}}\right)$$

Temperature effect is evaluated through:

- a linear correction of the coefficients A,B,C,E,F starting from a reference temperature (T_{ref}=338 K , ~65°C);
- a correction of ohmic loss (D_T), according to the change in ionic conductivity vs. T (ref. baseline membrane*);
- a correction of activation losses through the exchange current density i_0 (activation energy E_c assumed @ $66\frac{kJ}{mol}$ for O_2 reduction on Pt).

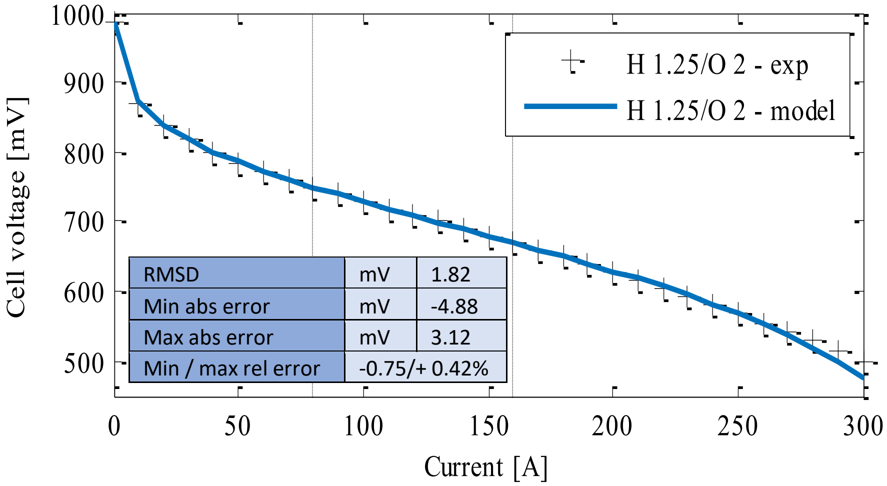
Reactant stoichiometry is evaluated through species molar fractions x_i vs. the ratio to stoichiometry of H_2 and O_2 (S_H, S_O) and relative humidity RH (affecting water fraction vs. saturation $x_{sat}(T)$).

Changes in losses vs. reactants concentration are taken into account through a dependence of exchange current i_0 and limiting current i_L on stoichiometry

* T. E. Springer, "Polymer Electrolyte Fuel Cell Model," J. Electrochem. Soc., 138, no. 8, 2334.

PEM FUEL CELL MODEL - III

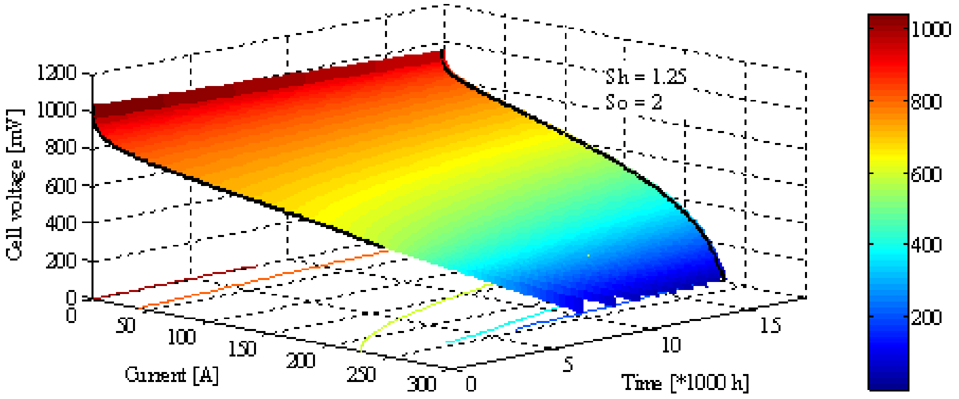
- ✓ Coefficients *A*-*F*, as well as exchange and limiting current densities i_o and i_L are regressed on experimental data from stacks operated by Nedstack in Lillo and Delfzijl plants, obtaining a very good fitting



RMSD	mV	1.82
Min abs error	mV	-4.88
Max abs error	mV	3.12
Min / max rel error	-0.75/+ 0.42%	

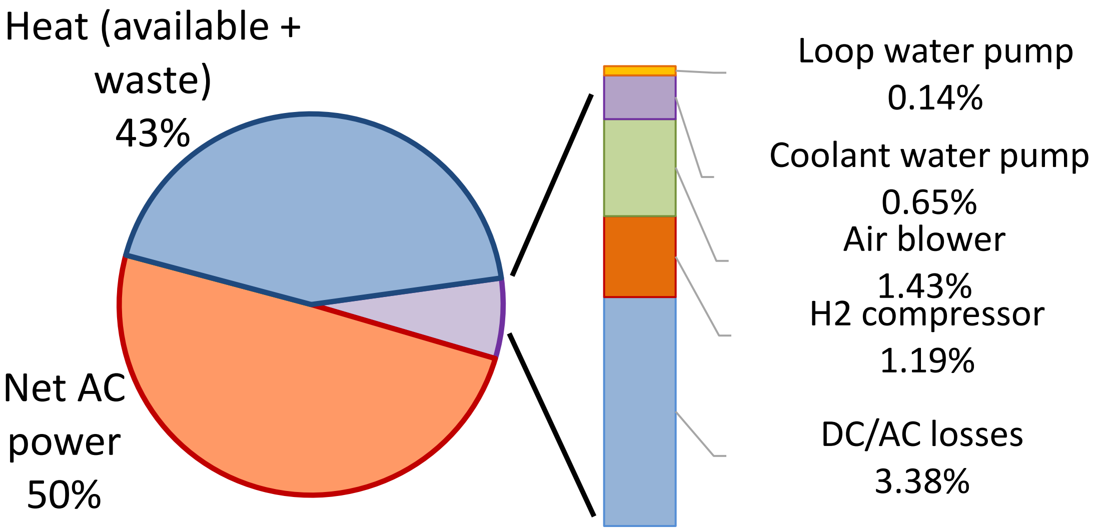
Regressed parameter	Value at BOL	Value at EOL
A [mV]	961,23	952,4
B [mV]	27,7	6,49
C [mV]	116,4	3,15
D [mΩ]	-0,267	-0,43
E [mV]	-40,3	-24,44
F [mV]	81,9	195,48
I_0 [mA]	187	97,15
$I_{L,1}$ [A]	334,6	-1120,2
$I_{L,2}$ [A]	-	322,2
$I_{L,3}$ [A]	-	-

- ✓ The model also takes into account the cell voltage decay vs. time through regression of the coefficients A-F/$I_{o,L}$ at BOL and EOL, allowing interpolation of mid-of-life conditions.



PLANT SIMULATIONS

Plant energy balance at BOL



- ✓ A large quantity of low temperature heat (@ ~63°C) can be exploited by an external user. The amount is dependent on environmental temperatures due to system heat losses.

  Compression and DC/AC conversion are the most significant losses.

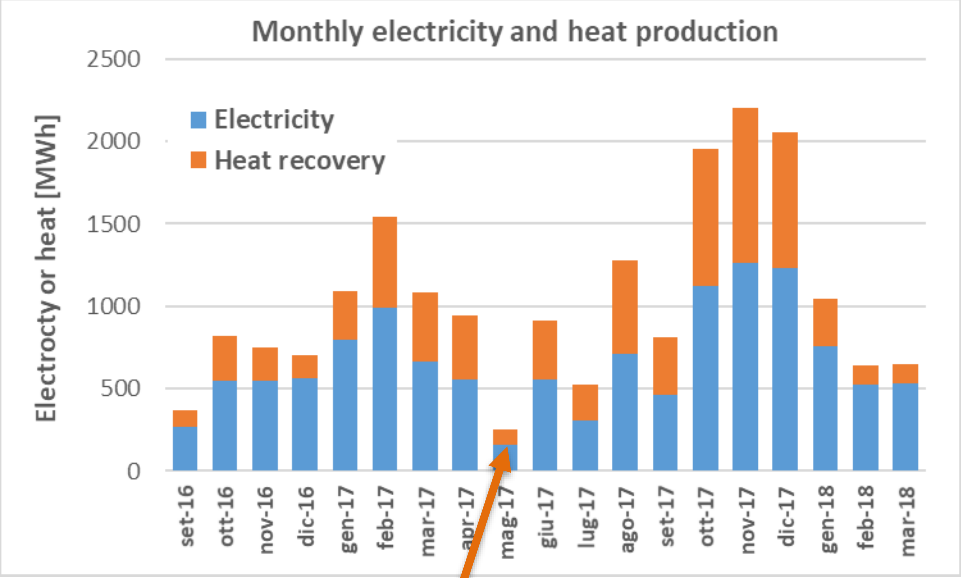
- ➢ The plant energy balance changes towards EoL, where the electric efficiency loss during expected lifetime (about 6%, based on plant simulation) is partially recovered as additional heat.

PLANT SIMULATION AND MEASURED RESULTS

Operating conditions				
Air inlet flow	Nm³/h	5314		
Stoichiometry cathode / anode	-	2.3 / 2.0		
T coolant, FC inlet	°C	60.0		
Power DC (gross)	kW	1653		
Results		Measurement	Model	Difference
H_2 inlet flow	Nm³/h	972	978	0.6%
Temperature air humidifier	°C	63.0	62.7	-0.4%
Coolant flow	m³/h	317	315	-0.6%
Coolant temperature at stack outlet	°C	64.7	63.9	-1.3%
Voltage (average)	V	728.7	742	1.8%
Current (average)	A	113.4	111	-1.8%
Auxiliary power	kW	106	105	-1.2%
Available Thermal power (HX2)	kW	-	735	-
Power AC (net)	kW	-	1450	-
Efficiency (gross)	%	56.7	56.4	-0.5%
Efficiency (net)	%	-	49.5	-
Net water production	kg/h	-	534	-

- Results of modelling activities @ BOL conditions have been positively validated vs. on-field data with low errors.
- The plant also produces 534 kg/h of demi water - a valuable contribute to the industrial site consumptions.

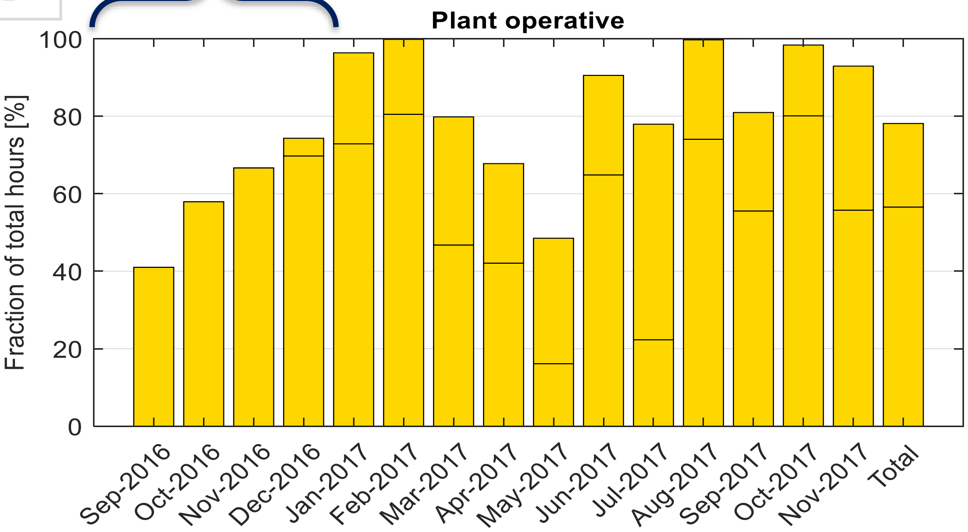
FIRST YEAR OPERATION RESULTS - I



The plant has been operative since Sept. 2016 and reached full-load capacity in Jan. 2017.

The plant has been active up to now for more than 11240 hours (vs. 13560 calendar hours).

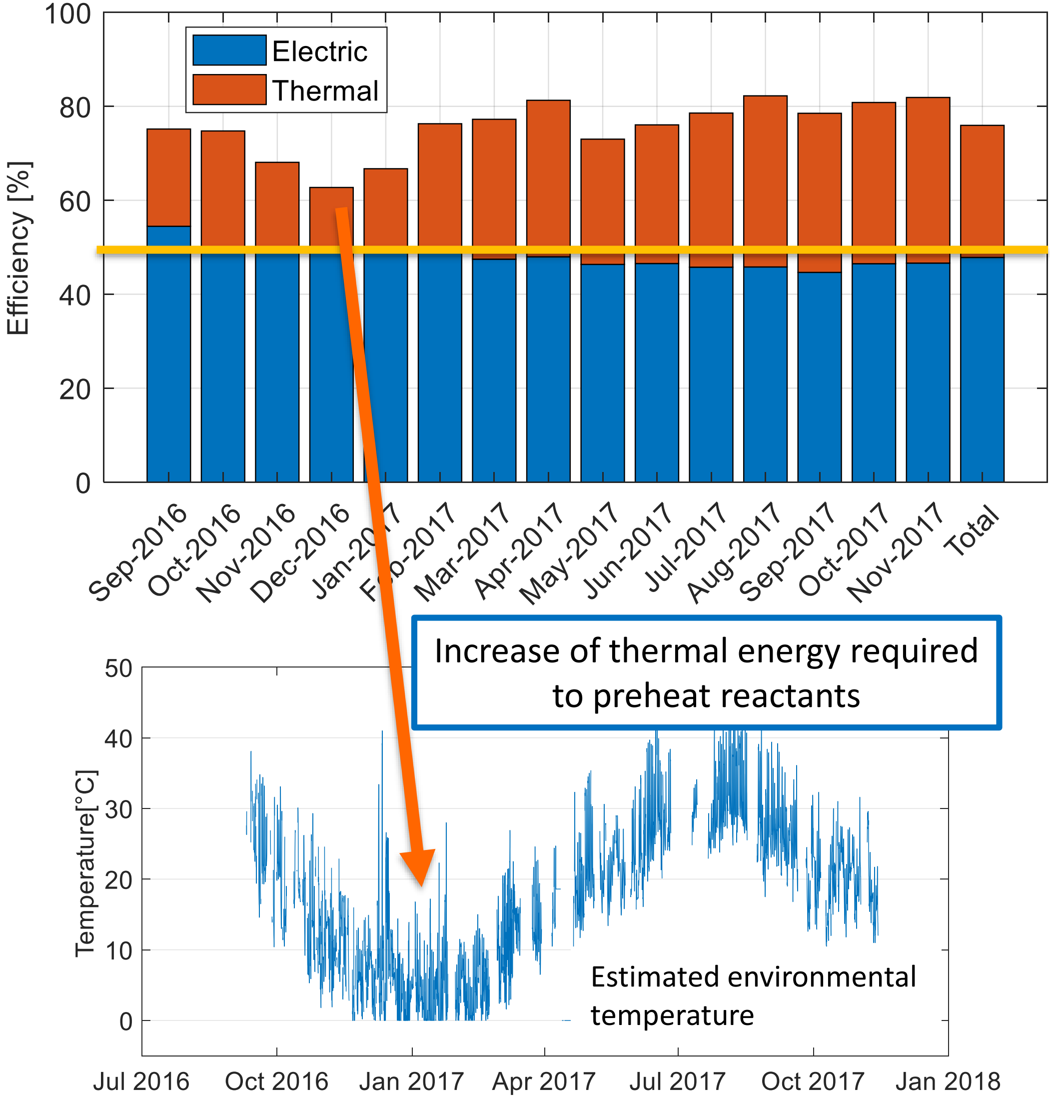
Initial plant operation with some limitations



Plant is often operated at part load (not all modules running) depending on hydrogen availability and grid limitations

Thermal energy is calculated from measurements - although currently not recovered by the chlor-alkali plant.

FIRST YEAR OPERATION RESULTS - II



Increase of thermal energy required to preheat reactants

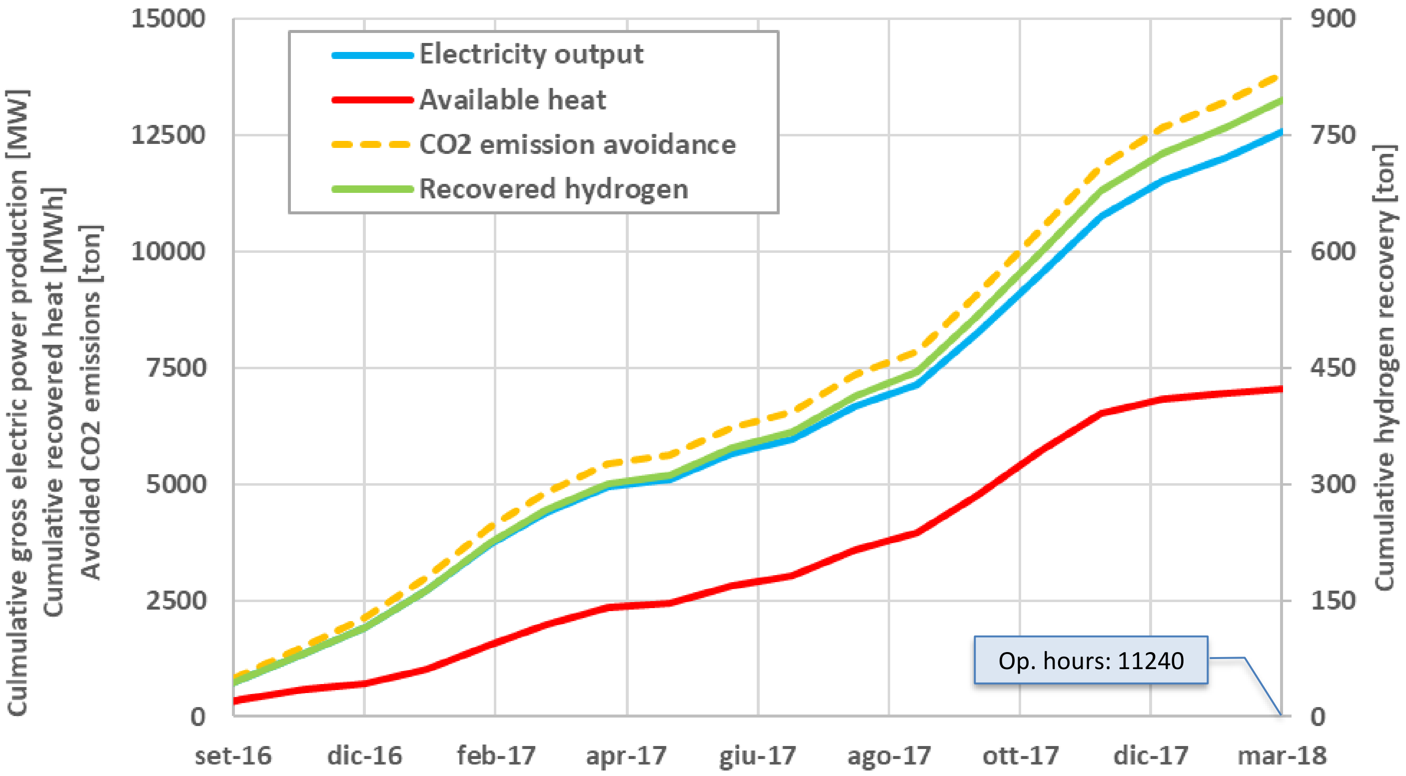
Estimated environmental temperature

- ✓ The measured **BOL electric efficiency** was 55%$_{LHV}$ and during the first year of operation the **average net electrical efficiency** has been ~49-50%$_{LHV}$ (56-57%$_{LHV}$ gross), aligned with project targets.
- ✓ Additional 26%$_{LHV}$ (average) can be recovered as **thermal energy** leading to a global first law efficiency of nearly 76%$_{LHV}$ (peaks over 80%)

Thermal recovery is strongly influenced by the cold winter climate in Yingkou, China. Thermal efficiency ranges from 32% to 12%.

PLANT GLOBAL PERFORMANCES

Globally, the plant produced more than 12 GWh_{el} making available over 7 GWh of thermal energy at about 65°C.



- ✓ More than 800 tons of hydrogen have been recovered, with an average electric efficiency of ~49%$_{LHV}$ and over 13000 tCO_2 emission avoidance

CONCLUSIONS & OUTLOOK

The coupling of a large scale PEM fuel cell system with a chlor-alkali industrial plant for byproduct hydrogen recovery is under demonstration with satisfying results.

- The DEMCOPEM 2MW plant has been built on time and is currently in operation, using long-life , high volume manufacturing process MEAs
- BOL performances are statisfactory and aligned with expectations (net electric efficiency 50%, large thermal recovery capability)
- Plant availability is high (~83%, substantially higher than uptime, influenced by OSBL limitations on H_2 & grid capacity)
- The plant shows excellent flexibility in terms of part-load, standby operation and on-off control (allowing very frequent startups when needed)
- Modelling activity yields results which are aligned with measured data

Next steps:

- Analysis of long-term plant performance data, decay phenomena, options for efficiency improvement
- Partial substitution of stacks with improved versions (MEA development) with further stabilisation against degradation, developed by Johnson Matthey)

Thank you for your attention!

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